Supporting Information (SI)

Fluorodinitroethylamino Functionalization Derivatives Based on Azole : A New Family of Insensitive Energetic Materials

Weixia Wang,[a] Guangbin Cheng,[a] Hualin Xiong[a] and Hongwei Yang[*] [a]

[a] School of Chemical Engineering, Nanjing University of Science and Technology, Xiaolingwei 200, Nanjing, Jiangsu, China, Fax:(+)86 25 8430 3286, E-mail: hyang@mail.njust.edu.cn

Table of Contents

1. Differential scanning caorimetry gravity (DSC) curves of compounds 6-11

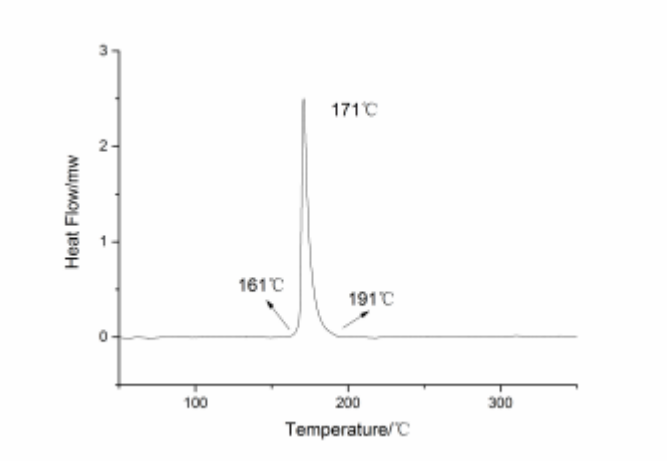


Fig. S1 DSC curves of **6** under nitrogen with a heating rate of 5 ℃ min^{-1}.

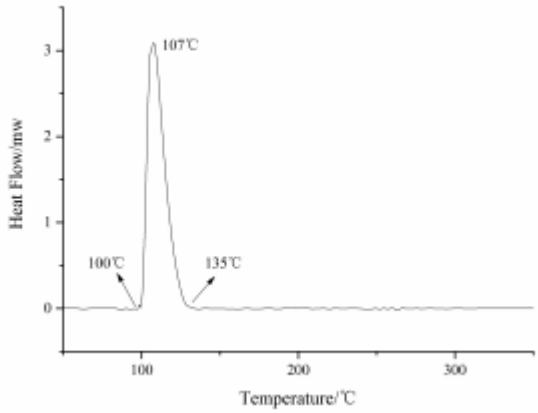


Fig. S2 DSC curves of **7** under nitrogen with a heating rate of 5 ℃ min^{-1}.

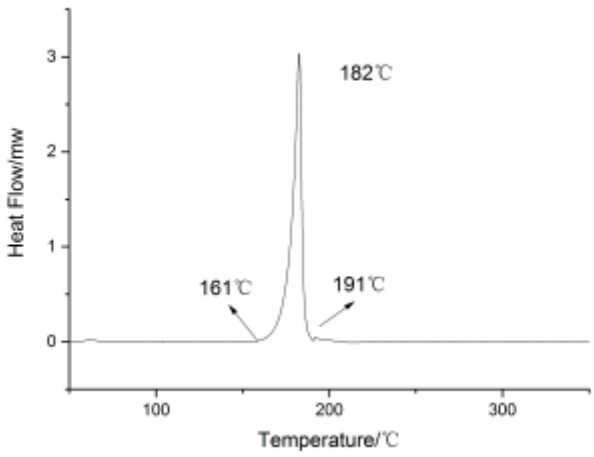


Fig. S3 DSC curves of **8** under nitrogen with a heating rate of 5 ℃ min^{-1}.

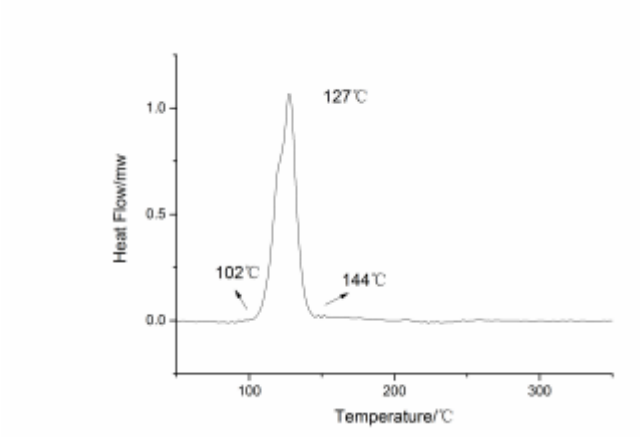


Fig. S4 DSC curves of **9** under nitrogen with a heating rate of 5 ℃ min^{-1}.

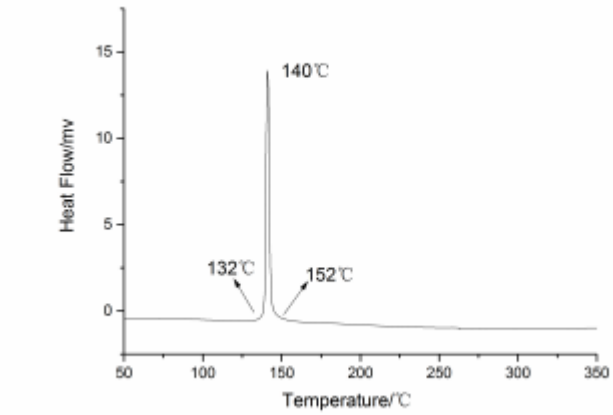


Fig. S5 DSC curves of **10** under nitrogen with a heating rate of 5 ℃ min^{-1}.

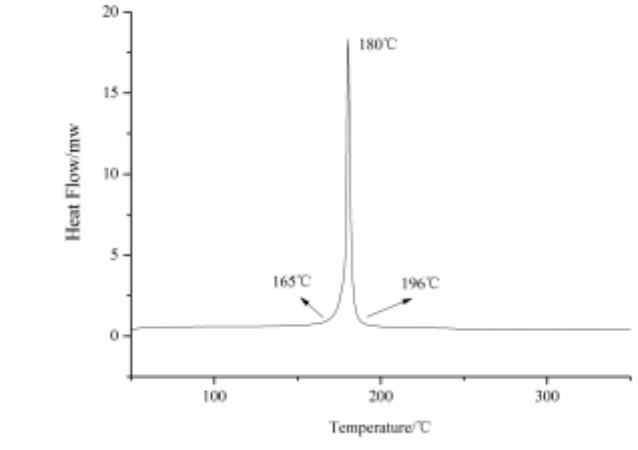
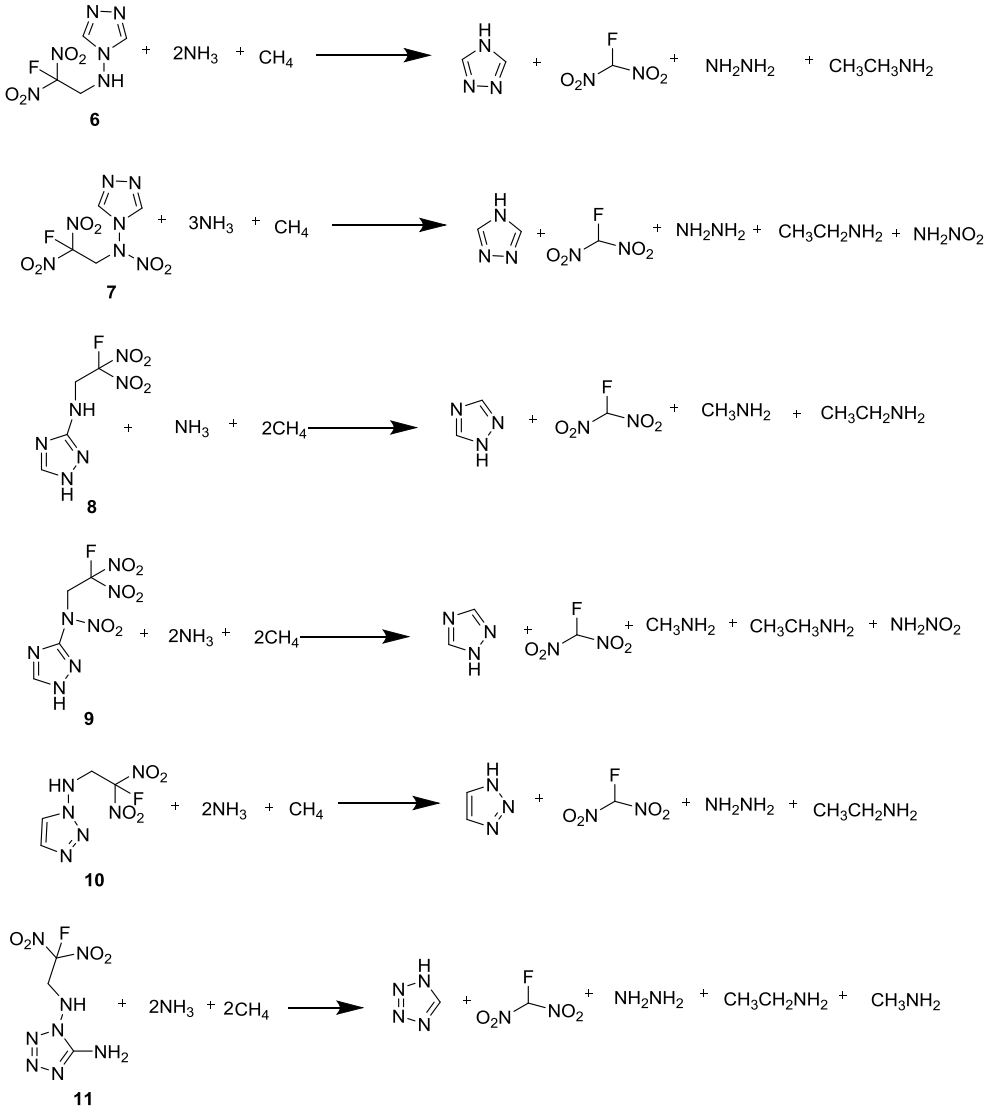


Fig. S6 DSC curves of **11** under nitrogen with a heating rate of 5 ℃ min^{-1}.

2. Computational data

Computations were performed by using the Gaussian09 suite of programs.[1] The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP)[2] functional with the 6-311+G** basis set.[3] 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.[4] 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 **6-11**, are listed in Scheme S1.



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

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 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).

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

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[5-7] or from the high-level computing such as CBS-4M.

Table S1 Ab initio computational values of fluorodinitroethyl-substituted aminoazoles derivatives

compounds	E_0/a.u.[a]	ZPE/ kJ mol^{-1}[b]	ΔH_T/ kJ mol^{-1}[c]	HOF/ kJ mol^{-1}[d]
NH_3	-56.58	86.27	10.05	-45.91[e]
CH_4	-40.53	112.26	10.04	-74.60[e]
4H-1,2,4-triazole	-242.31	148.18	12.29	206.74[f]
NH_2NH_2	-111.91	134.28	11.16	95.40[e]
$CH_3CH_2NH_2$	-135.22	232.76	14.37	-60.74[f]
$CHF(NO_2)_2$	-548.89	111.94	18.81	-212.35[f]
CH_3NH_2	-95.89	160.78	11.64	-22.50[e]
NH_2NO_2	-261.12	98.79	12.39	-3.90[e]
1H-1,2,4-triazole	-242.32	150.38	12.06	180.67[f]
1H-1,2,3-triazole	-242.30	150.23	12.05	233.71[f]
1H-tetrazole	-258.32	117.69	11.84	334.30[f]
6	-884.65	323.46	38.23	168.83
7	-1089.18	325.83	45.19	239.11
8	-884.71	326.70	38.44	-15.07

9	-1089.24	331.21	44.72	73.77
10	-884.64	323.92	37.96	181.77
11	-956.05	335.16	42.13	252.83

[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.

3. Single-crystal X-ray diffraction analysis of compound 6

Table S2 Selected bond lengths (Å) of **6**

Parameter	Å	Parameter	Å
C1-N2	1.298(4)	C4-F1	1.337(3)
C1-N3	1.359(3)	C4-N5	1.530(4)
C1-H1	0.95	C4-N6	1.534(4)
C2-N1	1.297(4)	N1-N2	1.404(3)
C2-N3	1.352(4)	N3-N4	1.408(3)
C2-H2	0.95	N4-H4A	0.83(3)
C3-N4	1.455(4)	N5-O1	1.214(3)
C3-C4	1.501(4)	N5-O2	1.219(3)
C3-H3A	0.99	N6-O3	1.209(3)
C3-H3B	0.99	N6-O4	1.216(3)

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

Table S3 Selected angles ( ) of of **6**

Parameter	°	Parameter	°
N2-C1-N3	110.4(3)	F1-C4-C3	113.4(2)
N2-C1-H1	124.8	F1-C4-N5	106.7(2)
N3-C1-H1	124.8	C3-C4-N5	113.4(2)
N1-C2-N3	110.7(3)	F1-C4-N6	106.8(2)
N1-C2-H2	124.6	C3-C4-N6	111.9(2)
N3-C2-H2	124.6	N5-C4-N6	104.0(2)
N4-C3-C4	107.7(2)	C2-N1-N2	106.7(2)
N4-C3-H3A	110.2	C1-N2-N1	106.8(2)
C4-C3-H3A	110.2	C2-N3-C1	105.2(2)
N4-C3-H3B	110.2	C2-N3-N4	126.3(2)
C4-C3-H3B	110.2	C1-N3-N4	128.3(2)
H3A-C3-H3B	108.5	N3-N4-C3	113.5(2)
N(3)-N(4)-H(4A)	105(2)	O(2)-N(5)-C(4)	116.8(2)
C(3)-N(4)-H(4A)	112(2)	O(3)-N(6)-O(4)	126.9(3)
O(1)-N(5)-O(2)	127.0(3)	O(3)-N(6)-C(4)	118.2(3)
O(1)-N(5)-C(4)	116.2(2)	O(4)-N(6)-C(4)	114.9(2)

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

Table S4 Selected torsion angles for **6**

Parameter	°	Parameter	°
C2-N1-N2-C1	0.3(3)	O1-N5-C4-F1	-42.0(3)
N2-N1-C2-N3	-0.3(3)	O2-N5-C4-F1	137.7(3)
N1-N2-C1-N3	-0.2(3)	O2-N5-C4-N6	-109.7(3)
C1-N3-N4-C3	-76.7(3)	O3-N6-C4-F1	3.5(3)
C2-N3-N4-C3	109.1(3)	O4-N6-C4-C3	-51.9(3)
N4-N3-C1-N2	-175.2(3)	O3-N6-C4-N5	-109.1(3)
C2-N3-C1-N2	0.0(3)	O4-N6-C4-N5	70.9(3)
N4-N3-C2-N1	175.5(3)	O4-N6-C4-F1	-176.5(2)
C1-N3-C2-N1	0.2(3)	O3-N6-C4-C3	128.1(3)
N3-N4-C3-C4	-102.3(3)	N4-C3-C4-N5	177.0(2)
O1-N5-C4-C3	-167.6(2)	N4-C3-C4-N6	-65.8(3)
O2-N5-C4-C3	12.1(4)	N4-C3-C4-F1	55.0(3)
O1-N5-C4-N6	70.6(3)		

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

Table S5 Hydrogen bonds present in **6**

D—H•••A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °	comment
N4—H4A•••N2	0.84(3)	2.25(3)	3.071(3)	166(3)	inter
C1—H1•••O3	0.95	2.56	3.359(4)	142	inter
C3—H3A•••N1	0.99	2.46	3.445(4)	177	inter

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

4. Single-crystal X-ray diffraction analysis of compound 9

Table S6 Selected bond lengths (Å) of **9**

Parameter	Å	Parameter	Å
F1-C4	1.330(12)	N4-N5	1.388(6)
F1'-C4'	1.319(10)	N4-C1	1.413(6)
F1A-C4A	1.353(12)	N4-C3	1.461(6)
O1-N5	1.210(5)	N4-C3'	1.460(6)
O2-N5	1.225(5)	N4-C3A	1.460(6)
O3-N6	1.203(12)	N6-C4	1.537(11)
O3'-N6'	1.228(10)	N6'-C4'	1.530(10)
O3A-N6A	1.214(12)	N6A-C4A	1.525(11)
O4 -N6	1.221(12)	N7-C4	1.531(11)
O4'-N6'	1.212(10)	N7'-C4'	1.538(10)
O4A-N6A	1.242(11)	N7A-C4A	1.521(12)
O5 -N7	1.223(14)	N1-H1A	0.84(5)
O5'-N7'	1.210(12)	C3-C4	1.497(12)
O5A-N7A	1.227(13)	C3'-C4'	1.518(11)
O6 -N7	1.214(18)	C3A-C4A	1.494(12)

O6'-N7'	1.218(14)	C2-H2	0.95
O6A-N7A	1.212(17)	C3-H3A	0.99
N1 -N2	1.359(5)	C3-H3B	0.99
N1 -C2	1.330(6)	C3'-H3'1	0.99
N2 -C1	1.321(6)	C3'-H3'2	0.99
N3 -C1	1.344(6)	C3A-H3A1	0.99
N3 -C2	1.322(6)	C3A-H3A2	0.99

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

Table S7 Selected angles ( ) of of **9**

Parameter	°	Parameter	°
N2-N1-C2	110.6(4)	O6A-N7A-C4A	116.7(13)
N1-N2-C1	100.8(4)	O5A-N7A-O6A	126.3(14)
C1-N3-C2	102.1(4)	O5A-N7A-C4A	117.0(14)
N5-N4-C1	117.4(4)	C2-N1-H1A	133(3)
N5-N4-C3	116.4(4)	N2-N1-H1A	117(3)
N5-N4-C3'	116.4(4)	N3-C1-N4	123.6(4)
N5-N4-C3A	116.4(4)	N2-C1-N4	120.0(4)
C1-N4-C3	120.0(4)	N2-C1-N3	116.3(4)
C1-N4-C3'	120.0(4)	N1-C2-N3	110.2(4)
C1-N4-C3A	120.0(4)	N4-C3-C4	109.7(6)
O1-N5-O2	126.3(4)	N4-C3'-C4'	109.9(5)
O1-N5-N4	117.0(4)	N4-C3A-C4A	108.3(6)
O2-N5-N4	116.6(4)	F1-C4-C3	113.4(11)
O4-N6-C4	114.6(15)	F1-C4-N6	105.6(12)
O3-N6-O4	127.9(16)	F1-C4-N7	107.7(13)
O3-N6-C4	117.5(14)	N7-C4-C3	112.6(10)
O3'-N6'-O4'	125.6(11)	N6-C4-C3	114.0(11)
O3'-N6'-C4'	116.3(10)	N6-C4-N7	102.7(11)
O4'-N6'-C4'	118.1(11)	F1'-C4'-N7'	107.2(8)
O3A-N6A-O4A	128.9(14)	F1'-C4'-N6'	110.3(8)
O3A-N6A-C4A	117.0(13)	N6'-C4'-C3'	110.2(7)
O4A-N6A-C4A	114.1(14)	F1'-C4'-C3'	115.2(8)
O6-N7-C4	117.3(13)	N6'-C4'-N7'	103.4(8)
O5-N7-O6	127.8(14)	N7'-C4'-C3'	109.9(7)
O5-N7-C4	114.8(14)	F1A-C4A-N7A	108.0(12)
O5'-N7'-C4'	115.2(9)	F1A-C4A-C3A	108.0(10)
O6'-N7'-C4'	116.0(10)	N6A-C4A-C3A	117.4(11)
O5'-N7'-O6'	128.5(11)	N7A-C4A-C3A	114.8(10)

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

Table S8 Selected torsion angles for **9**

Parameter	°	Parameter	°
C2-N1-N2-C1	-0.4(5)	C2-N3-C1-N4	-177.2(4)

N2-N1-C2-N3	0.5(5)	C1-N4-N5-O1	171.7(4)
N1-N2-C1-N4	177.6(4)	N5-N4-C1-N3	-80.1(6)
N1-N2-C1-N3	0.3(5)	C1-N4-N5-O2	-9.7(6)
C1-N3-C2-N1	-0.3(5)	N5-N4-C1-N2	102.8(5)
C2-N3-C1-N2	0.0(5)		

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

Table S9 Hydrogen bonds present in **9**.

D—H•••A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °	comment
N1—H1A •••N3	0.84(6)	2.12(6)	2.90(6)	155(4)	inter
C2—H2 ••• O1	0.95	2.55	3.45(6)	158	inter

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

5. Single-crystal X-ray diffraction analysis of compound 10

Table S10 Selected bond lengths (Å) of **10**

Parameter	Å	Parameter	Å
F1-C4	1.334(14)	N4-C3	1.465(4)
F1'-C4'	1.344(12)	N5-C4	1.545(16)
O1-N5	1.208(14)	N5'-C4'	1.525(15)
O1'-N5'	1.216(13)	N6-C4	1.567(16)
O2-N5	1.218(14)	N6'-C4'	1.514(14)
O2'-N5'	1.219(13)	N4-H4A	0.87(2)
O3-N6	1.197(14)	C1-C2	1.359(5)
O3'-N6'	1.215(12)	C3-C4	1.480(16)
O4-N6	1.208(14)	C3'-C4'	1.513(14)
O4'-N6'	1.193(12)	C1-H1	0.95
N1-C2	1.345(5)	C2-H2	0.95
N1-N4	1.401(4)	C3-H3B	0.99
N1-N2	1.342(4)	C3-H3A	0.99
N2-N3	1.318(4)	C3'-H3'2	0.99
N3-C1	1.351(5)	C3'-H3'1	0.99
N4-C3'	1.465(4)		

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

Table S11 Selected angles ( ) of of **9**

Parameter	°	Parameter	°
N2-N1-N4	121.7(3)	N6-C4-C3	111.3(13)
N2-N1-C2	112.2(3)	N5-C4-N6	102.1(14)
N4-N1-C2	126.0(3)	N5-C4-C3	114.9(11)
N1-N2-N3	105.9(3)	F1-C4-N5	105.5(16)
N2-N3-C1	109.0(3)	F1-C4-C3	115.4(15)
N1-N4-C3'	111.7(2)	F1-C4-N6	106.7(13)

N1-N4-C3	111.7(2)	F1'-C4'-N6'	108.3(13)
O1-N5-O2	128(2)	F1'-C4'-C3'	111.3(13)
O1-N5-C4	117(2)	F1'-C4'-N5'	107.5(15)
O2-N5-C4	114.8(19)	N5'-C4'-C3'	111.7(11)
O2'-N5'-C4	115.7(17	N6'-C4'-C3'	111.2(11)
O1'-N5'-O2	127(2	N5'-C4'-N6'	106.6(13)
O1'-N5'-C4	117.0(18	N3-C1-H1	125
O3-N6-C4	112.8(16)	C2-C1-H1	125
O4-N6-C4	113.7(17)	C1-C2-H2	128
O4'-N6'-C4	118.7(19	C4-C3-H3A	111
O3'-N6'-O4	125(2	C4-C3-H3B	111
O3'-N6'-C4	116.1(16	H3A-C3-H3B	109
C3'-N4-H4A	111(2)	N4-C3-H3B	111
N1-N4-H4A	106.9(19)	N4-C3-H3A	111
C3-N4-H4A	111(2)	H3'-C3'-H3'2	108
N3-C1-C2	109.3(3)	C4'-C3'-H3'2	110
N1-C2-C1	103.6(3)	N4-C3'-H3'1	110
N4-C3-C4	105.6(7)	N4-C3'-H3'2	110
N4-C3'-C4'	108.6(6)	C4'-C3'-H3'1	110

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

Table S12 Selected torsion angles for **10**

Parameter	°	Parameter	°
N4-N1-N2-N3	179.4(3)	O1'-N5'-C4'-N6'	-99(2)
C2-N1-N2-N3	0.4(3)	O2'-N5'-C4'-N6'	81(2)
N2-N1-N4-C3'	66.5(4)	O2'-N5'-C4'-F1'	-35(2)
C2-N1-N4-C3'	-114.6(3)	O3'-N6'-C4'-F1'	-171(2)
N2-N1-C2-C1	-0.4(4)	O3'-N6'-C4'-N5'	73(2)
N4-N1-C2-C1	-179.4(3)	O4'-N6'-C4'-C3'	128(2)
N1-N2-N3-C1	-0.2(4)	O4'-N6'-C4'-N5'	-110(2)
N2-N3-C1-C2	0.0(4)	O4'-N6'-C4'-F1'	5(3)
N1-N4-C3'-C4'	130.4(6)	O3'-N6'-C4'-C3'	-49(2)
O1'-N5'-C4'-F1'	145(2)	N3-C1-C2-N1	0.3(4)
O1'-N5'-C4'-C3'	23(2)	N4-C3'-C4'-N5'	-172.4(10)
O2'-N5'-C4'-C3'	-157.0(16)	N4-C3'-C4'-N6'	-53.4(12)
N4-C3'-C4'-F1'	67.4(13)		

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

Table S13 Hydrogen bonds present in **10**.

D—H•••A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °	comment
N4—H4 •••N3	0.87(3)	2.11(3)	2.910(4)	154(3)	inter
C3—H3'1 ••• O3'	0.99	2.56	3.53(2)	164	inter
C3—H3'2 ••• O4'	0.99	2.34	3.031(14)	126	inter

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

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

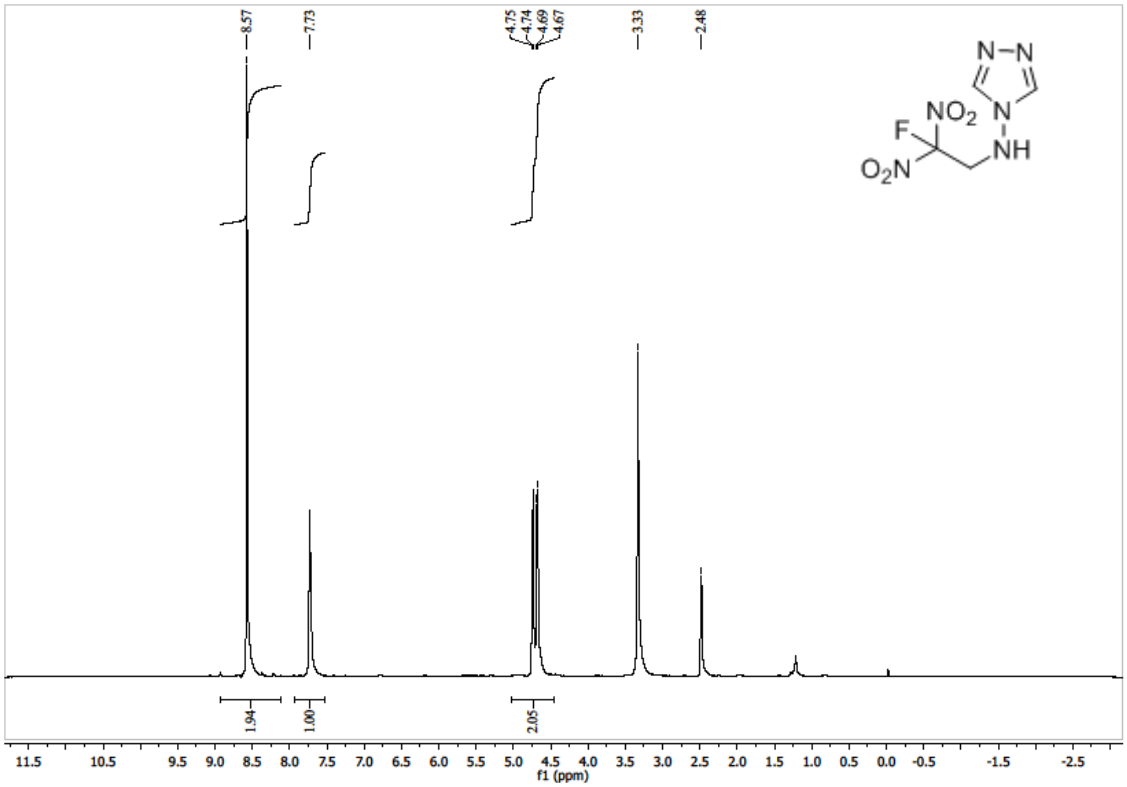


Fig. S7 ^{1}H-NMR spectrum of **6** in DMSO-d_6.

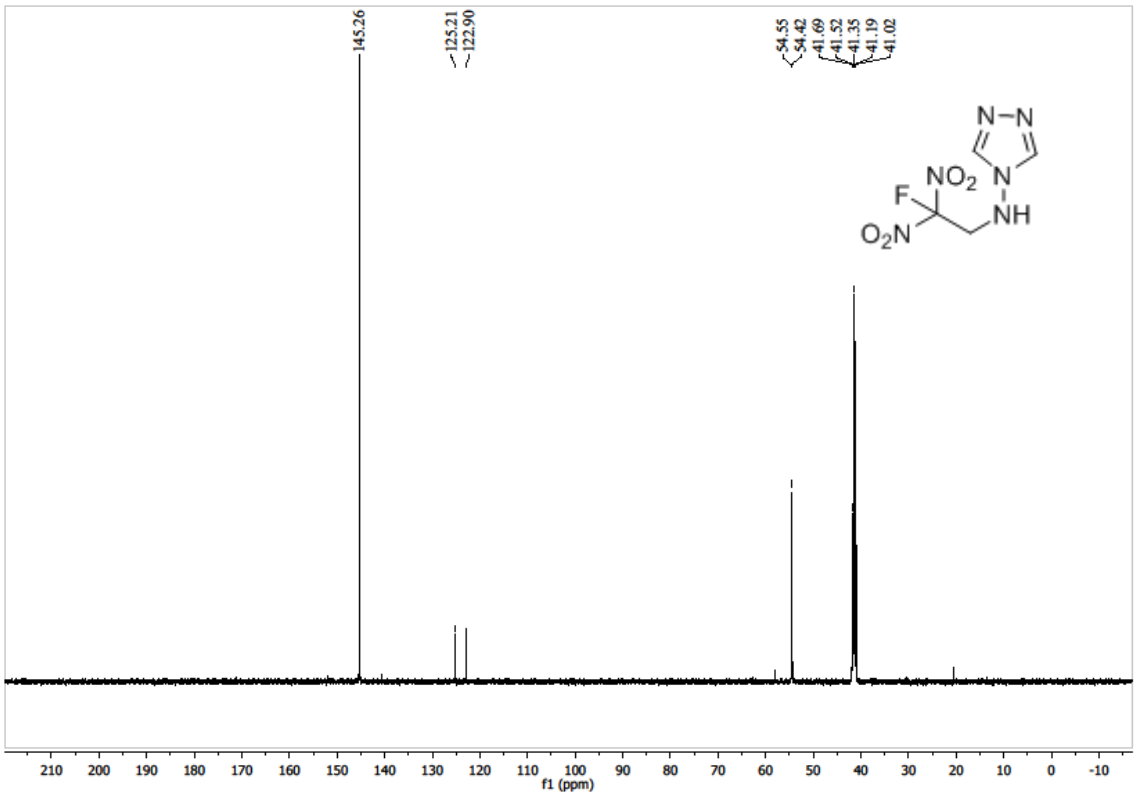


Fig. S8 ^{13}C-NMR spectrum of **6** in DMSO-d_6.

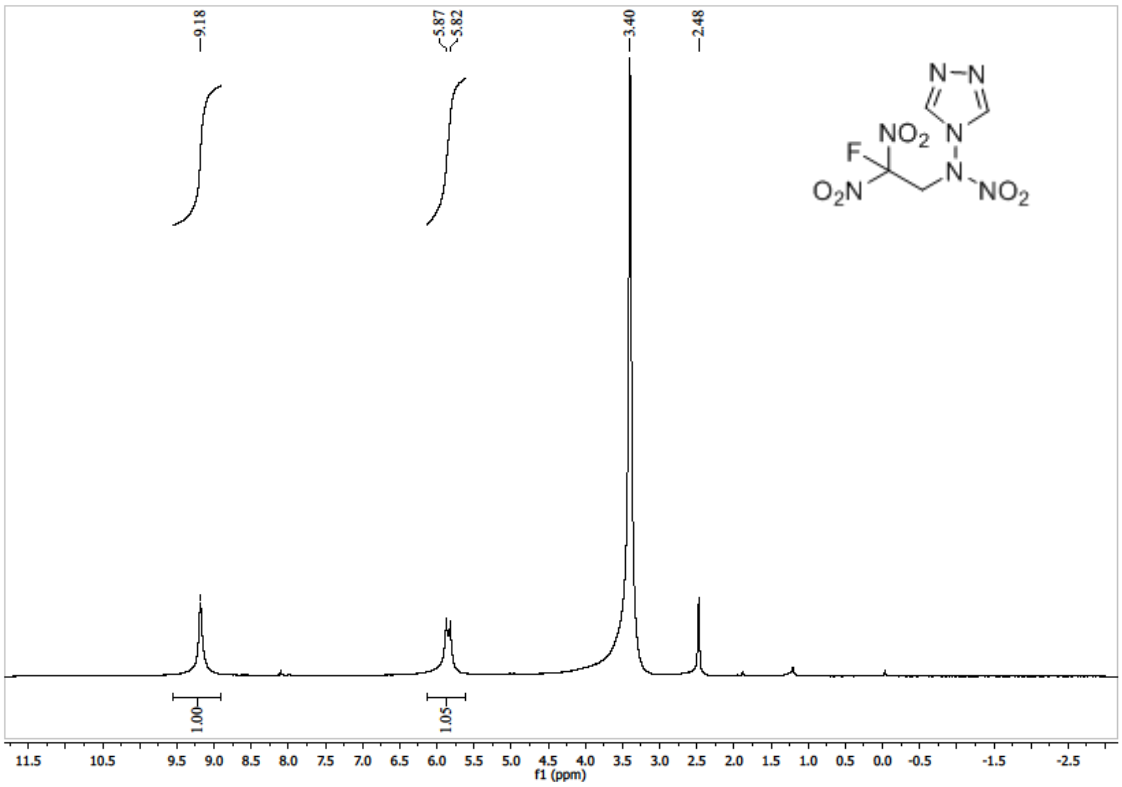


Fig. S9 ^{1}H-NMR spectrum of **7** in DMSO-d_6.

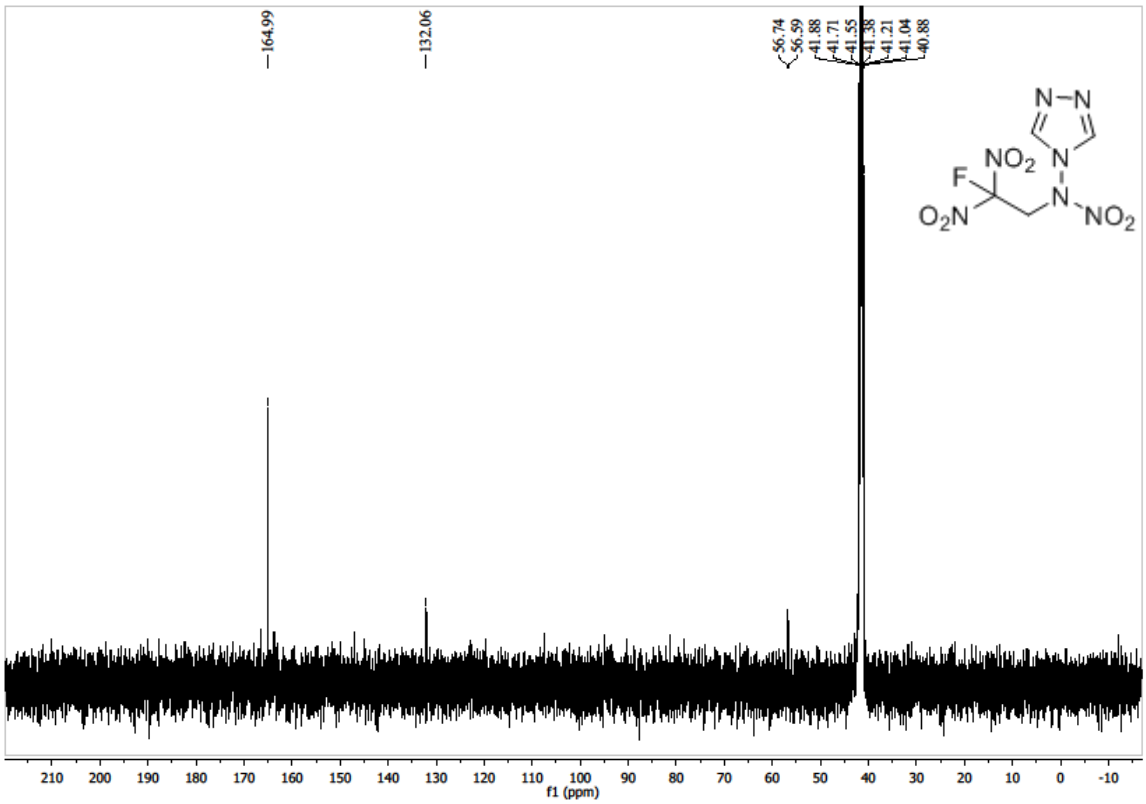


Fig. S10 ^{13}C-NMR spectrum of **7** in DMSO-d_6.

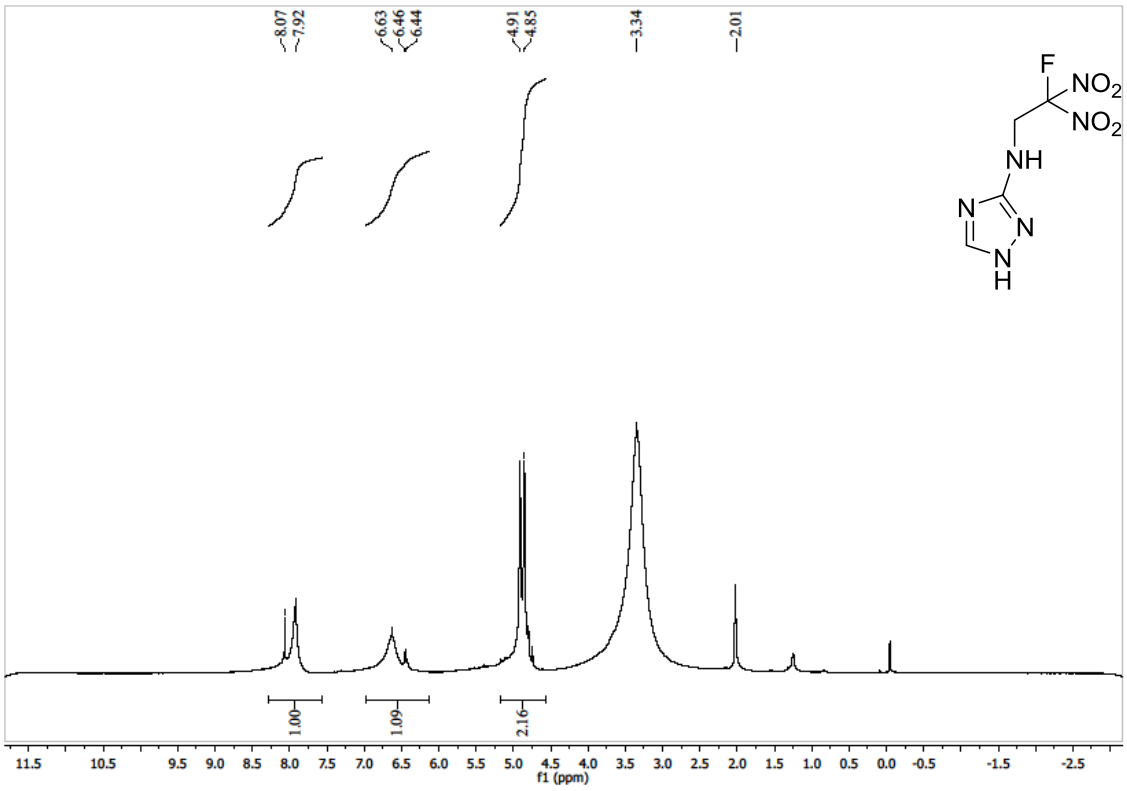


Fig. S11 [1]H-NMR spectrum of **8** in Acetone-d_6.

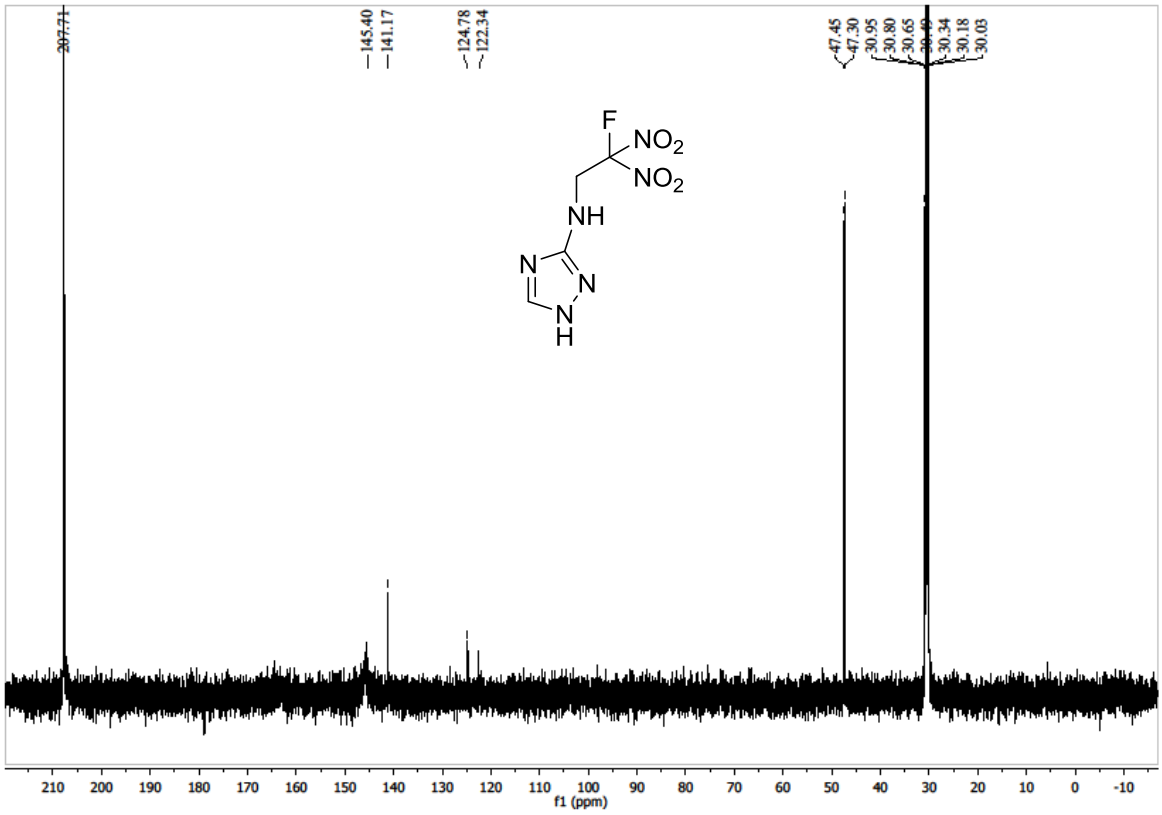


Fig. S12 [13]C-NMR spectrum of **8** in Acetone-d_6.

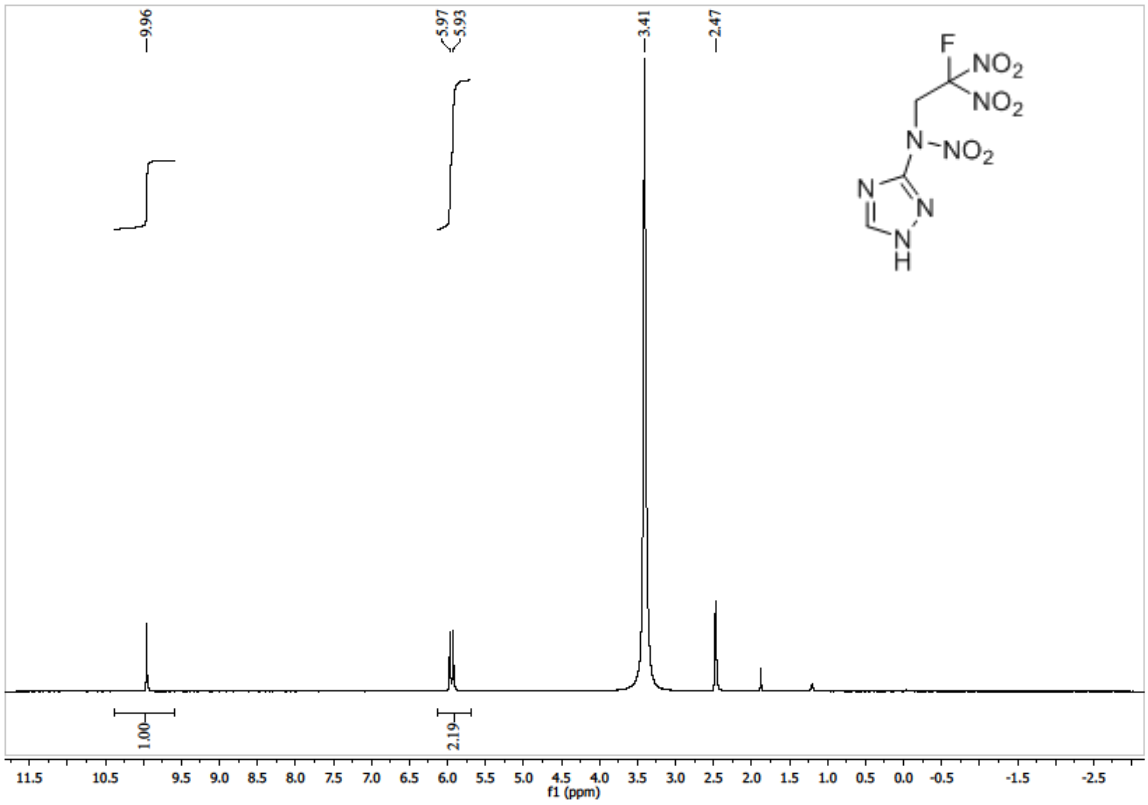


Fig. S13 ^{1}H-NMR spectrum of **9** in DMSO-d_6.

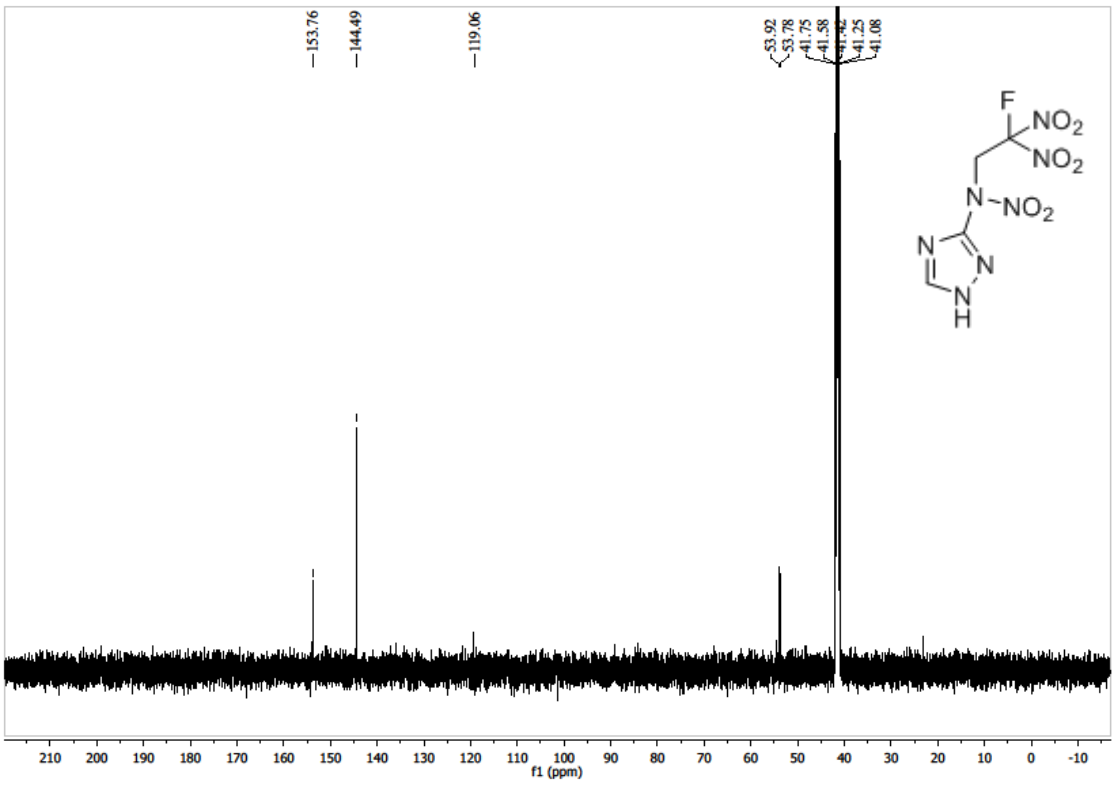


Fig. S14 ^{13}C-NMR spectrum of **9** in DMSO-d_6.

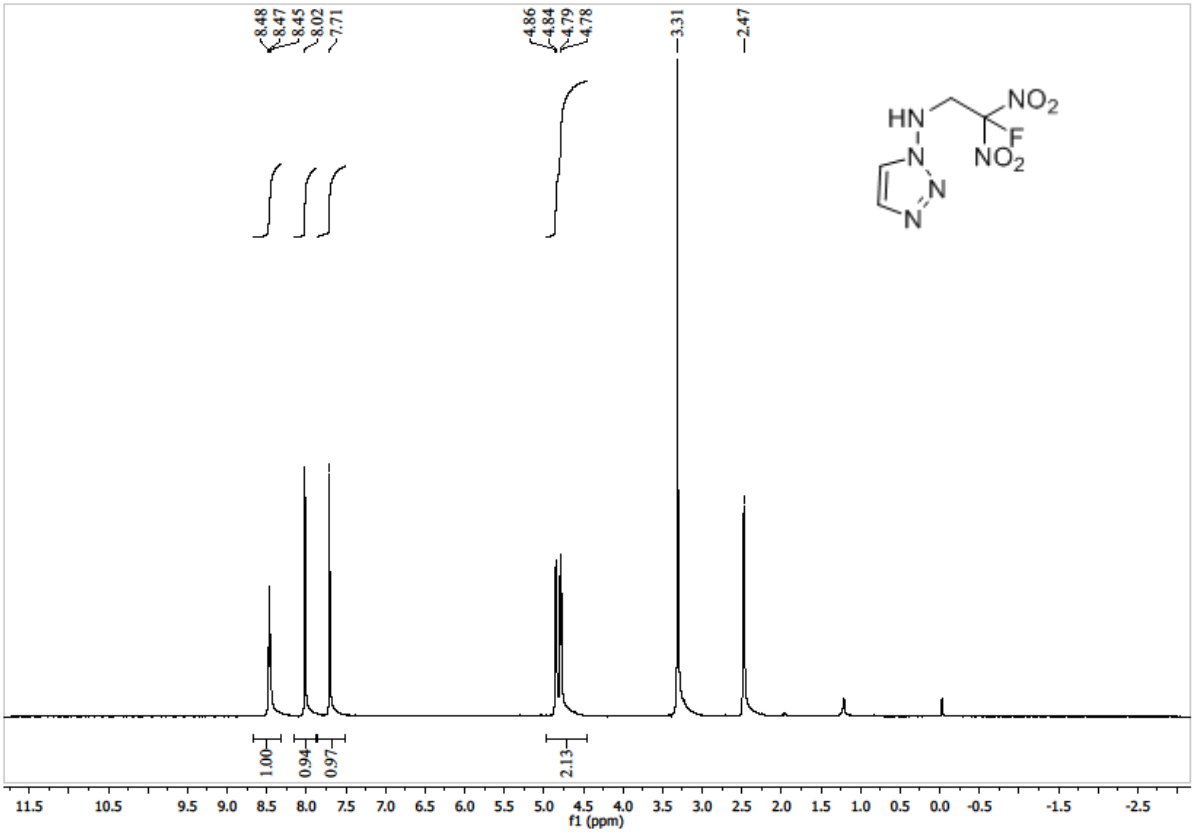


Fig. S15[1]H-NMR spectrum of **10** in DMSO-d_6.

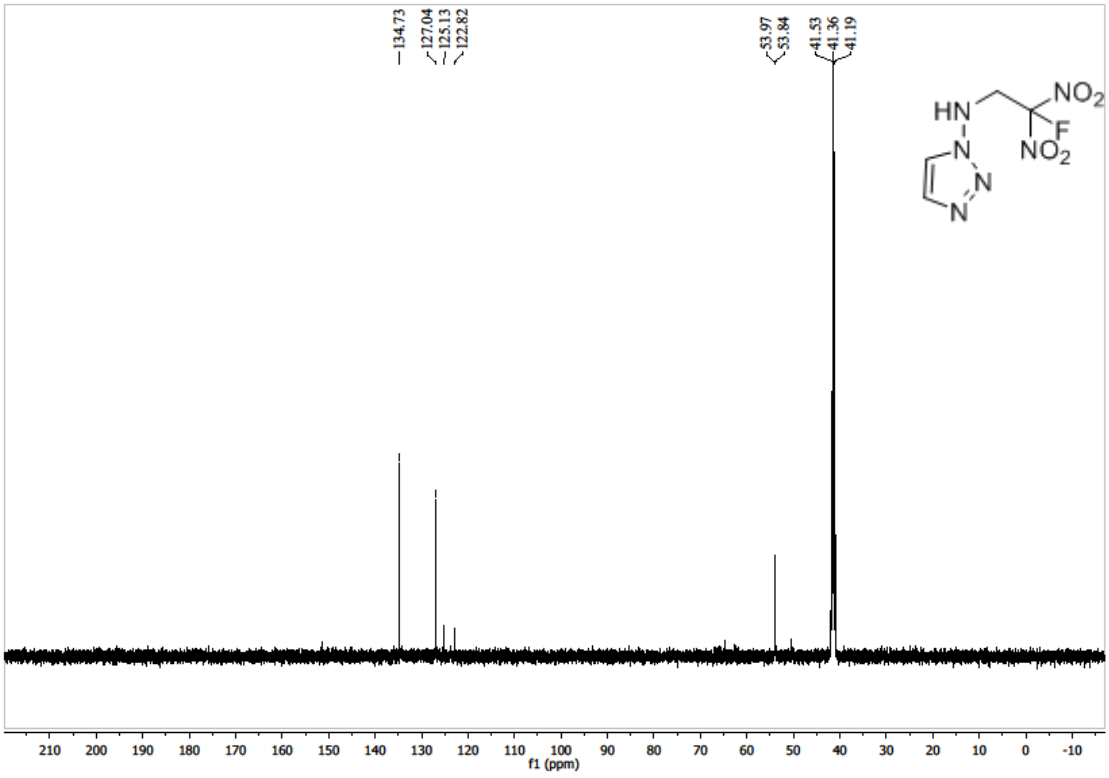


Fig. S16 [13]C-NMR spectrum of **10** in DMSO-d_6.

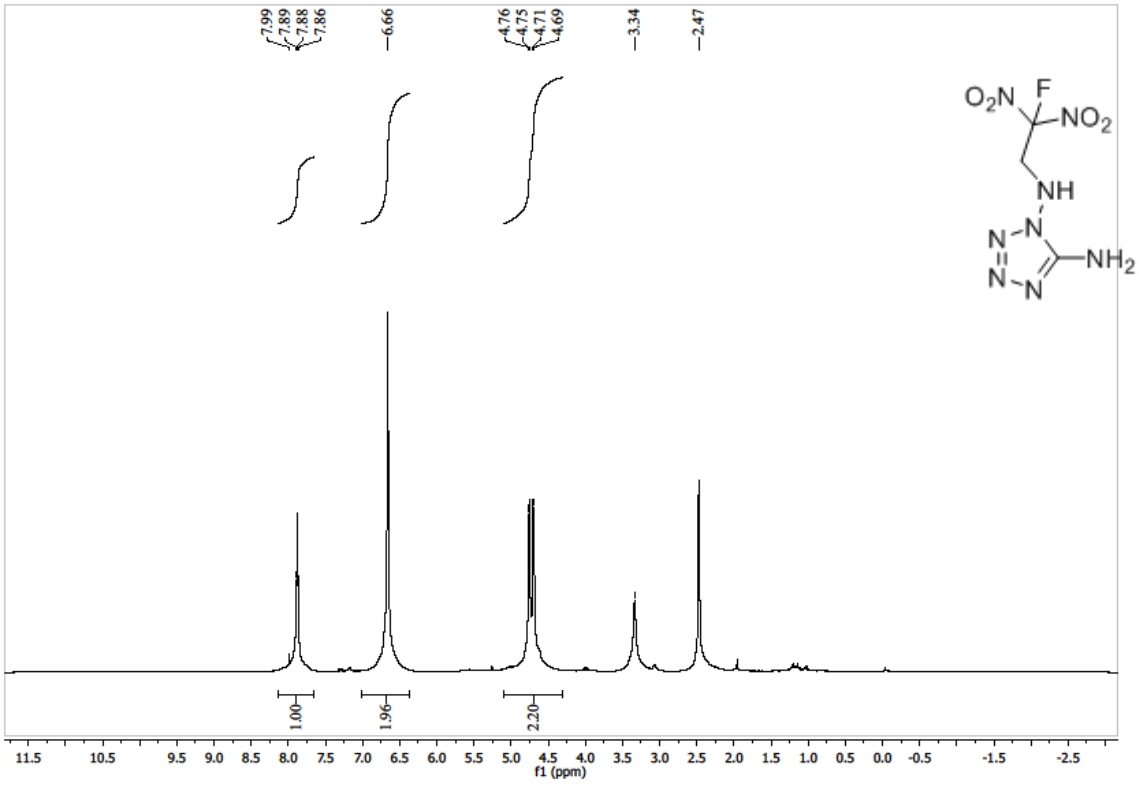


Fig. S17 ^{1}H-NMR spectrum of **11** in DMSO-d_6.

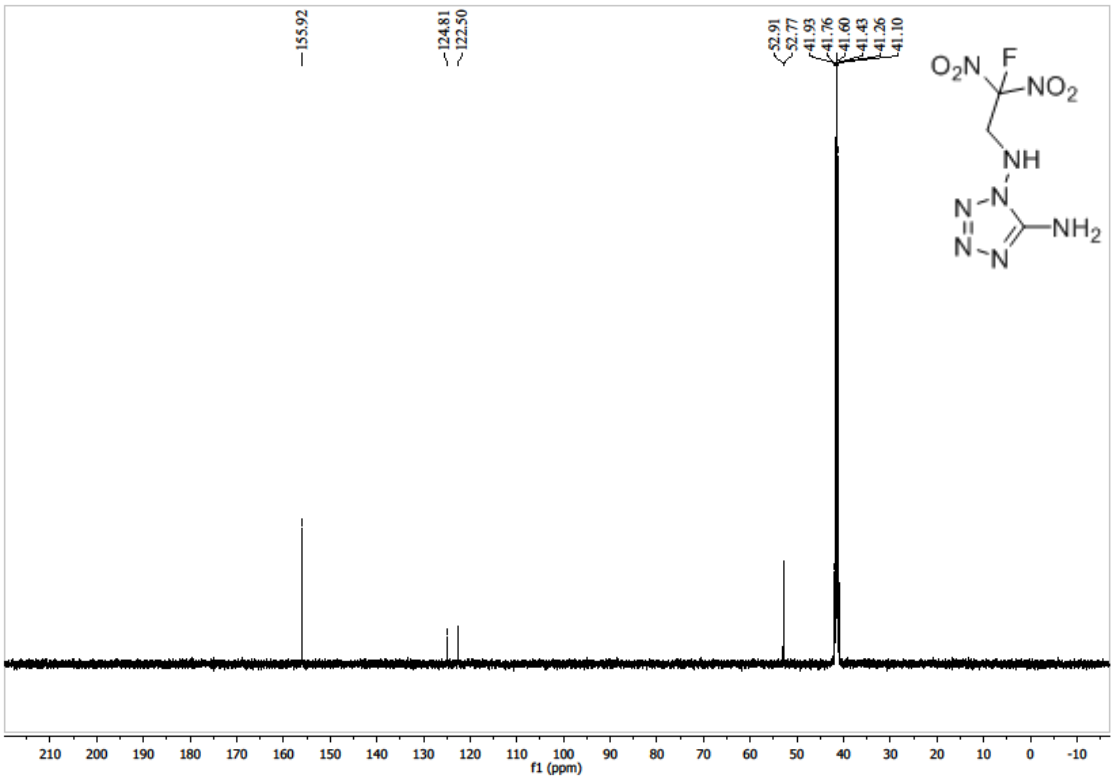


Fig. S18 ^{13}C-NMR spectrum of **11** in DMSO-d_6.

References

1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian 09, revision A. 01; Gaussian, Inc.: Wallingford, CT, 2009.

2 (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652; (b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem*, 1994, **98**, 11623-11627.

3 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213-222.

4 J. W. Ochterski, G. A. Petersson and J. A. Montgomery, *J. Chem. Phys*, 1996, **104**, 2598.

5 D. R. Lide, *CRC Handbook of Chemistry and Physics*, 88th ed. (Internet Version 2008), CRC Press/Taylor and Francis, Boca Raton, 2007-2008.

6 N. Fischer, T. M. Klapötke and J. Stierstorfer, *Z. Anorg. Allg. Chem*, 2009, **635**, 271-281.

7 Y.-H. Joo, J. H. Chung, S. G. Cho and E. M. Goh, *New. J. Chem*, 2013, **37**, 1180-1188.

8 M. J. Kamlet and S. J. Jacobs, *J. Chem. Phys*, 1968, **48**, 3685-3692.