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High-performing and Thermally Stable Energetic 3,7-Diamino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazole derivatives

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1. Crystal Structure Data

Table S1. Crystal data and structure refinement for **4**.

Identification code	**4**	
CCDC number	1526400	
Empirical formula	$C_3H_5N_7O_3$	
Formula weight	187.14	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.6446(6) Å	α□= 90°
	b = 14.4368(7) Å	β□= 96.954(2)°
	c = 7.7331(4) Å	γ□ = 90°
Volume	1401.27(12) $Å^3$	
Z	8	
Density (-123 °C)	1.774 Mg/m^3	
Denisty (20 °C)	1.738 Mg/m^3	
Absorption coefficient	0.155 mm^{-1}	
F(000)	768	
Crystal size	0.258 × 0.215 × 0.029 mm^3	
Theta range for data collection	2.150 to 26.360°.	
Index ranges	-15<=h<=15, -18<=k<=18, -9<=l<=9	
Reflections collected	16794	
Independent reflections	2858 [R_{int} = 0.0349]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7460 and 0.6876	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2858 / 8 / 257	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R_1 = 0.0367, wR_2 = 0.0928	
R indices (all data)	R_1 = 0.0545, wR_2 = 0.1011	
Largest diff. peak and hole	0.229 and -0.231 e.$Å^{-3}$	

Table S2. Crystal data and structure refinement for **7**.

Identification code	**7**	
CCDC Number	1526401	
Empirical formula	$C_8H_{16}N_{20}O_7$	
Formula weight	504.41	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.9443(6) Å	α□= 90°
	b = 22.3674(10) Å	β□= 103.600(2)°
	c = 6.8059(3) Å	γ□ = 90°
Volume	1915.26(15) $Å^3$	
Z	4	
Density (-123°C)	1.749 Mg/m^3	
Density (20°C)	1.712 Mg/m^3	
Absorption coefficient	0.151 mm^{-1}	
F(000)	1040	
Crystal size	0.295 × 0.081 × 0.030 mm^3	
Theta range for data collection	3.176 to 26.368°.	
Index ranges	-16<=h<=16, -25<=k<=27, -8<=l<=8	
Reflections collected	18805	
Independent reflections	3923 [R_{int} = 0.0529]	
Completeness to theta = 25.000°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3923 / 6 / 340	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R_1 = 0.0387, wR_2 = 0.0850	
R indices (all data)	R_1 = 0.0699, wR_2 = 0.0963	
Largest diff. peak and hole	0.253 and -0.270 e.$Å^{-3}$	

Table S3. Hydrogen bonds for **4** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6)...O(2)	0.88	2.19	2.651(2)	112.6
N(6)-H(6)...O(26A)	0.88	1.94	2.747(4)	151.8
N(6)-H(6)...O(26B)	0.88	1.82	2.649(4)	157.1
N(9)-H(9)...O(13)#1	0.88	2.05	2.9269(19)	174.9
N(9)-H(9)...O(14)#1	0.88	2.39	2.997(2)	126.4
N(18)-H(18)...O(14)	0.88	2.14	2.6051(19)	112.2
N(18)-H(18)...O(25)#3	0.88	1.88	2.718(2)	159.9
N(21)-H(21)...O(1)	0.88	2.49	3.198(2)	137.6
N(21)-H(21)...N(4)	0.88	1.98	2.841(2)	165.5
C(22)-H(22)...O(13)#2	0.95	2.52	3.102(2)	119.3
O(25)-H(25A)...N(7)	0.821(10)	2.411(16)	3.124(2)	146(2)
O(25)-H(25A)...O(26A)#4	0.821(10)	2.43(2)	3.047(7)	132(2)
O(25)-H(25B)...O(2)#5	0.823(10)	2.139(13)	2.9008(19)	154(2)
O(26A)-H(26A)...O(1)#5	0.834(10)	2.096(18)	2.761(3)	136(2)
O(26A)-H(26B)...N(19)#5	0.838(10)	2.315(15)	2.967(3)	134.9(17)

Symmetry transformations used to generate equivalent atoms:
#1 x,y+1,z #2 -x+2,y+1/2,-z+1/2 #3 x,y-1,z
#4 x,-y+3/2,z-1/2 #5 -x+1,y+1/2,-z+3/2

Table S4. Hydrogen bonds for **7** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(14)-H(14A)...O(2)#1	0.88	1.97	2.748(2)	146.7
N(14)-H(14A)...N(3)#1	0.88	2.68	3.517(2)	158.9
N(14)-H(14B)...O(35)#1	0.88	2.02	2.893(2)	174.3
N(16)-H(16)...O(1)#1	0.88	2.63	3.363(2)	142.0
N(16)-H(16)...N(30)#1	0.88	2.30	3.003(2)	137.2
C(21)-H(21)...O(7)#2	0.95	2.44	2.976(2)	116.0
C(21)-H(21)...N(33)#2	0.95	2.53	3.297(3)	137.8
N(23)-H(23B)...N(11)#3	0.91(2)	2.68(2)	3.565(2)	164.9(19)
N(23)-H(23B)...O(12)#3	0.91(2)	1.99(2)	2.826(2)	152(2)
N(23)-H(23A)...N(8)	0.96(2)	2.23(2)	3.148(3)	160.7(19)
N(23)-H(23A)...O(13)	0.96(2)	2.44(2)	3.021(2)	119.1(17)
N(24)-H(24A)...N(10)#4	0.88	2.05	2.890(2)	159.4
N(24)-H(24B)...N(17)#1	0.88	2.17	3.028(2)	164.7
N(26)-H(26)...O(2)#4	0.88	1.98	2.749(2)	145.8
N(26)-H(26)...N(3)#4	0.88	2.59	3.461(2)	172.7
N(26)-H(26)...N(4)#4	0.88	2.38	3.202(2)	155.2

C(31)-H(31)...O(1)	0.95	2.54	3.126(2)	120.0
C(31)-H(31)...N(6)	0.95	2.51	3.350(3)	147.8
N(33)-H(33B)...O(34)	0.91(3)	2.56(3)	3.371(3)	149(2)
N(33)-H(33A)...O(35)#5	0.91(3)	2.09(3)	2.977(3)	166(2)
O(34)-H(34A)...N(27)#6	0.839(10)	2.135(14)	2.942(2)	161(3)
O(34)-H(34B)...O(13)#2	0.835(10)	2.303(15)	3.072(2)	154(3)
O(35)-H(35B)...N(8)#7	0.833(10)	2.268(10)	3.101(2)	178(3)
O(35)-H(35B)...O(13)#7	0.833(10)	2.54(3)	2.976(2)	113(2)
O(35)-H(35A)...O(34)#8	0.841(10)	2.005(10)	2.844(3)	175(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1 #2 -x,-y+1,-z+1 #3 x,-y+1/2,z+1/2
#4 -x+1,y+1/2,-z+1/2 #5 -x+1,-y+1,-z #6 x,-y+3/2,z+1/2
#7 x+1,y,z #8 -x+1,y-1/2,-z+1/2

2. Theoretical Calculation

The gas phase enthalpies of formation were calculated based on G2 method. The enthalpy of reaction is obtained by combining the MP2/6–311++G** energy difference for the reactions, the scaled zero point energies (ZPE), values of thermal correction (HT), and other thermal factors. The solid state heats of formation of compounds **3** and **4** were calculated with Trouton's rule according to equation (1) (*T* represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition).

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

For energetic salts **5** **11**, the solid-phase enthalpy of formation is obtained using a Born−Haber energy cycle. For the compound which is a hydrate (**4** and **6**), the solid-phase enthalpy of formation is obtained by adding the gas phase heat of formation of anhydrous compound to that of water (-241.8 kJ mol^{-1}).

Table S5. Calculated the solid state heat of formation (*HOF*)

Compound	ΔH_L (kJ mol^{-1})	ΔH_f^{Cation} (kJ mol^{-1})	ΔH_f^{Anion} (kJ mol^{-1})	ΔH_f^{298} (kJ mol^{-1})
5	495.13	1137.35	-277.8	364.4
6	503.70	1137.35	-307.9	325.8
7	1126.37	1137.35	263.3	1411.6
8	1055.32	1137.35	463.5	1682.9
9	1052.54	1137.35	631.0	1853.2
10	1056.83	1137.35	664.1	1882.0
11	516.31	770	364.41	618.1

3. NMR spectra

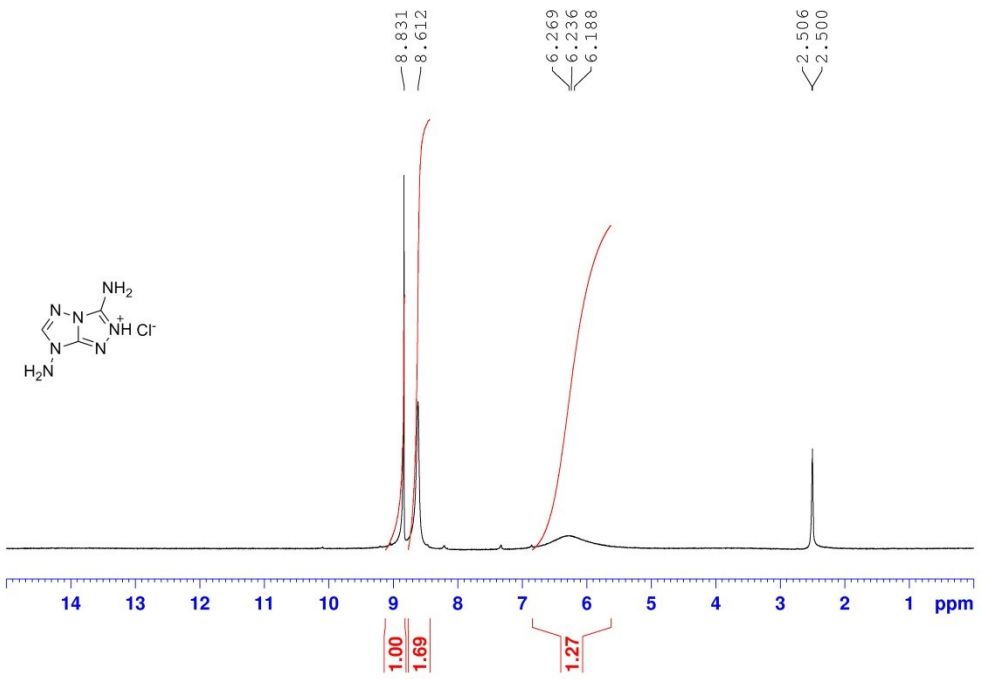

Fig. S1. ^{1}H NMR spectrum of **2**

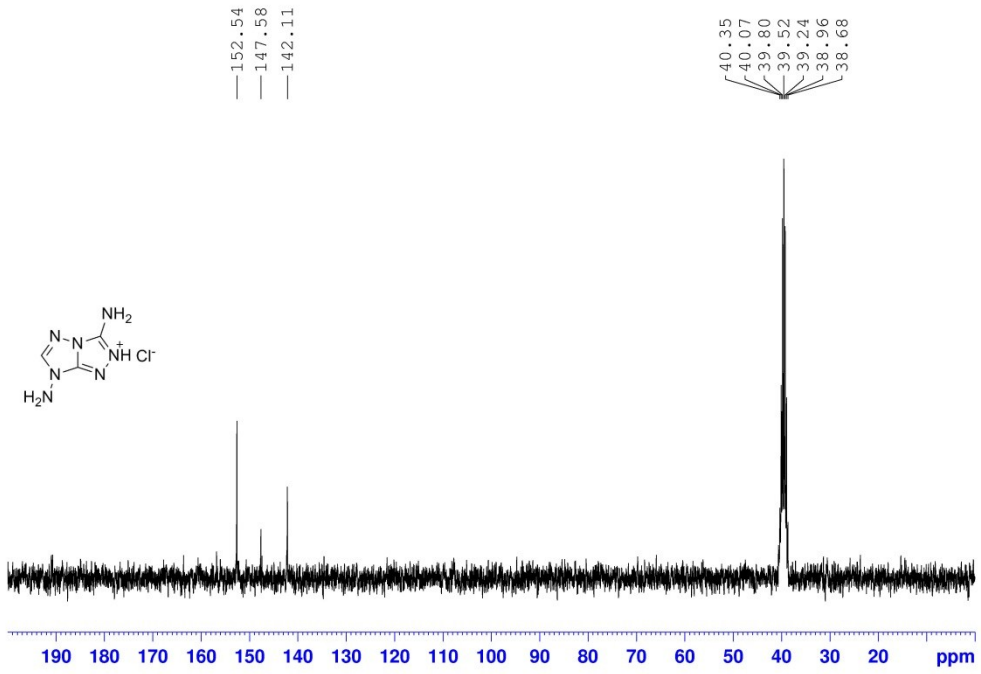

Fig. S2. ^{13}C NMR spectrum of **2**

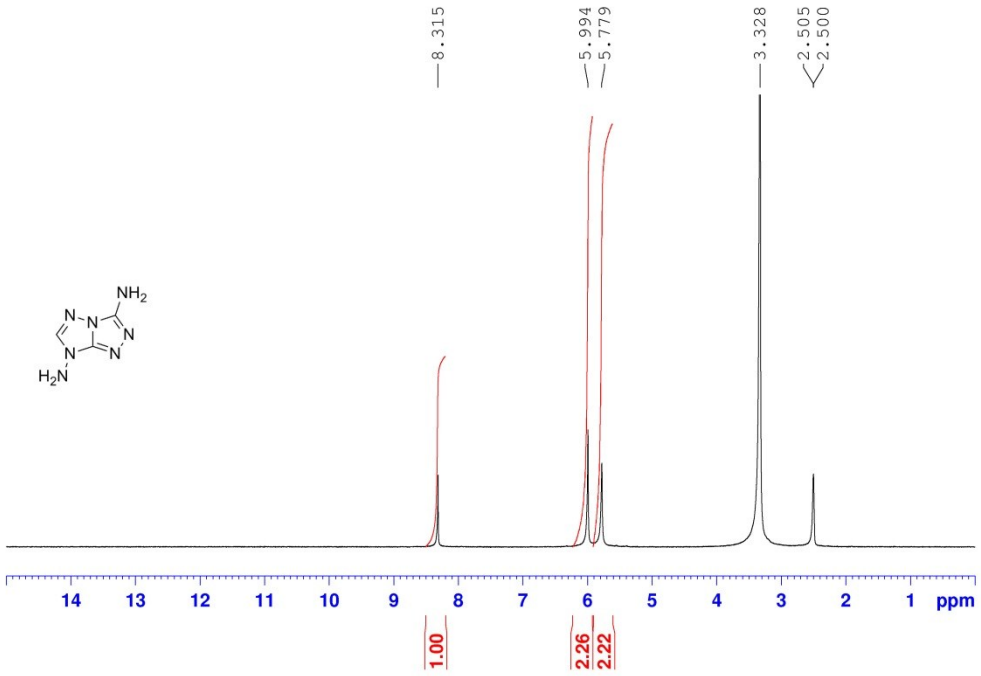

Fig. S3. ^{1}H NMR spectrum of **3**

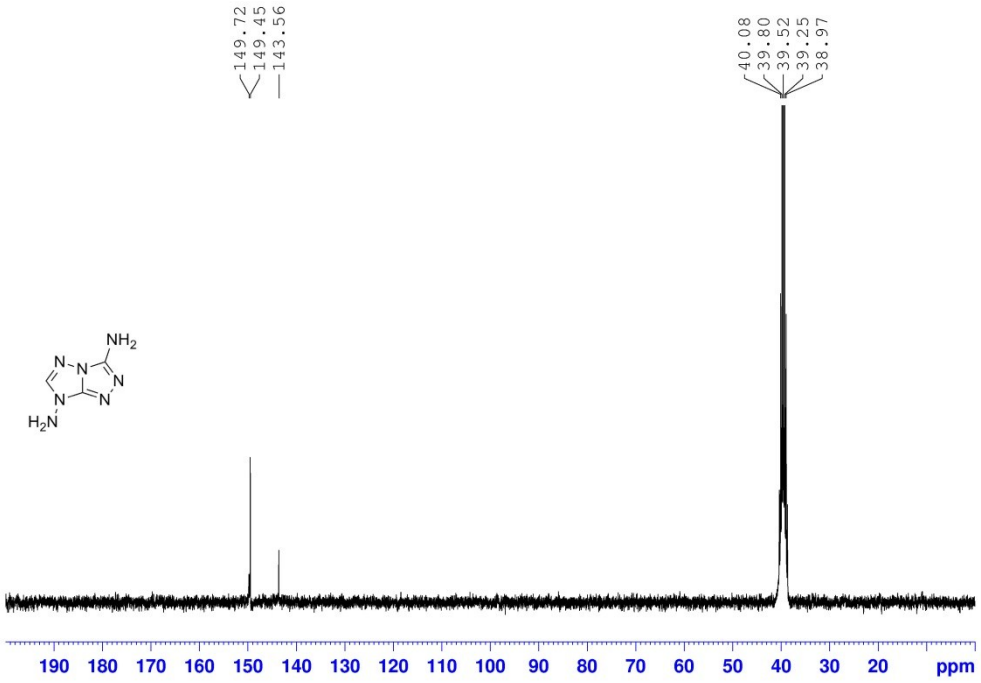

Fig. S4. ^{13}C NMR spectrum of **3**

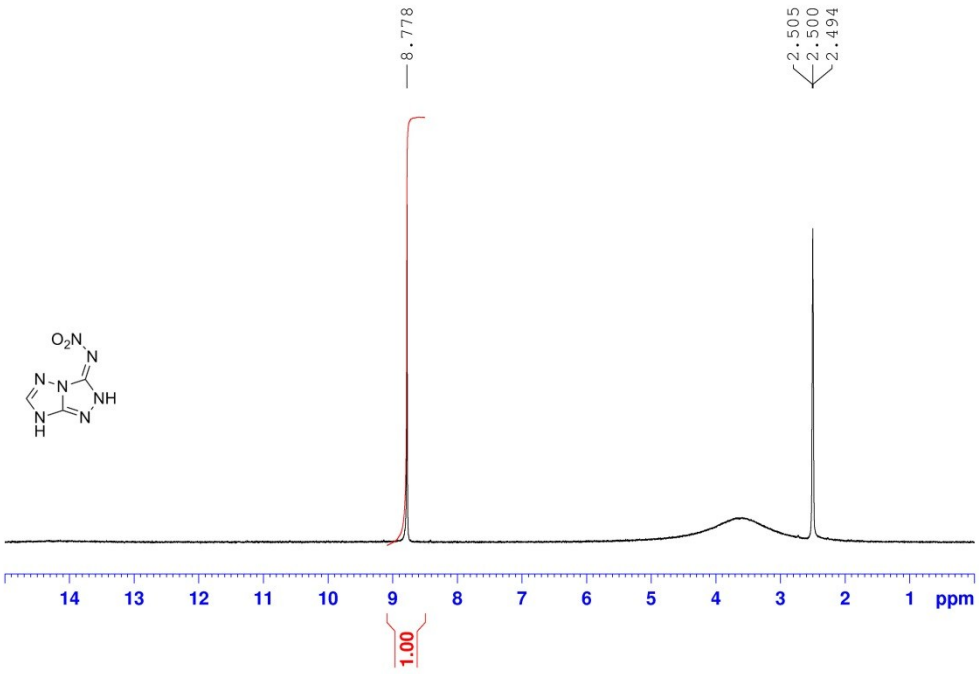

Fig. S5. ^{1}H NMR spectrum of **4**

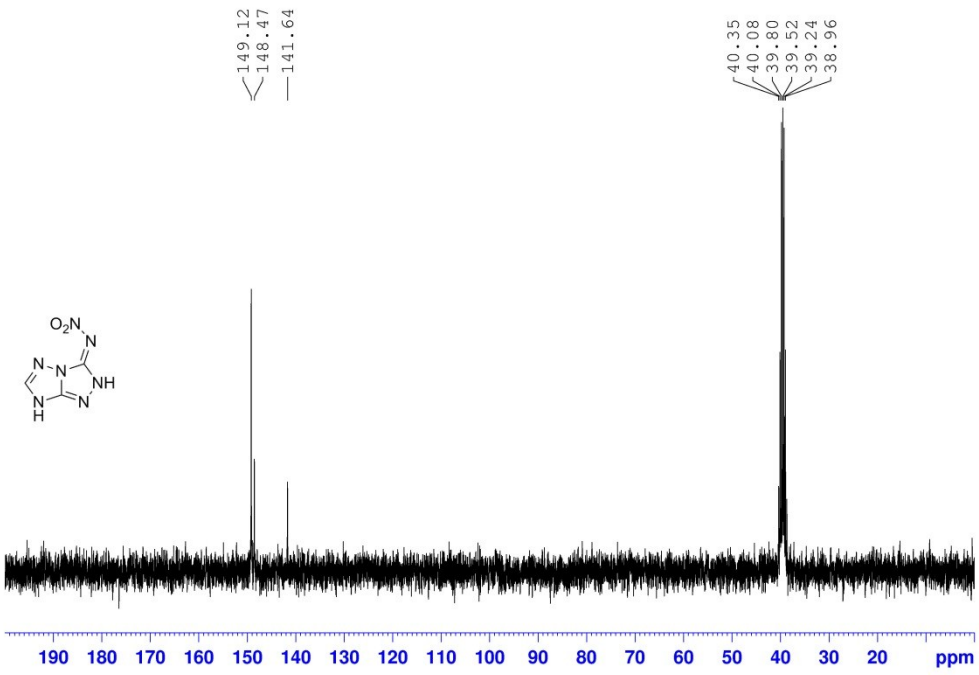

Fig. S6. ^{13}C NMR spectrum of **4**

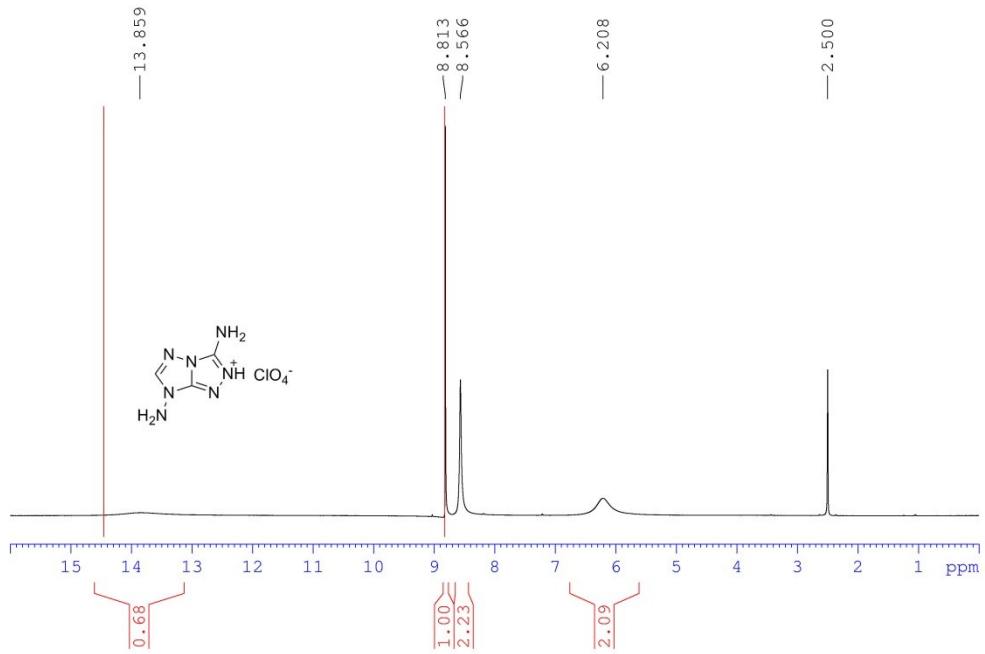

Fig. S7. ^{1}H NMR spectrum of **5**

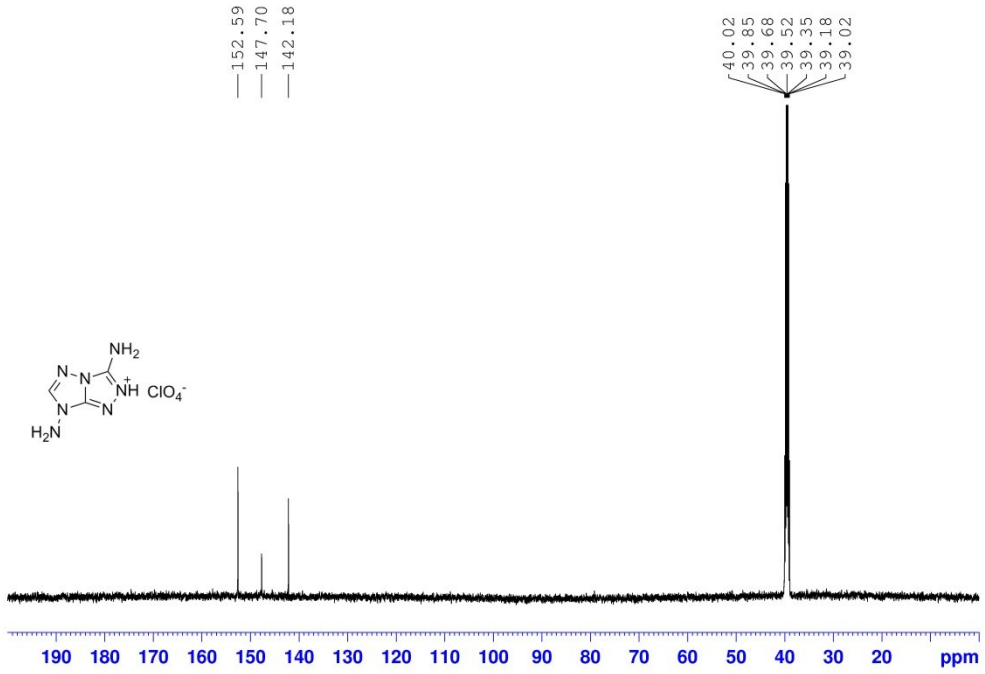

Fig. S8. ^{13}C NMR spectrum of **5**

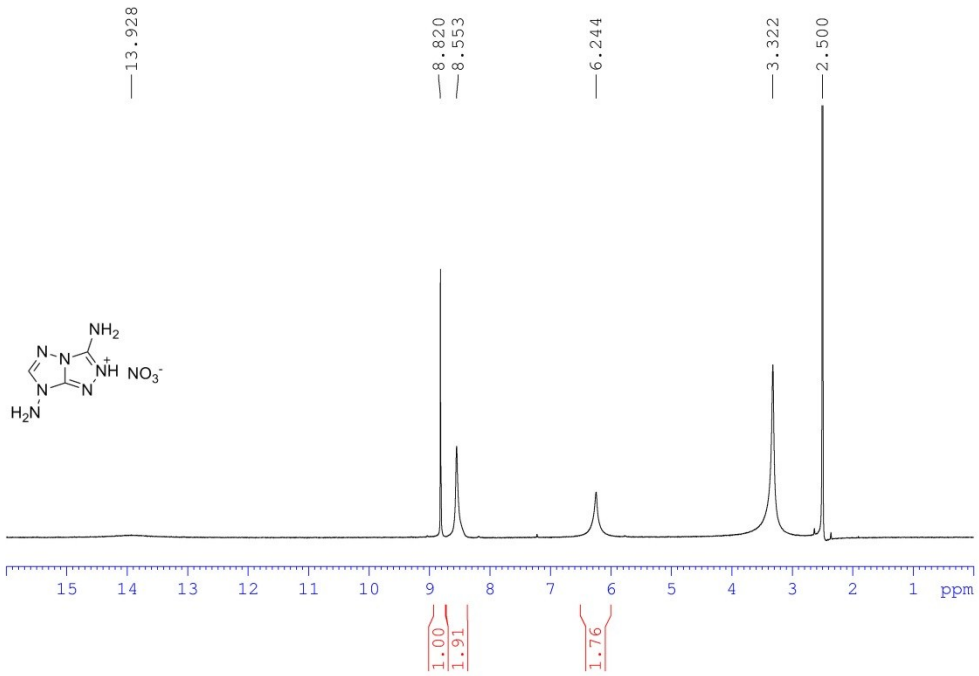

Fig. S9. ^{1}H NMR spectrum of **6**

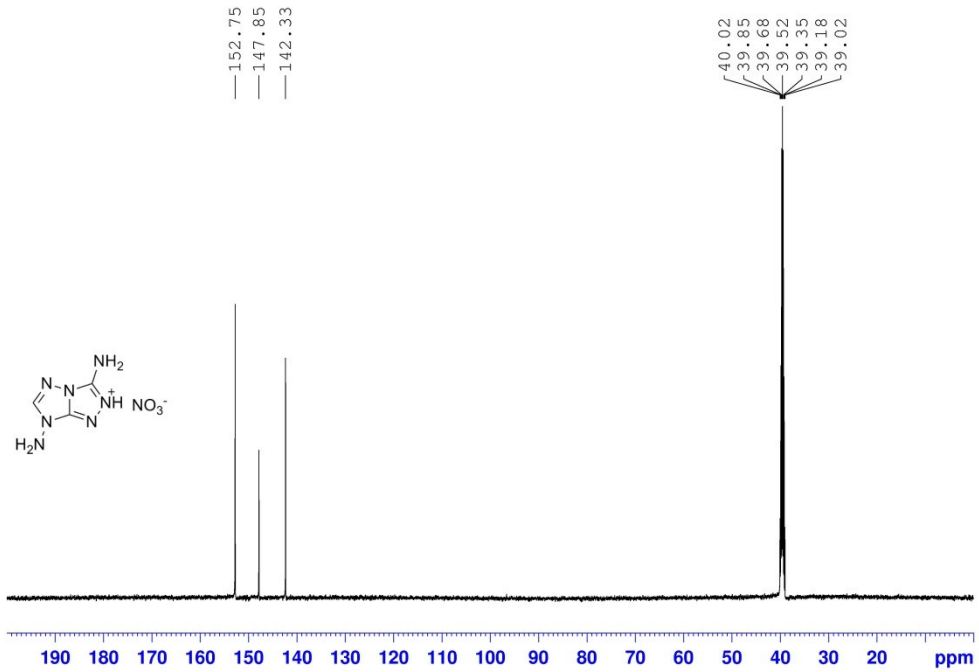

Fig. S10. ^{13}C NMR spectrum of **6**

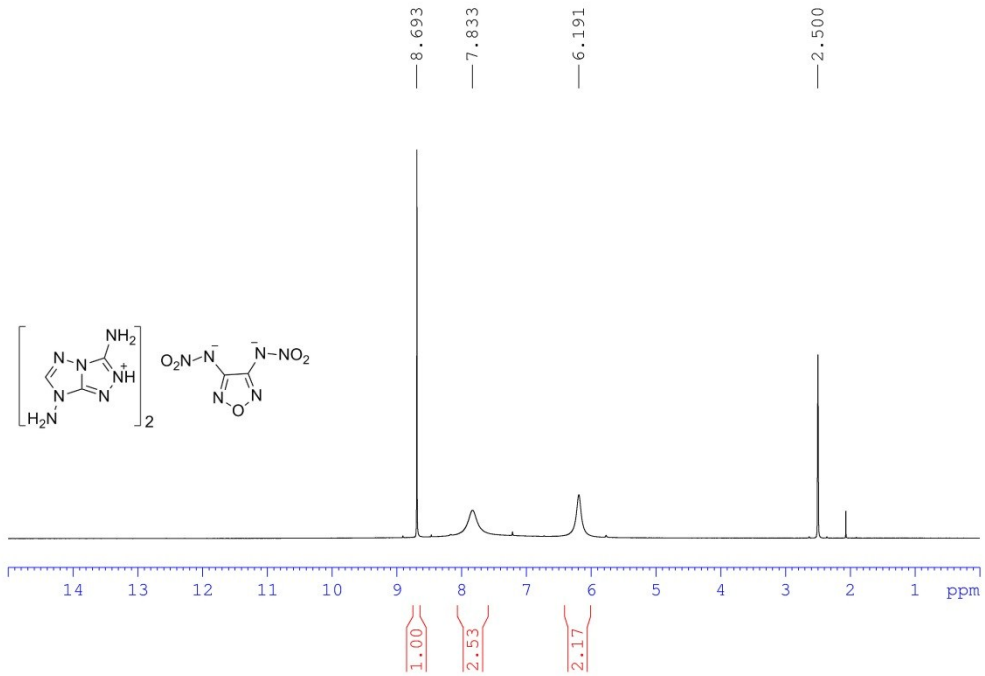

Fig. S11. ^{1}H NMR spectrum of **7**

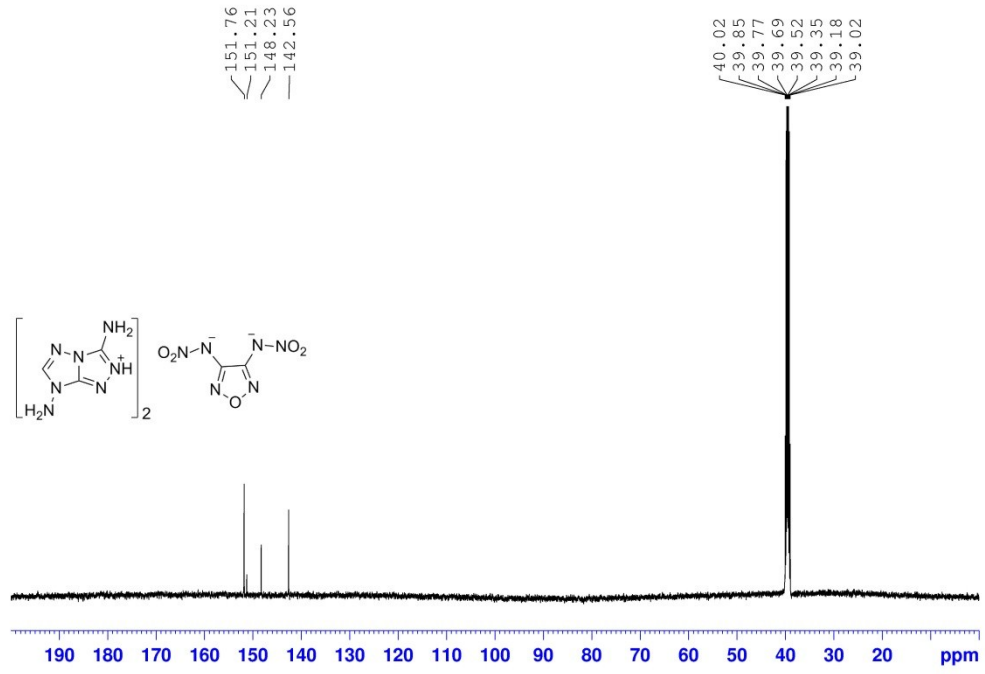

Fig. S12. ^{13}C NMR spectrum of **7**

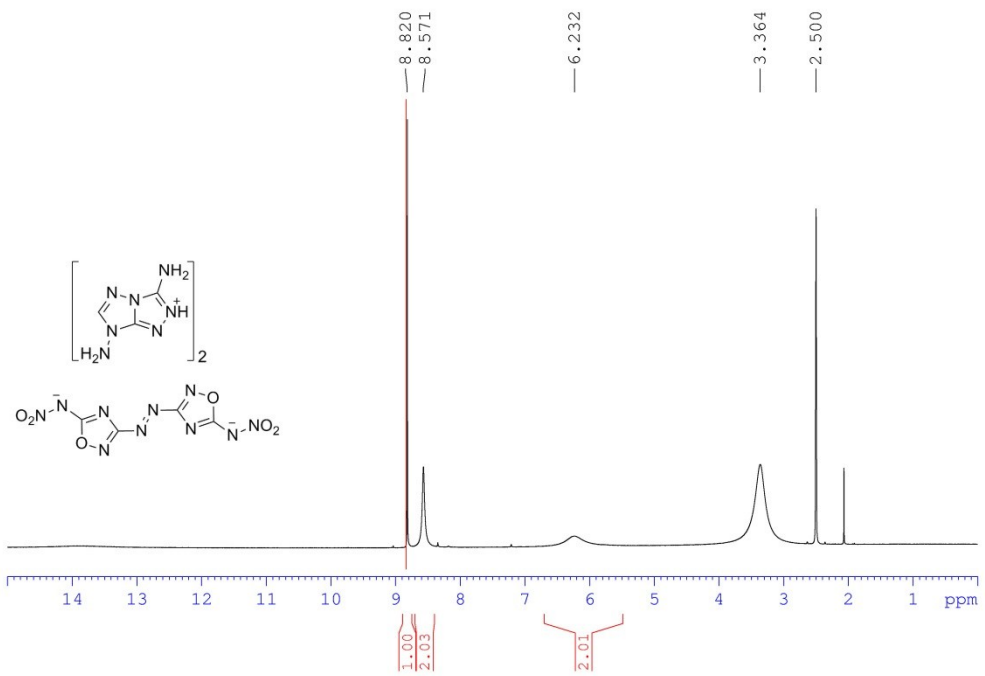

Fig. S13. ^{1}H NMR spectrum of **8**

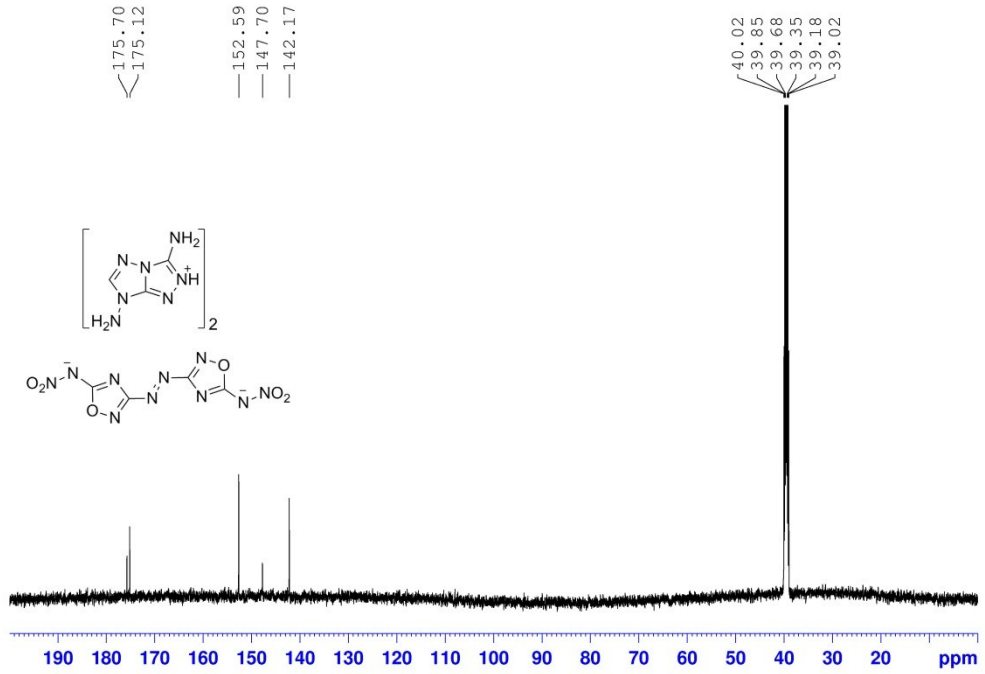

Fig. S14. ^{13}C NMR spectrum of **8**

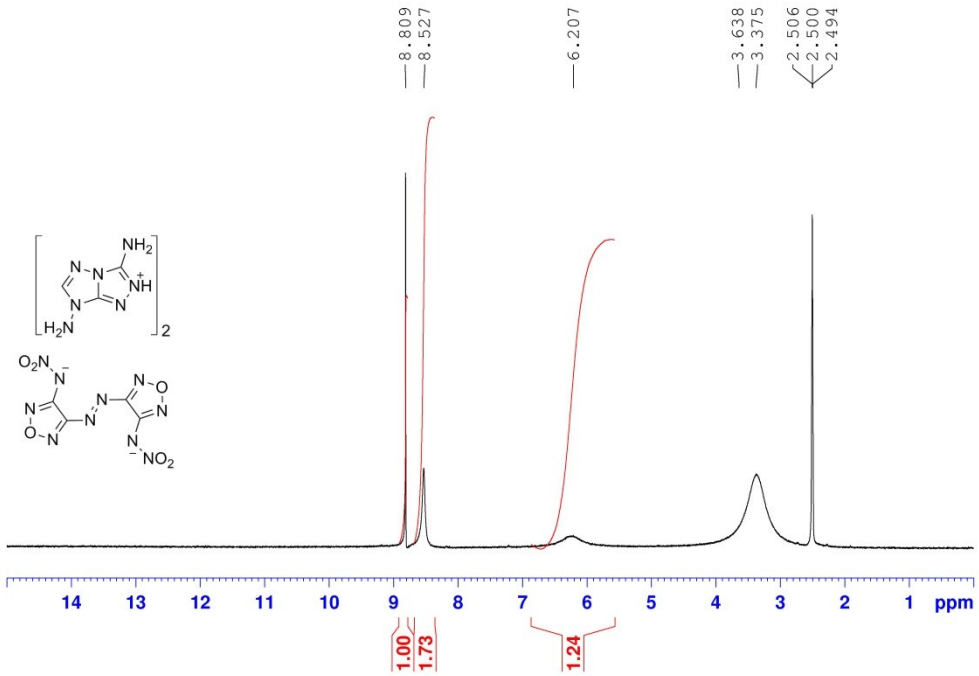

Fig. S15. ^{1}H NMR spectrum of **9**

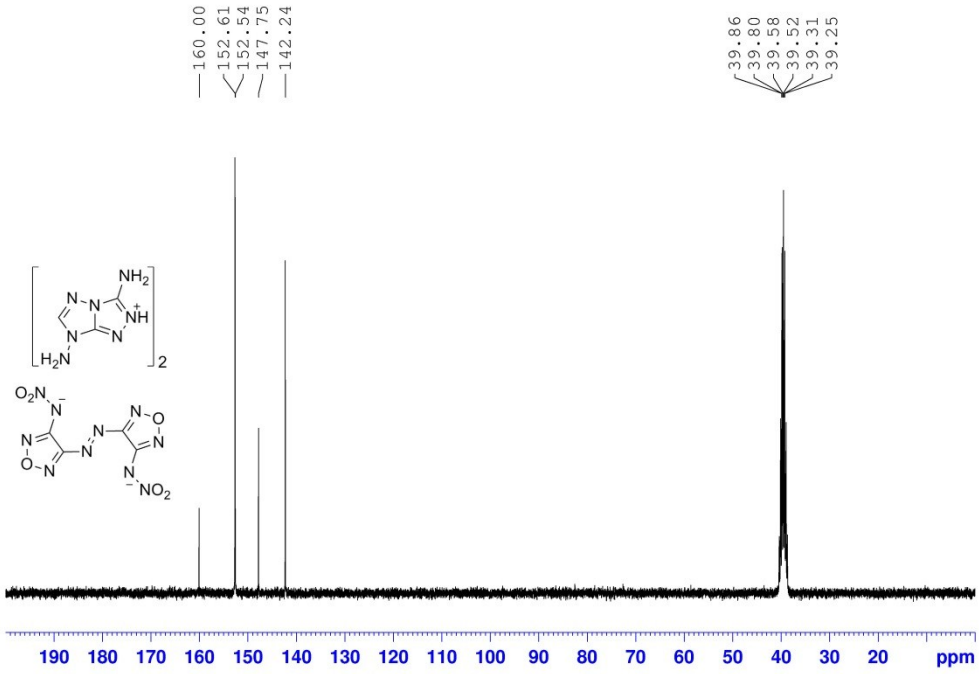

Fig. S16. ^{13}C NMR spectrum of **9**

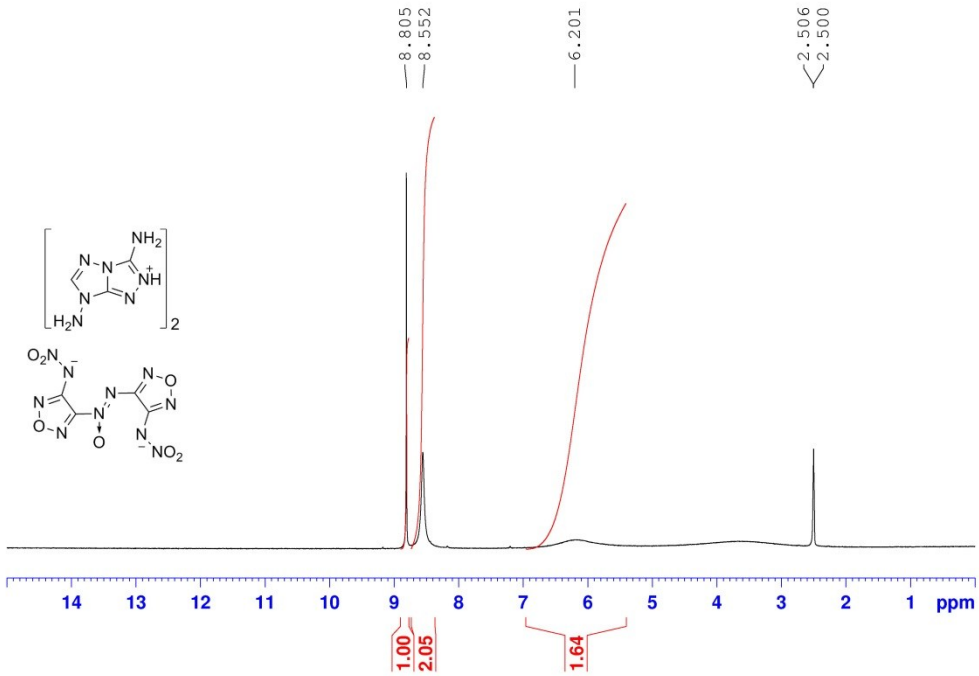

Fig. S17. ^{1}H NMR spectrum of **10**

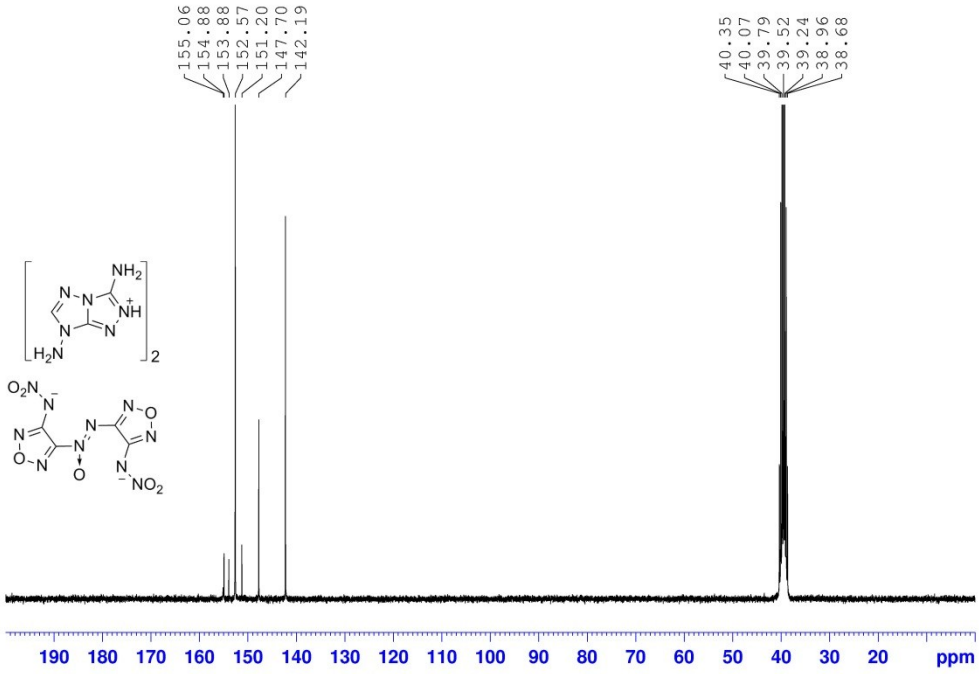

Fig. S18. ^{13}C NMR spectrum of **10**

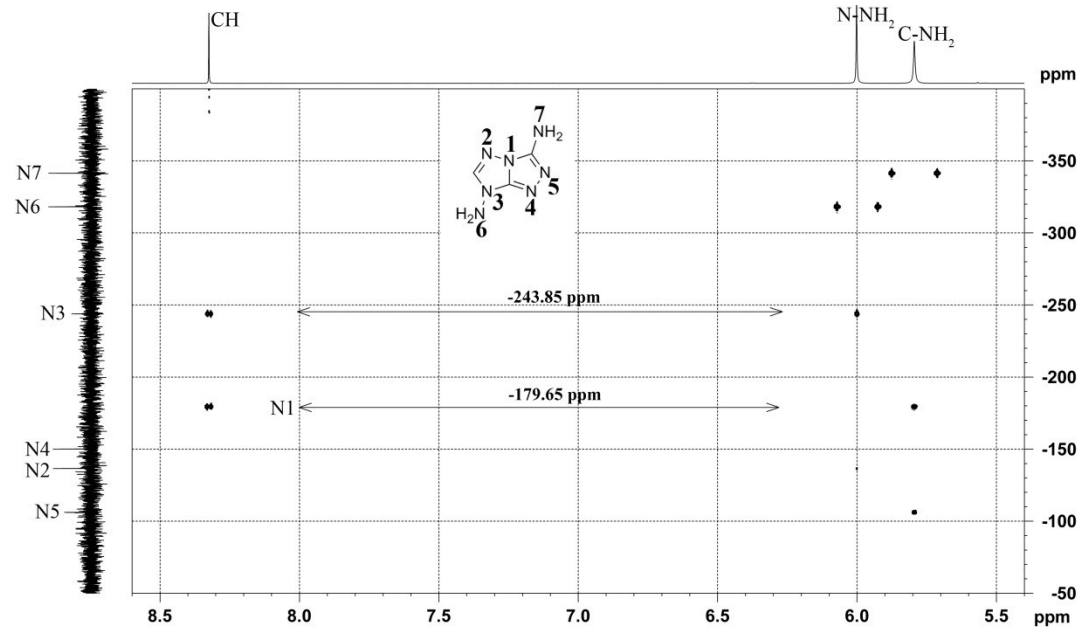

Fig. S19. ^{1}H-^{15}N HMBC spectrum of **3**

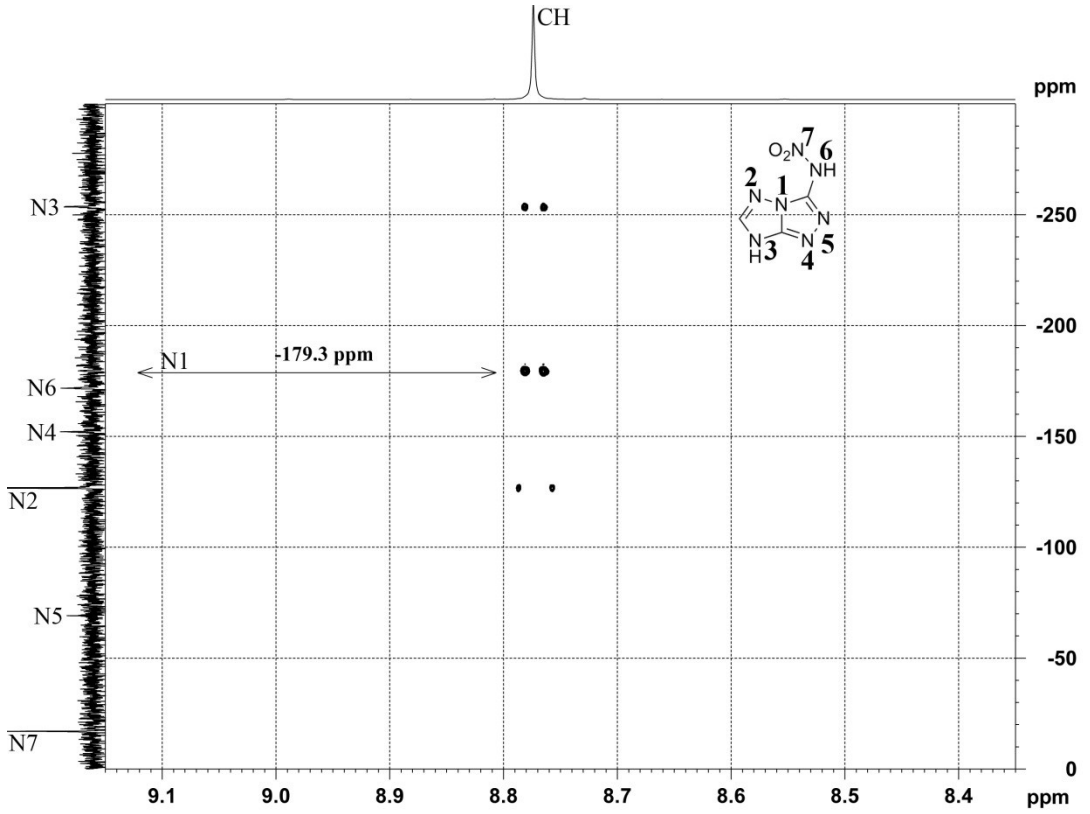

Fig. S20. ^{1}H-^{15}N HMBC spectrum of **4**