Electronic Supporting Information

Design and synthesis of N-methylene-C linked tetrazole and nitramino-1,2,4-triazole: an approach to promising energetic materials

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1 Crystal Structure Data

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

Identification code	**4**	
CCDC number	1480143	
Empirical formula	$C_4 H_9 N_{11} O_3$	
Formula weight	259.22	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.0682(5) Å	α = 90°.
	b = 9.9430(5) Å	β = 97.5240(10)°.
	c = 10.5715(6) Å	γ = 90°.
Volume	1049.18(10) $Å^3$	
Z	4	
Density (-123°C)	1.641 Mg/m^3	
Density (20°C)	1.623 Mg/m^3	
Absorption coefficient	0.139 mm^{-1}	
F(000)	536	
Crystal size	0.444 x 0.418 x 0.060 mm^3	
Theta range for data collection	2.824 to 28.695°.	
Index ranges	-13<=h<=13, -13<=k<=13, -14<=l<=14	
Reflections collected	10921	
Independent reflections	2708 [R_{int} = 0.0159]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7460 and 0.7063	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2708 / 0 / 165	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R_1 = 0.0313, wR_2 = 0.0859	
R indices (all data)	R_1 = 0.0334, wR_2 = 0.0887	
Largest diff. peak and hole	0.284 and -0.350 $e.Å^{-3}$	

Table S2. Crystal data and structure refinement for **6**.

Identification code	**6**	
CCDC number	1480144	
Empirical formula	$C_4 H_{13} N_{13} O_7$	
Formula weight	355.27	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 3.8438(8) Å	α = 90°.
	b = 14.463(3) Å	β = 90.988(3)°.
	c = 23.861(5) Å	γ = 90°.
Volume	1326.3(5) $Å^3$	
Z	4	
Density (-123°C)	1.779 Mg/m^3	
Density (20°C)	1.748 Mg/m^3	
Absorption coefficient	0.162 mm^{-1}	
Max. and min. transmission	0.5637 and 0.7460	
F(000)	736	
Crystal size	0.220 x 0.040 x 0.040 mm^3	
Theta range for data collection	1.707 to 29.992°.	
Index ranges	-5<=h<=5, -19<=k<=20, -30<=l<=32	
Reflections collected	14056	
Independent reflections	3749 [R_{int} = 0.1177]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3749 / 3 / 227	
Goodness-of-fit on F^2	0.970	
Final R indices [I>2sigma(I)]	R_1 = 0.0610, wR_2 = 0.1097	
R indices (all data)	R_1 = 0.1541, wR_2 = 0.1363	
Largest diff. peak and hole	0.409 and -0.338 $e.Å^{-3}$	

Table S3. Crystal data and structure refinement for 7.

Identification code	**7**	
CCDC number	1480145	
Empirical formula	$C_4H_3N_{11}O_4$, $2(H_5N_2)$, $1/2(H_2O)$	
Formula weight	344.30	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 16.6803(14) Å	α = 90°.
	b = 3.7404(3) Å	β = 90°.
	c = 42.897(4) Å	γ = 90°.
Volume	2676.4(4) $Å^3$	
Z	8	
Density (-123°C)	1.709 Mg/m^3	
Density (20°C)	1.685 Mg/m^3	
Absorption coefficient	1.295 mm^{-1}	
Max. and min. transmission	0.7531 and 0.5874	
F(000)	1432	
Crystal size	0.160 x 0.050 x 0.030 mm^3	
Theta range for data collection	2.060 to 68.228°.	
Index ranges	-20<=h<=20, -4<=k<=3, -41<=l<=48	
Reflections collected	12868	
Independent reflections	4085 [R_{int} = 0.0526]	
Completeness to theta = 67.679°	96.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4085 / 16 / 458	
Goodness-of-fit on F^2	1.076	
Final R indices [I>2sigma(I)]	R_1 = 0.0493, wR_2 = 0.1281	
R indices (all data)	R_1 = 0.0510, wR_2 = 0.1299	
Absolute structure parameter	0.4(2)	
Largest diff. peak and hole	0.545 and -0.348 e.$Å^{-3}$	

Table S4. Hydrogen bonds for **4** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6)...O(1)	0.88	2.11	2.5871(10)	113.6
N(16)-H(16A)...N(7)#2	0.88	2.39	3.1999(12)	153.6
N(16)-H(16B)...O(2)#3	0.88	2.18	2.9805(11)	150.7
O(17)-H(17)...O(1)#5	0.84	1.93	2.7631(10)	174.2
N(18)-H(18A)...N(9)#6	0.91	1.93	2.7981(11)	159.9
N(18)-H(18B)...O(2)#7	0.91	1.90	2.7958(11)	166.4
N(18)-H(18B)...N(3)#7	0.91	2.49	3.3666(11)	160.7
N(18)-H(18C)...N(13)#8	0.91	2.03	2.9114(11)	163.1

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

Table S5. Hydrogen bonds for **6** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6)...O(2)	0.88	2.13	2.611(3)	113.4
N(6)-H(6)...N(13)#1	0.88	2.22	3.055(3)	157.8
N(20)-H(20B)...O(19)#2	0.91	1.92	2.812(3)	165.2
N(20)-H(20A)...N(4)	0.91	1.97	2.845(3)	160.5
O(21)-H(21)...N(9)#2	0.84	1.79	2.621(3)	167.7
N(22)-H(22C)...O(19)#3	0.91	2.14	2.956(3)	149.0
N(22)-H(22B)...O(18)#4	0.91	2.23	2.908(3)	131.3
N(22)-H(22A)...O(24)#2	0.91	1.86	2.767(3)	174.8
O(23)-H(23)...N(14)#4	0.84	1.85	2.680(3)	170.4
O(24)-H(24B)...O(2)#3	0.831(10)	2.194(12)	3.019(3)	172(4)
O(24)-H(24A)...N(7)#5	0.831(10)	2.38(3)	2.994(3)	131(3)

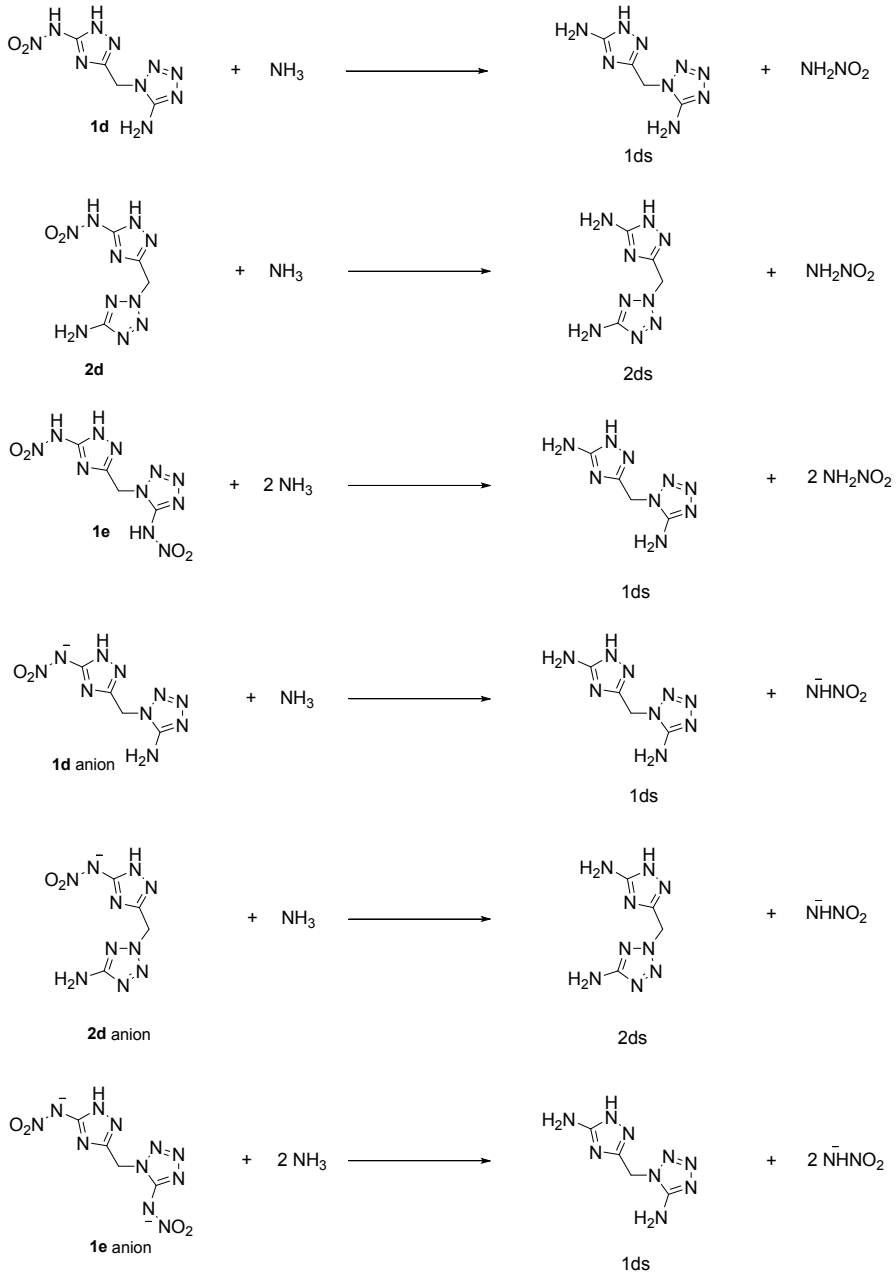
Symmetry transformations used to generate equivalent atoms:
#1 -x+2,y-1/2,-z+1/2 #2 -x+1,-y+1,-z+1 #3 -x+2,-y+1,-z+1
#4 x,y-1,z #5 x,-y+3/2,z+1/2

Table S6. Hydrogen bonds for **7** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6)...O(1)	0.88	2.03	2.535(5)	115.3
N(6)-H(6)...N(13)#1	0.88	2.15	2.943(5)	149.5
N(25)-H(25)...O(20)	0.88	2.05	2.546(5)	115.0
N(25)-H(25)...N(32)#2	0.88	2.15	2.946(5)	151.0
N(39)-H(39A)...O(21)#3	0.91	2.05	2.919(5)	158.0
N(39)-H(39C)...O(47)	0.91	2.18	2.960(5)	143.6
N(40)-H(40A)...N(28)#4	0.908(14)	2.10(2)	2.985(6)	165(5)
N(40)-H(40B)...O(20)#3	0.915(14)	2.21(4)	2.966(5)	140(5)
N(41)-H(41B)...N(14)#1	0.91	2.00	2.881(6)	161.2
N(41)-H(41C)...O(37)	0.91	2.02	2.851(7)	151.1
N(42)-H(42A)...N(7)	0.915(14)	2.195(16)	3.106(6)	174(5)
N(42)-H(42B)...O(18)	0.913(14)	2.216(18)	3.120(6)	170(5)
N(43)-H(43A)...N(33)#2	0.91	1.98	2.863(6)	162.1
N(43)-H(43C)...O(18)#2	0.91	2.08	2.878(6)	146.4
N(44)-H(44A)...O(37)	0.915(14)	2.16(2)	3.055(6)	165(5)
N(44)-H(44B)...N(26)	0.914(14)	2.22(2)	3.107(6)	164(5)
N(45)-H(45A)...O(2)#1	0.91	2.12	2.929(5)	148.4
N(45)-H(45A)...O(21)#5	0.91	2.35	2.803(5)	110.2
N(45)-H(45B)...O(47)#5	0.91	2.15	2.947(6)	145.6
N(46)-H(46A)...O(1)#1	0.909(14)	2.11(3)	2.961(5)	156(5)
N(46)-H(46B)...N(9)#6	0.910(14)	2.083(17)	2.986(6)	172(5)
O(47)-H(47B)...N(23)	0.822(14)	2.25(2)	3.035(6)	160(6)
O(47)-H(47A)...N(4)#7	0.823(14)	2.225(17)	3.039(6)	171(6)

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

2 Theoretical Calculations



Scheme S1. Isodesmic reactions

Table S1. Calculated zero point energy (*ZPE*), values of the correction (H_r), total energy (E_0) and gas phase heats of formation (*HOF*)

Species	*ZPE*	H_r	E_0	corrected E_0	*HOF* (kJ mol^{-1})
1d	0.152204	0.166437	-851.88753	-851.72718	555.303446
2d	0.152113	0.166593	-851.8920287	-851.73152	555.8469444
1e	0.154239	0.170958	-1055.959161	-1055.79437	608.2414761
1d anion	0.139321	0.15281	-851.3886417	-851.24140	401.4549518
2d anion	0.139129	0.153027	-851.3818416	-851.23438	431.8344718
1e anion	0.127708	0.143729	-1054.854823	-1054.71620	580.4663442
1ds	0.149669	0.16167	-647.8144792	-647.65880	505.5[a]
2ds	0.14967	0.161905	-647.8180796	-647.66216	508.6[a]
NH_2NO_2	0.039257	0.043909	-260.4931748	-260.45804	-6.11[a]
NH_3	0.034384	0.038203	-56.4154647	-56.37864	-45.9[b]
$NHNO_2$ anion	0.026168	0.030444	-259.936099	-259.90670	-6.74[a]

[a] Data obtained from G2.

[b] Data are from Ref. [D. R. Lide, ed., CRC Handbook of Chemistry and Physics, 88th Edition (Internet Version 2008), CRC Press/Taylor and Francis, Boca Raton, FL.].

Table S2. 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})
4	473.0994451	669.5	401.45	597.9
5	480.338003	669.5	434.83	621.0
6	1275.947408	669.5	580.5	643.5
7	1270.39435	770	580.5	850.1
8	1293.833856	626.4	580.5	539.4

3 NMR Spectra

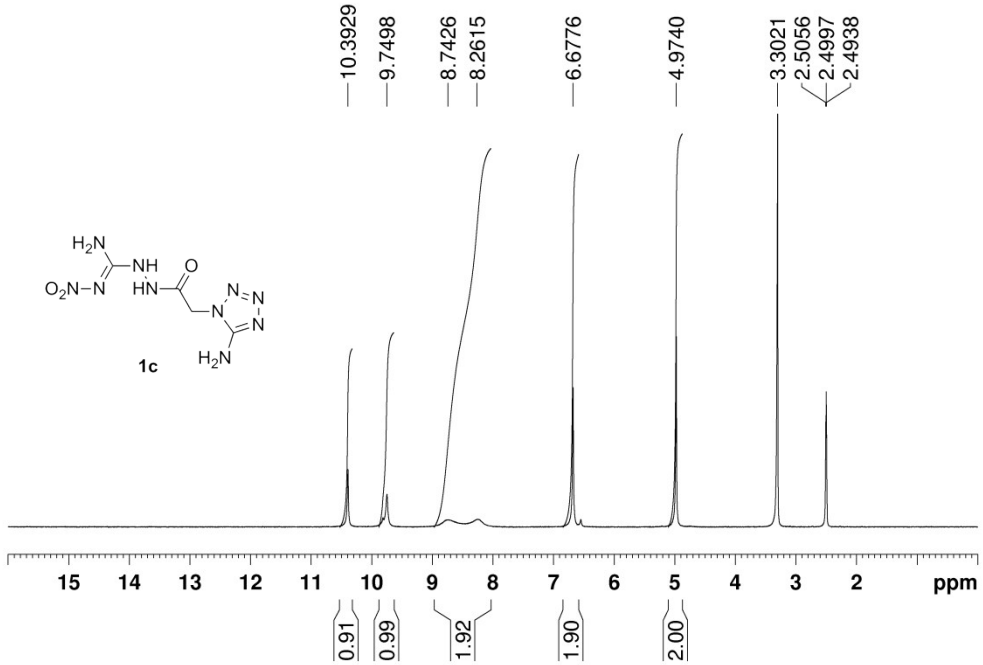


Figure S1. [1]H NMR spectrum of **1c**

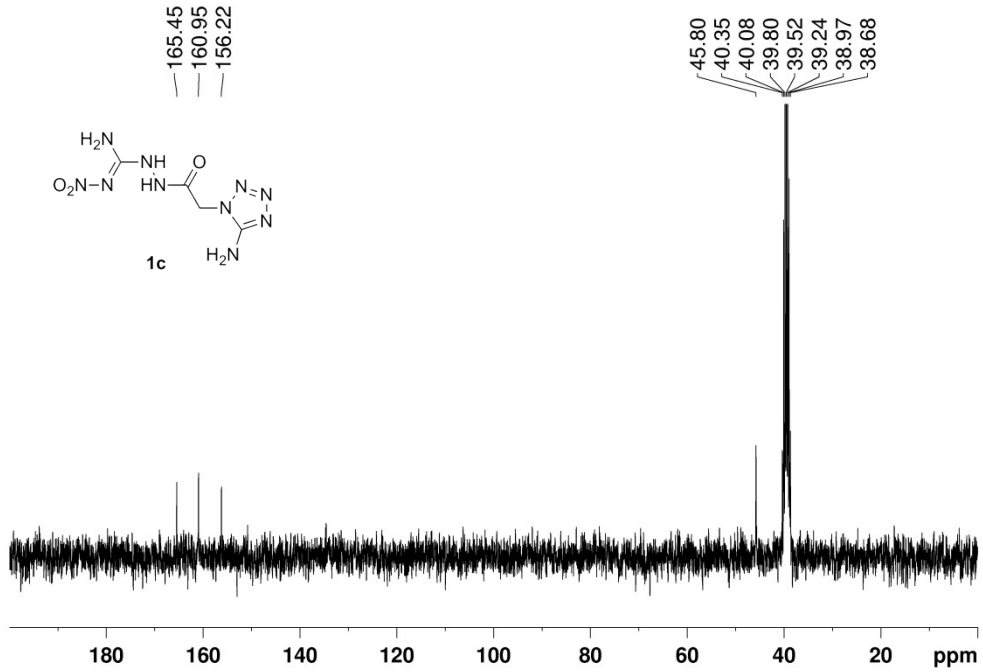


Figure S2 [13]C NMR spectrum of **1c**

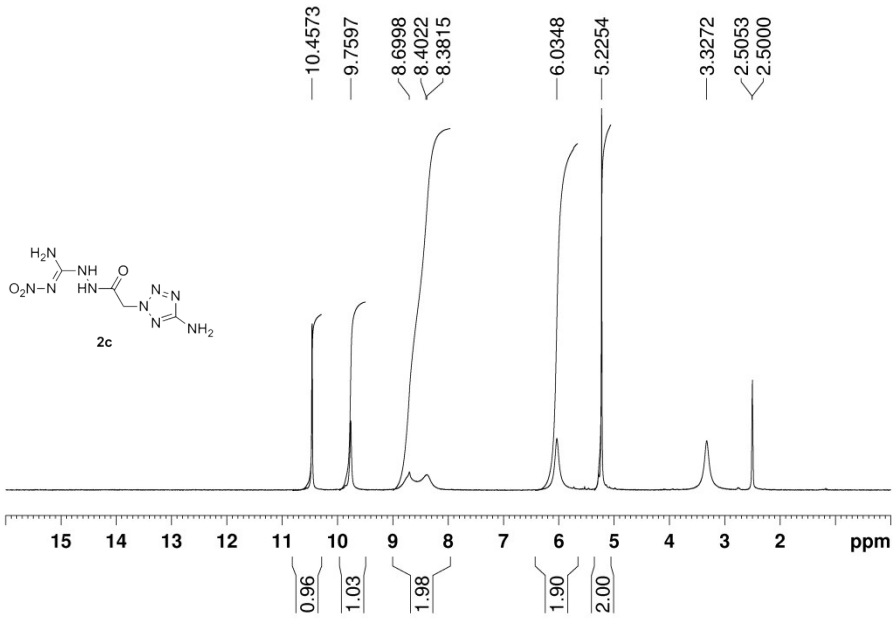


Figure S3. ^{1}H NMR spectrum of **2c**

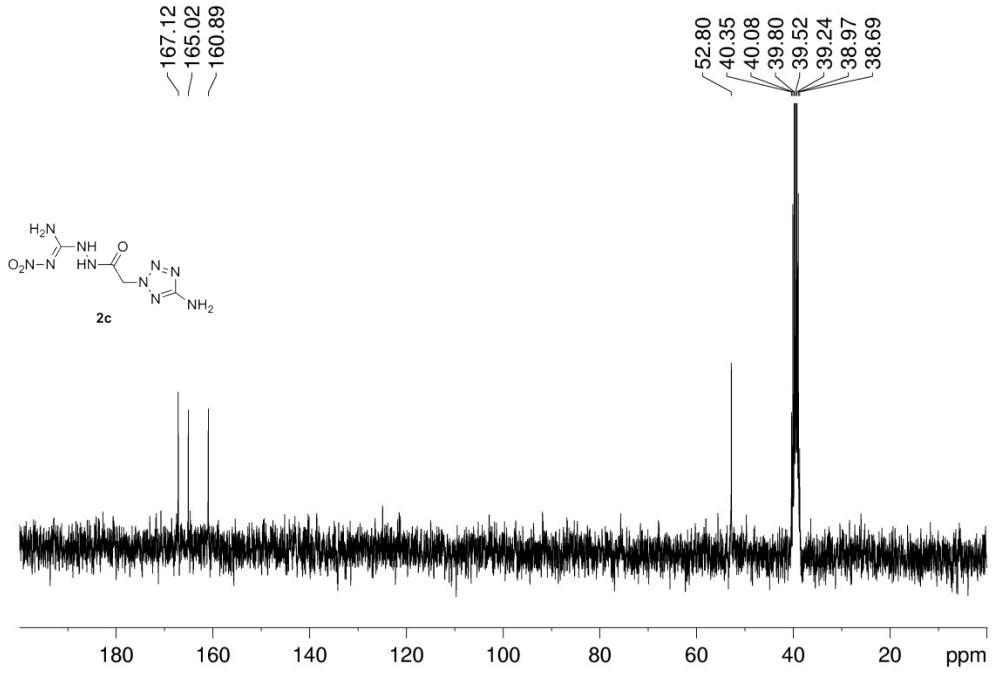


Figure S4. ^{13}C NMR spectrum of **2c**

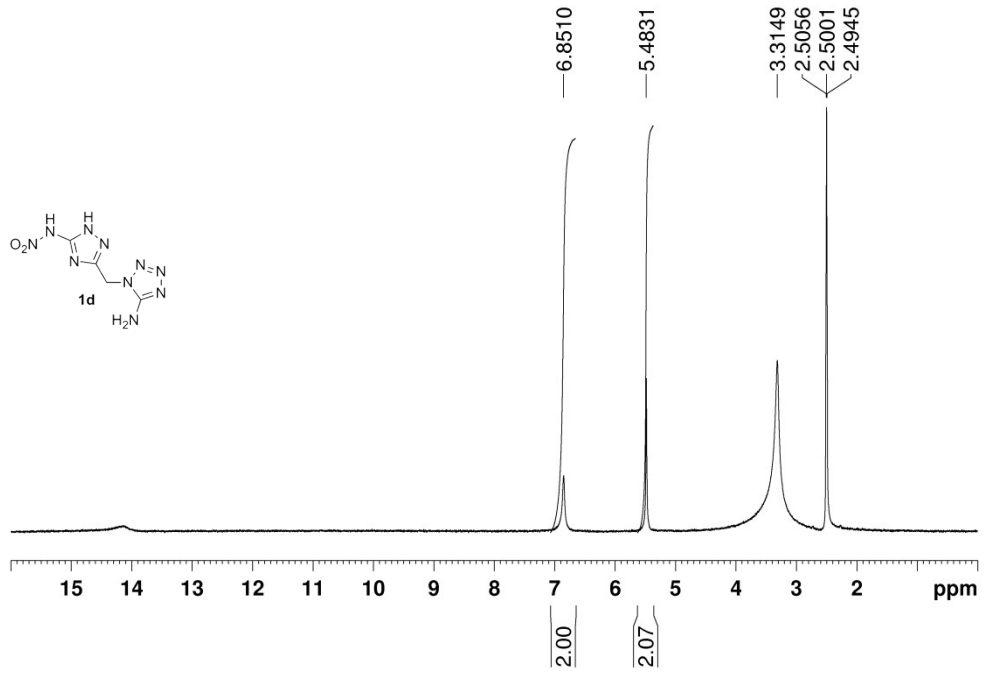


Figure S5. ^{1}H NMR spectrum of **1d**

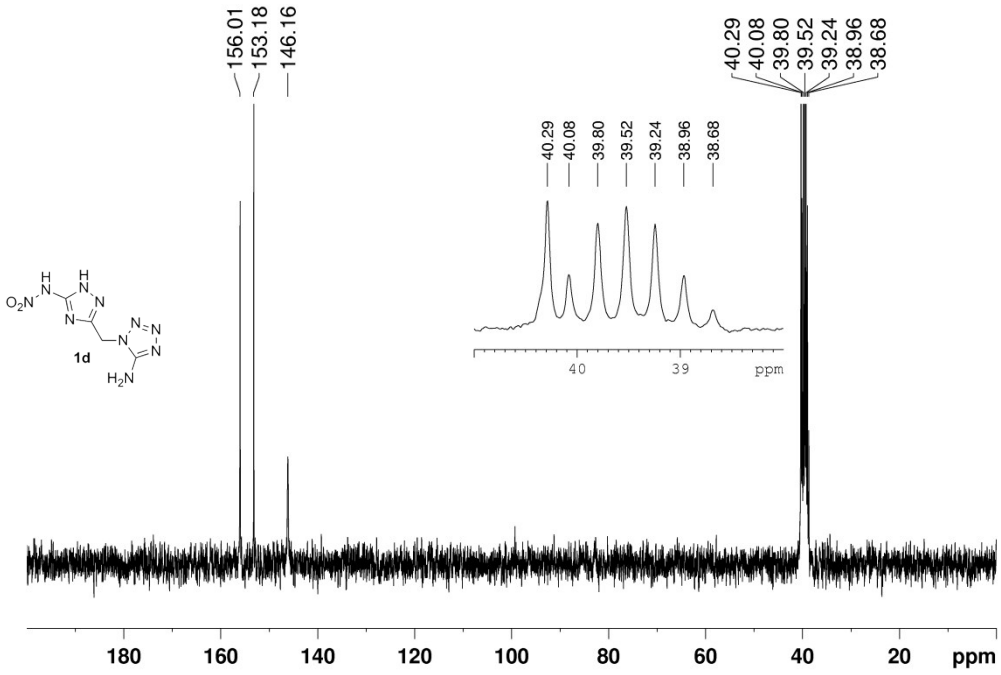


Figure S6. ^{13}C NMR spectrum of **1d**

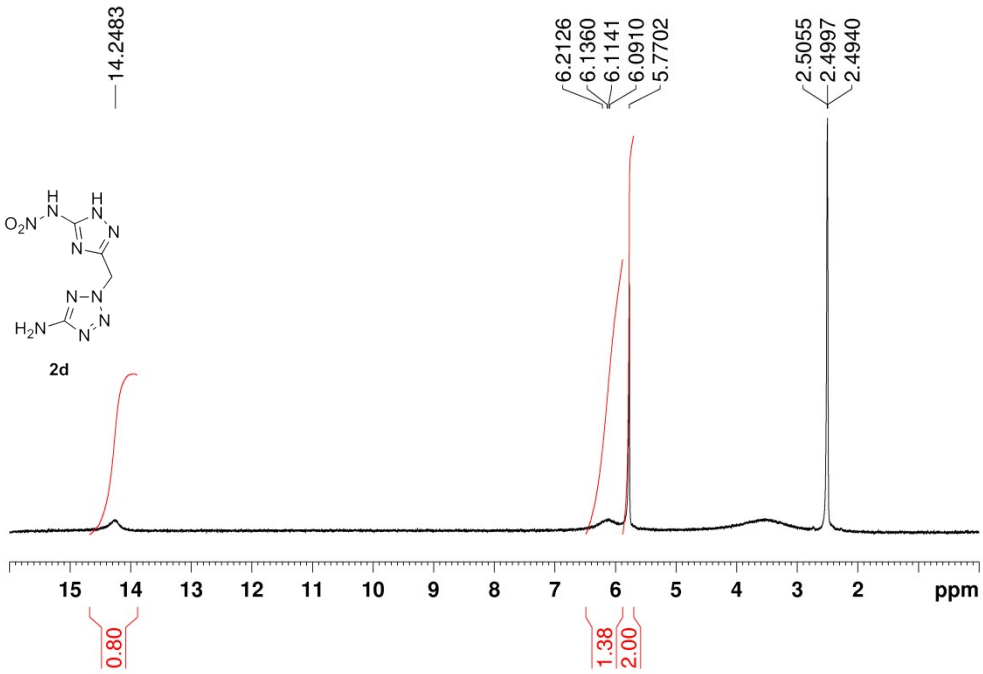


Figure S7. ^{1}H NMR spectrum of **2d**

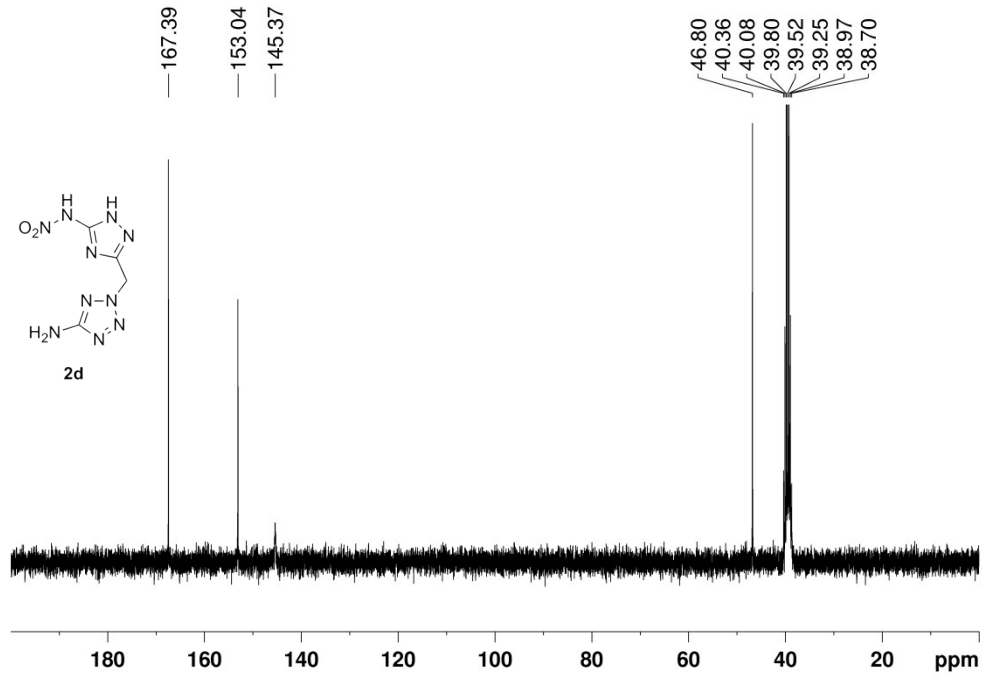


Figure S8. ^{13}C NMR spectrum of **2d**

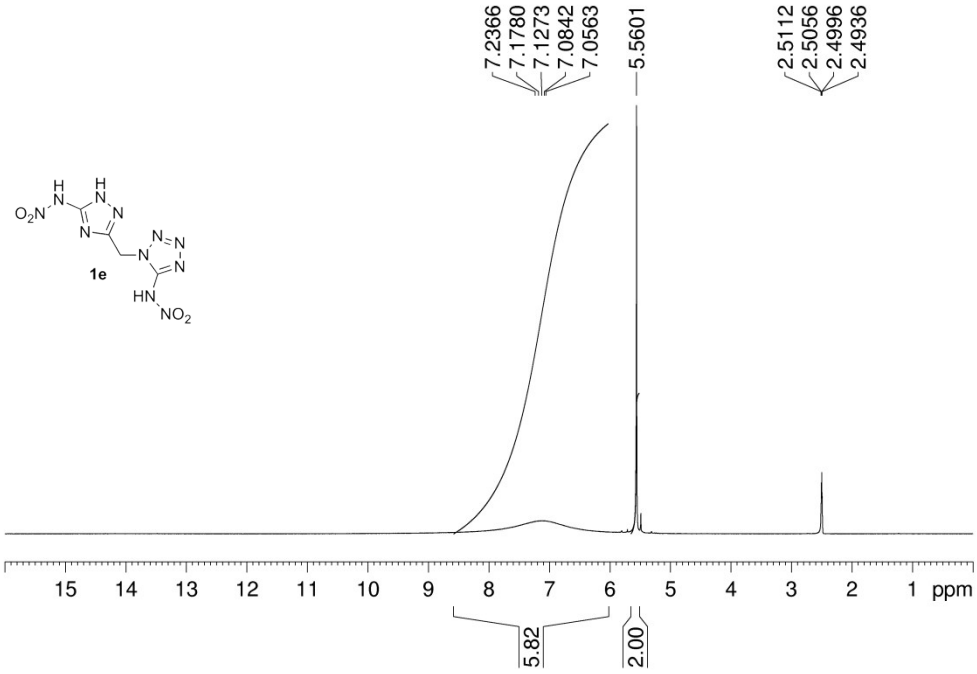


Figure S9. ^{1}H NMR spectrum of **1e**

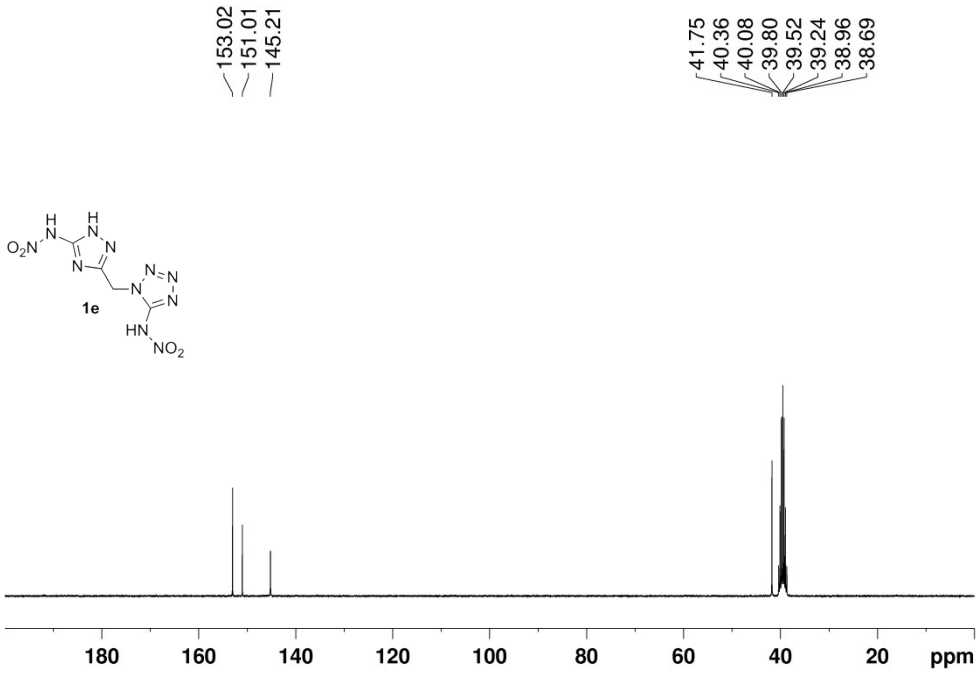


Figure S10. ^{13}C NMR spectrum of **1e**

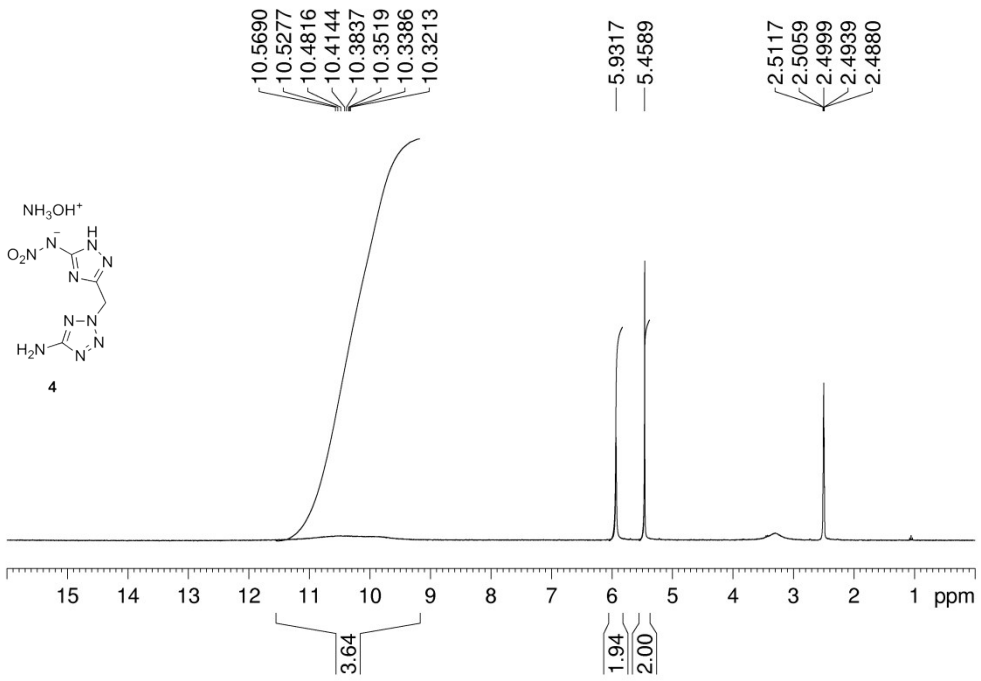


Figure S11. ^{1}H NMR spectrum of **4**

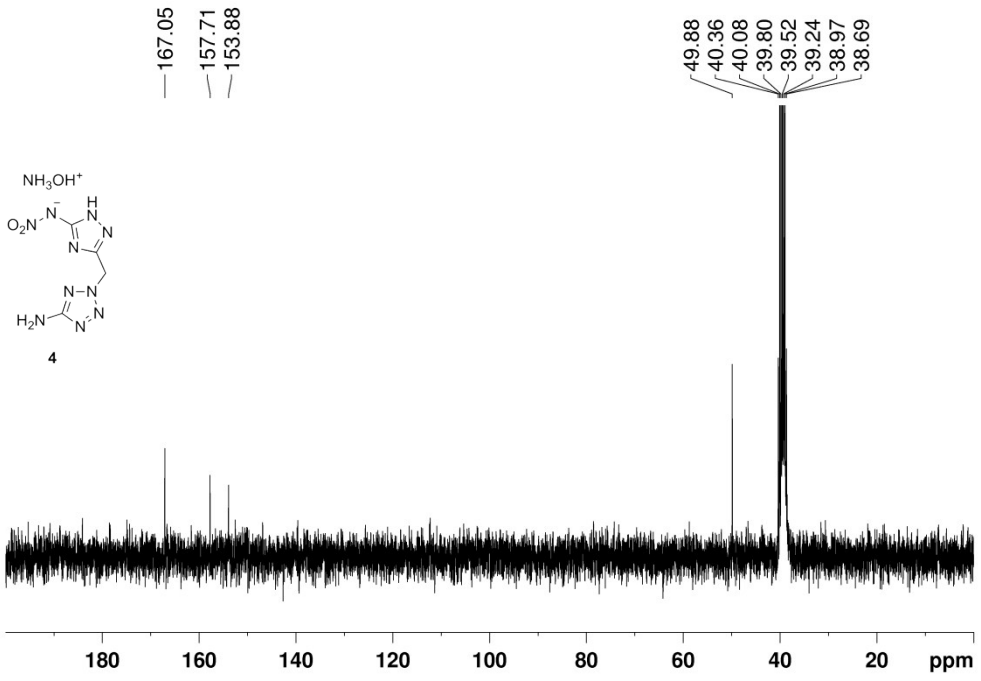


Figure S12. ^{13}C NMR spectrum of **4**

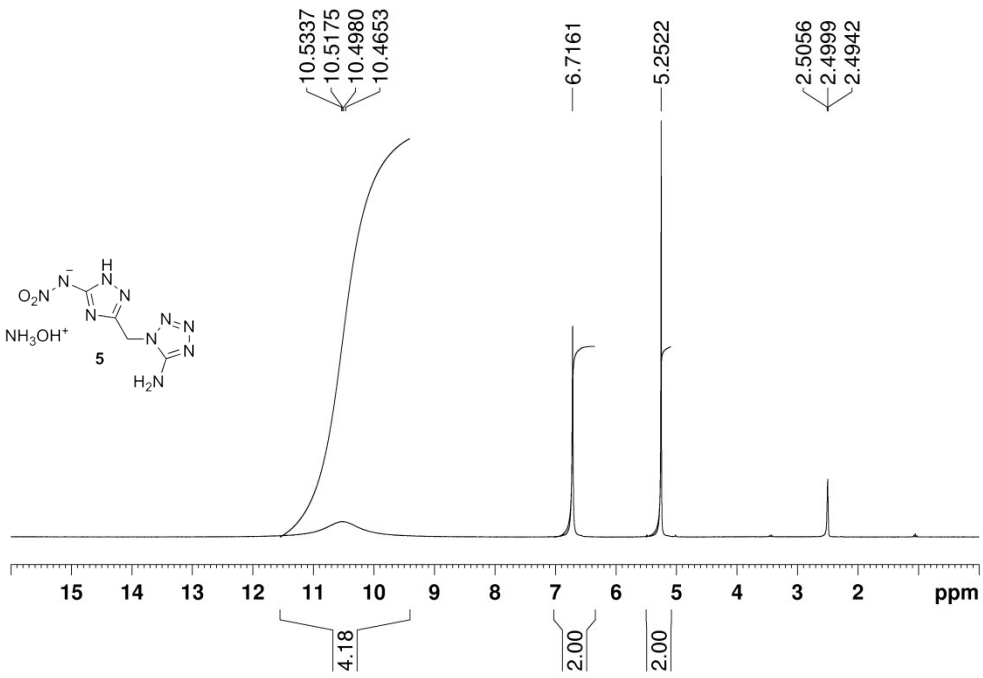


Figure S13. ^{1}H NMR spectrum of **5**

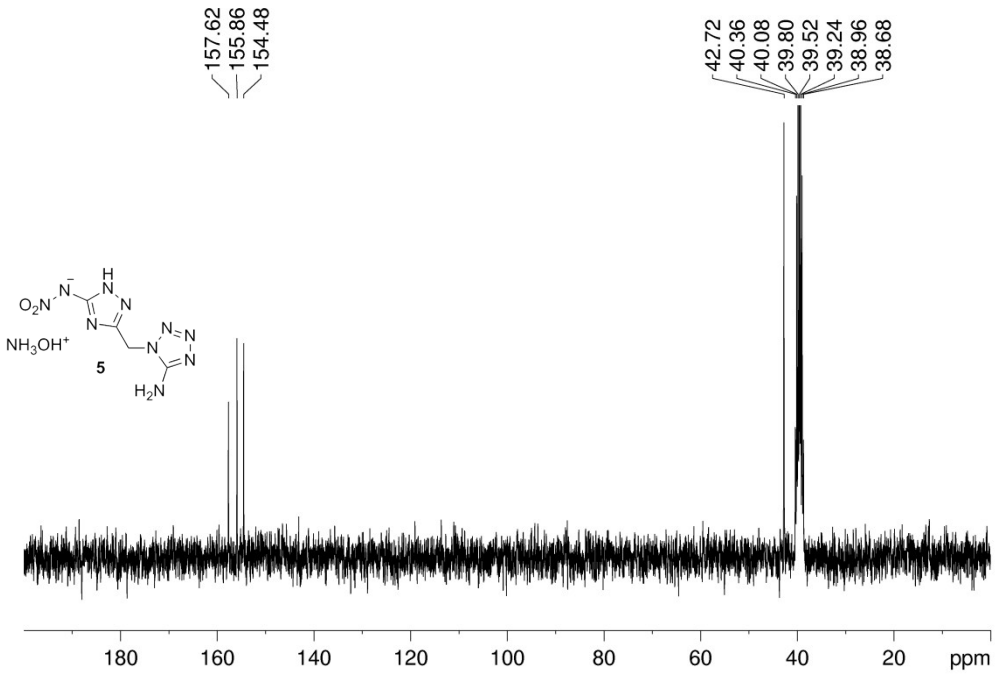


Figure S14. ^{13}C NMR spectrum of **5**

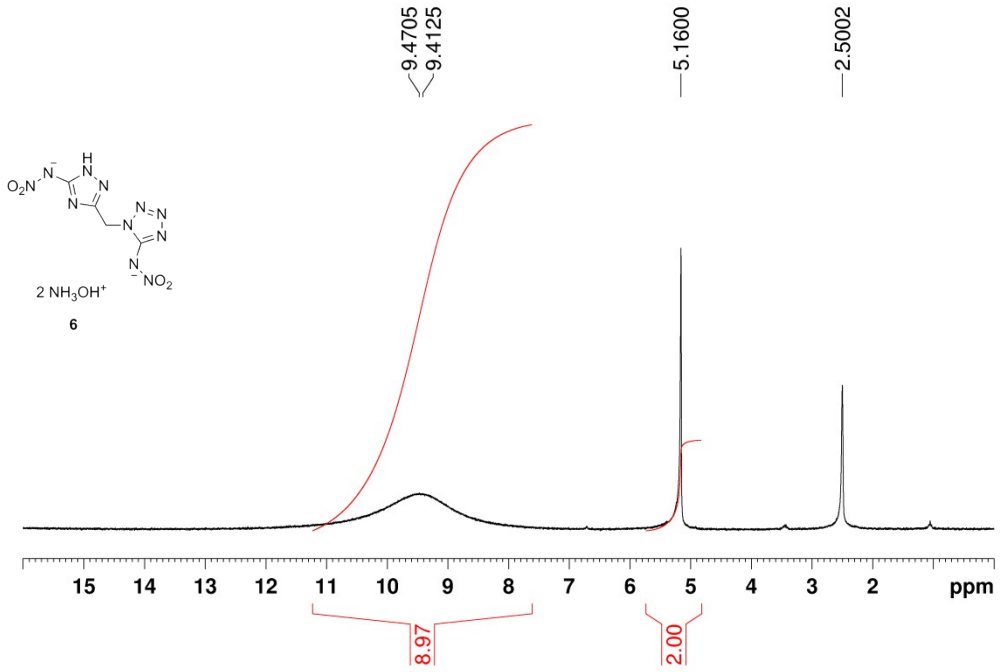


Figure S15. ^{1}H NMR spectrum of **6**

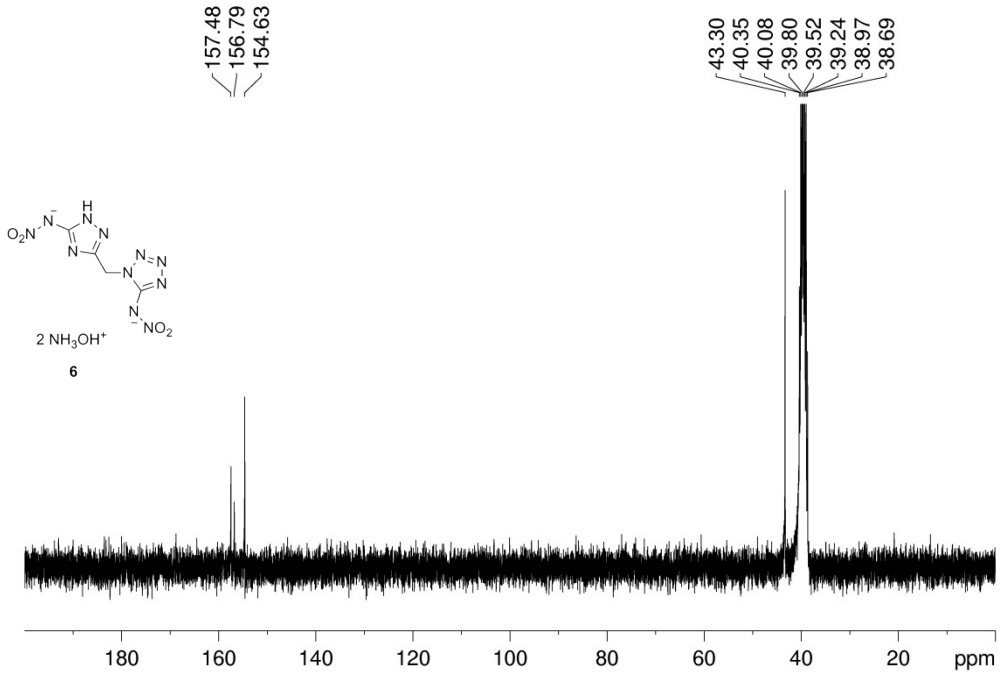


Figure S16. ^{13}C NMR spectrum of **6**

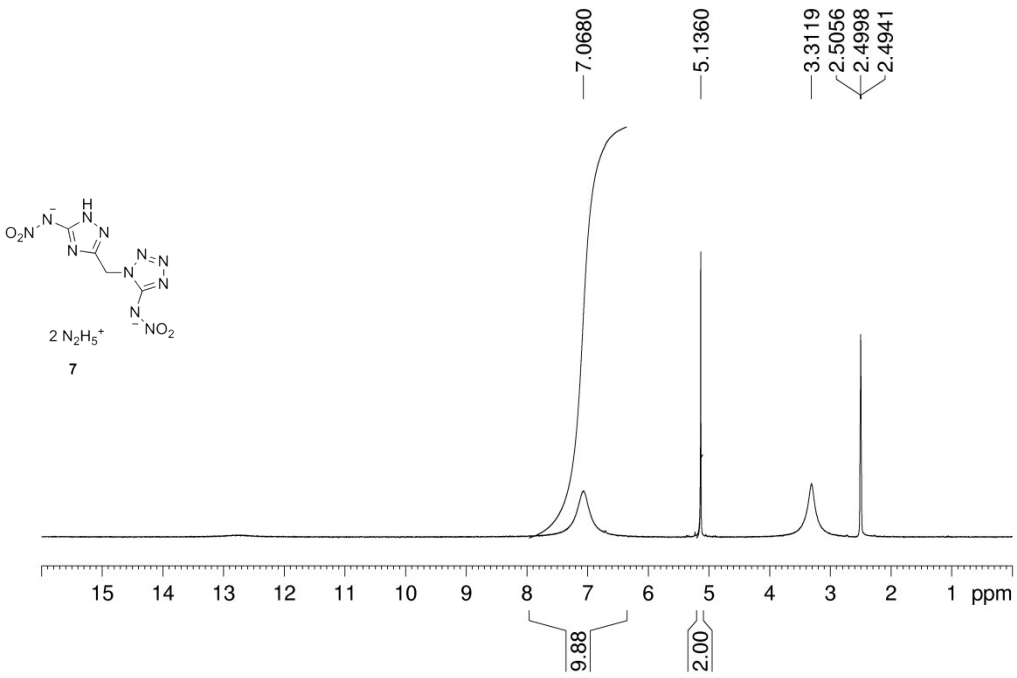


Figure S17. ^{1}H NMR spectrum of **7**

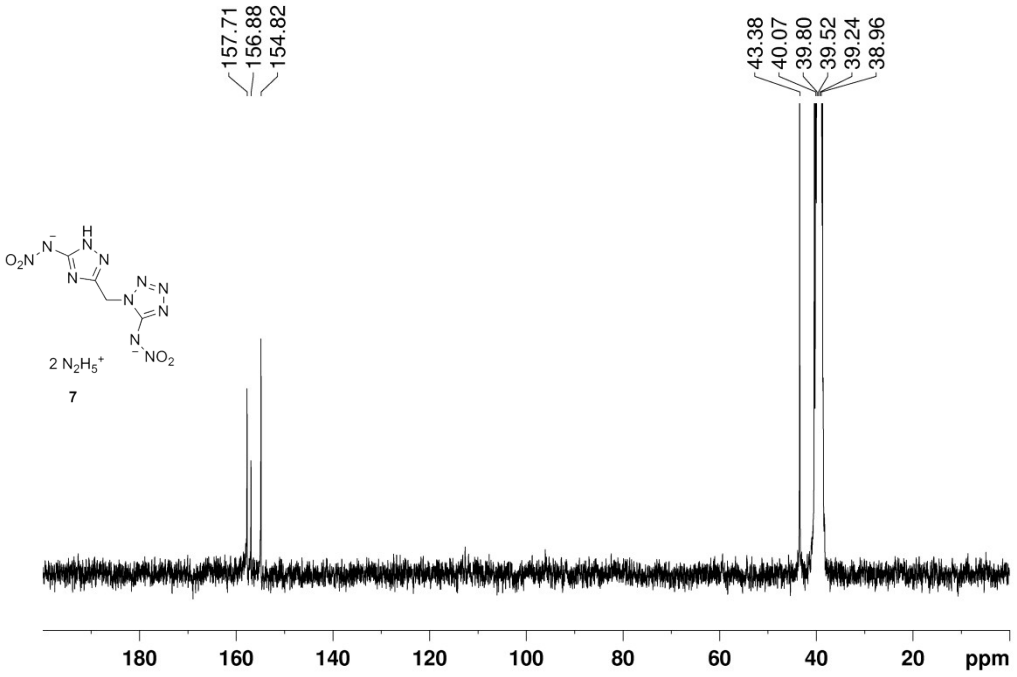


Figure S18. ^{1}H NMR spectrum of **7**

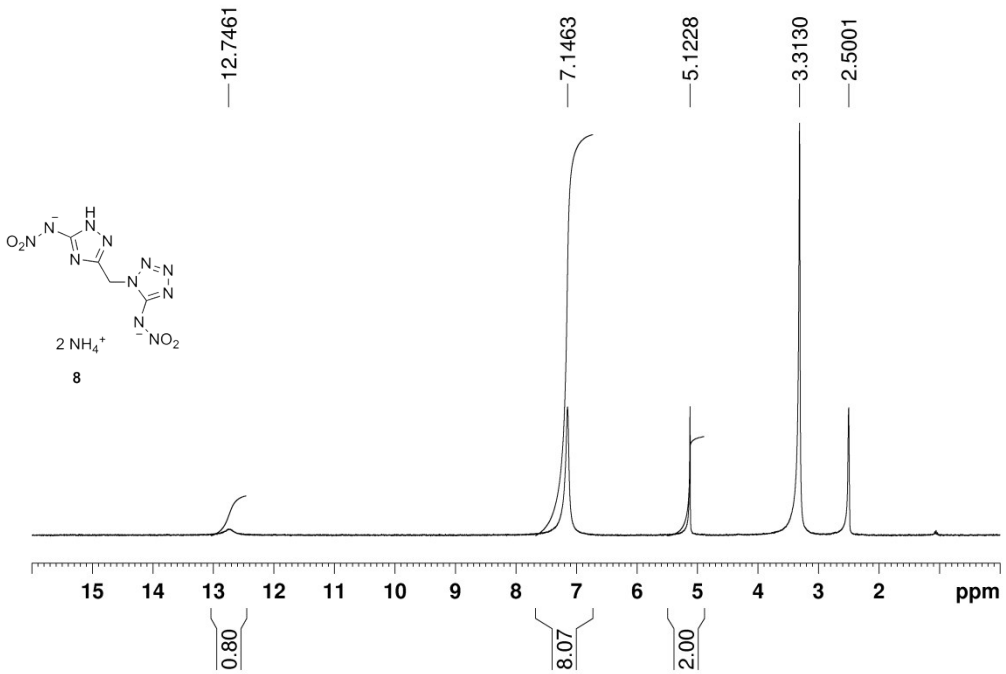


Figure S19. ^{1}H NMR spectrum of **8**

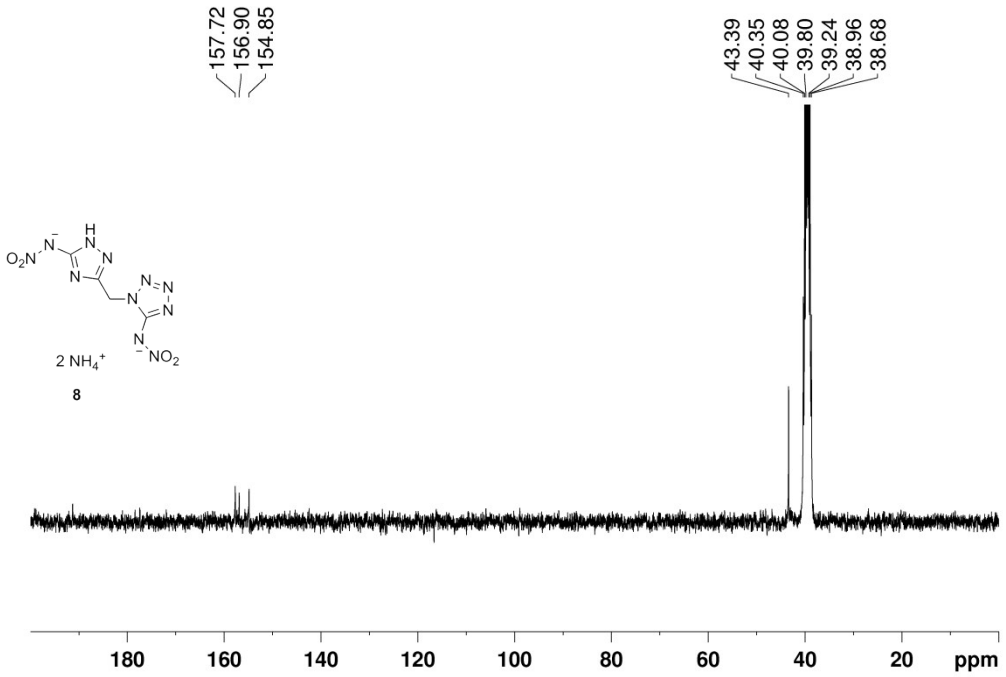
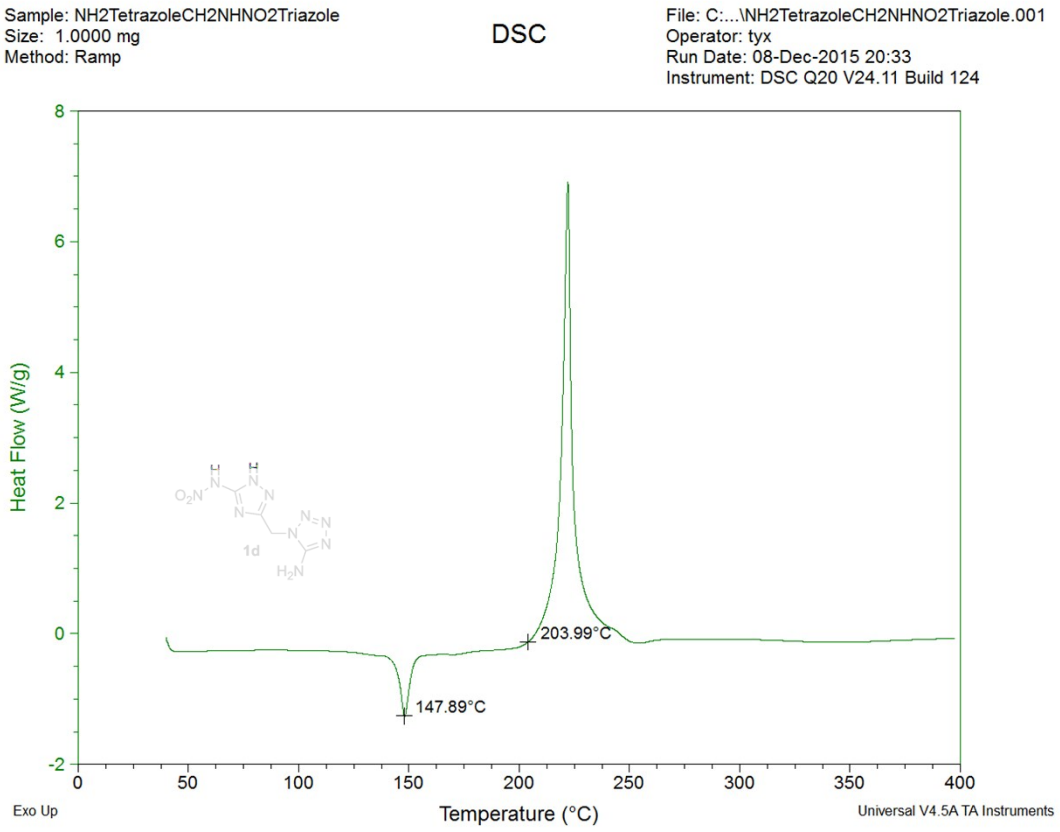
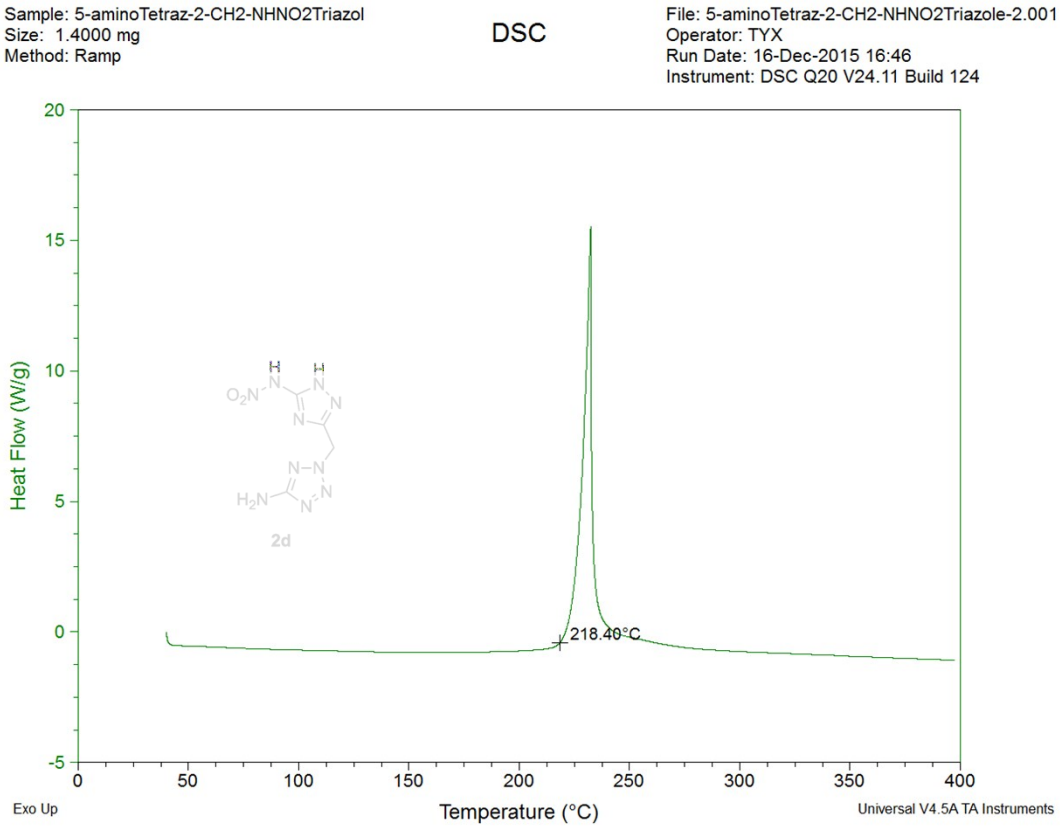


Figure S20. ^{13}C NMR spectrum of **8**

4 DSC plots

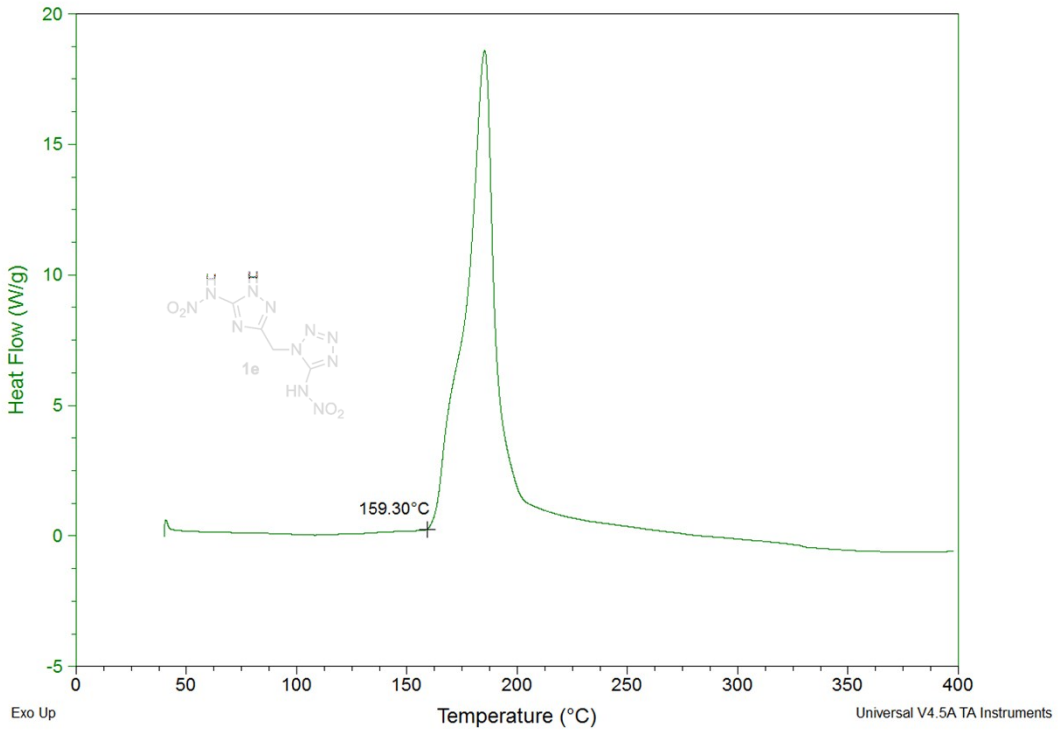

Sample: NH2TetrazoleCH2NHNO2Triazole
Size: 1.0000 mg
Method: Ramp
DSC
File: C:...\NH2TetrazoleCH2NHNO2Triazole.001
Operator: tyx
Run Date: 08-Dec-2015 20:33
Instrument: DSC Q20 V24.11 Build 124
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments
203.99°C
147.89°C
1d


Sample: 5-aminoTetraz-2-CH2-NHNO2Triazol
Size: 1.4000 mg
Method: Ramp
DSC
File: 5-aminoTetraz-2-CH2-NHNO2Triazole-2.001
Operator: TYX
Run Date: 16-Dec-2015 16:46
Instrument: DSC Q20 V24.11 Build 124
Heat Flow (W/g)
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments
218.40°C
2d

Sample: NHNO2T-1CH2-NHNO2Triz ZX
Size: 0.5000 mg
Method: Ramp

DSC

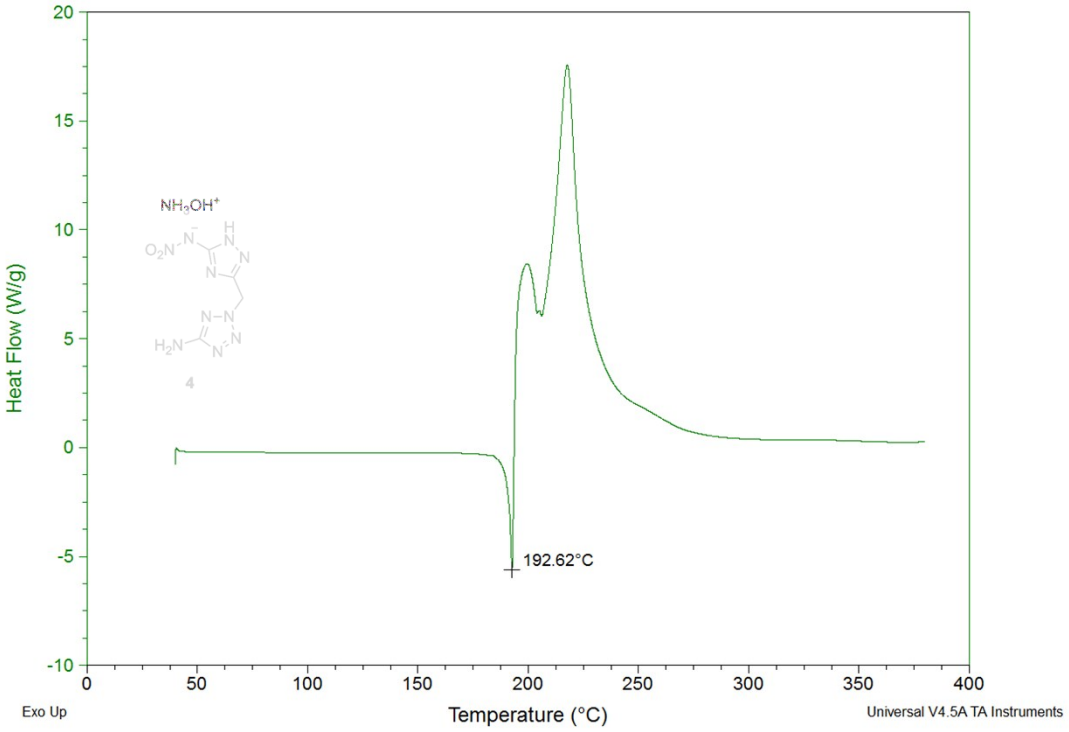
File: C:...\NHNO2T-1CH2-NHNO2Triz ZX.001
Operator: TYX
Run Date: 18-Jan-2016 10:21
Instrument: DSC Q20 V24.11 Build 124



Sample: NH2T-2CH2-NHNO2Triz NH3OH
Size: 0.9000 mg
Method: Ramp

DSC

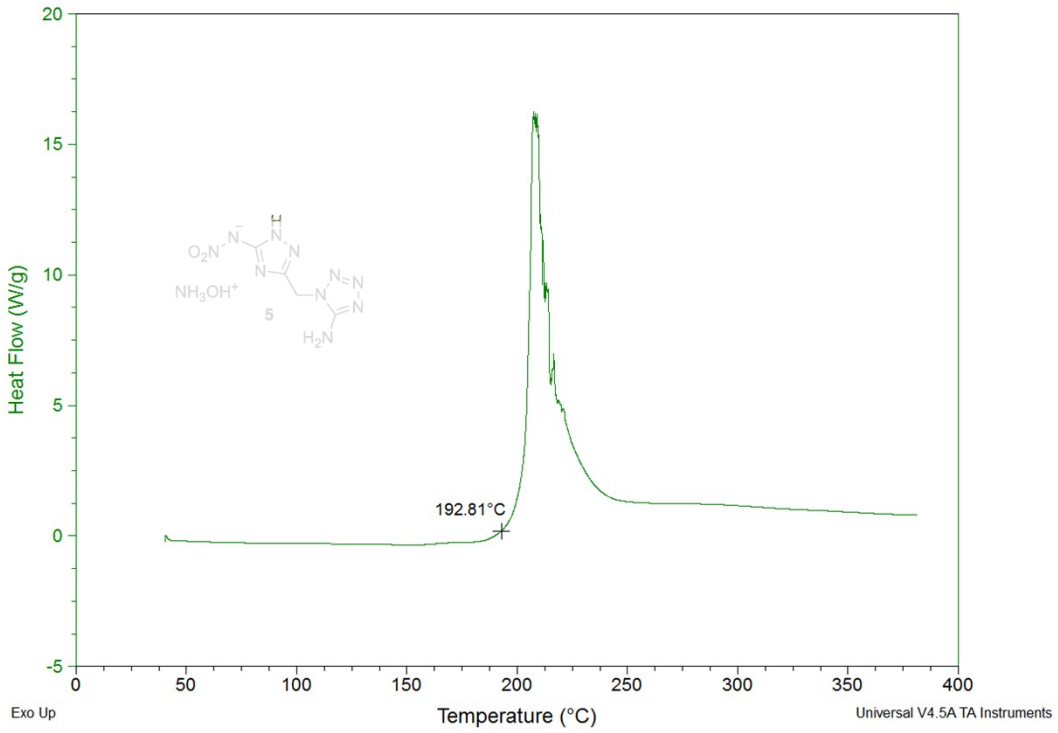
File: C:...\NH2T-2CH2-NHNO2Triz NH3OH.001
Operator: tyx
Run Date: 19-Jan-2016 21:16
Instrument: DSC Q20 V24.11 Build 124



Sample: NH2T-1CH2-NHNO2Triz NH3OH
Size: 1.4000 mg
Method: Ramp

DSC

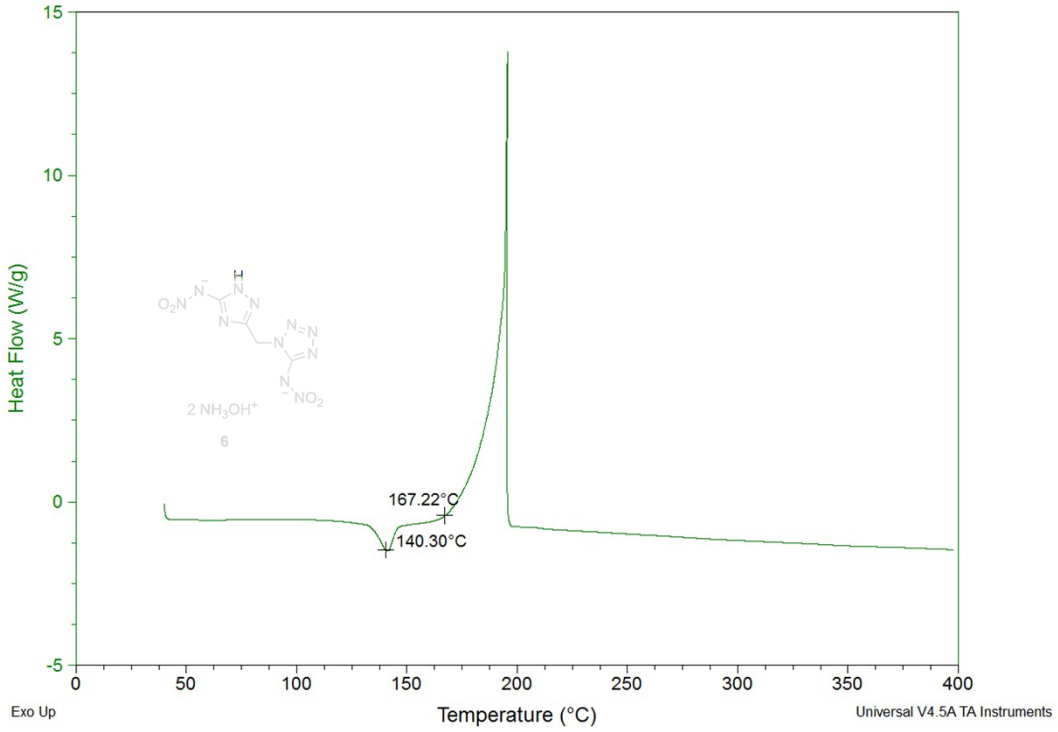
File: C:...\NH2T-1CH2-NHNO2Triz NH3OH.001
Operator: tyx
Run Date: 19-Jan-2016 20:35
Instrument: DSC Q20 V24.11 Build 124



Sample: NHNO2T-1CH2-NHNO2Triz 2NH3OH-2
Size: 1.0000 mg
Method: Ramp

DSC

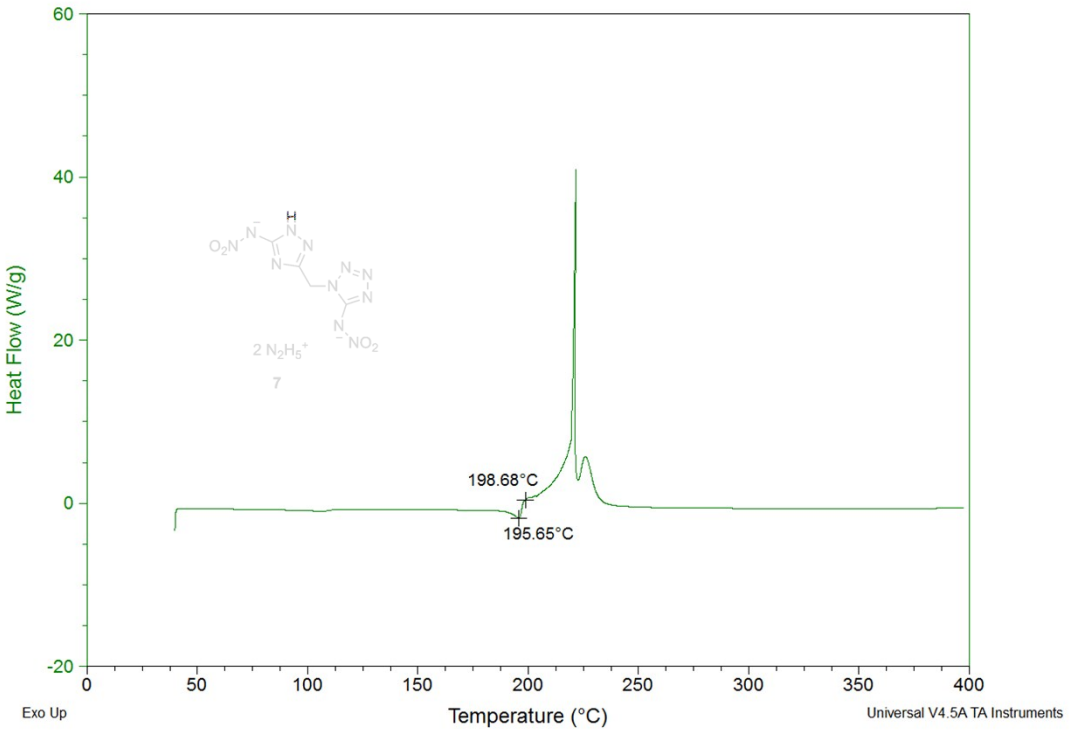
File: C:...\NHNO2T-1CH2-NHNO2Triz 2NH3OH-2.(
Operator: tyx
Run Date: 25-Mar-2016 09:01
Instrument: DSC Q20 V24.11 Build 124



Sample: NHNO2T-1CH2-NHNO2Triz 2NH2h5+-5
Size: 1.1000 mg
Method: Ramp

DSC

File: ...\NHNO2T-1CH2-NHNO2Triz 2NH2h5+-5.00
Operator: TYX
Run Date: 13-Apr-2016 08:40
Instrument: DSC Q20 V24.11 Build 124



Sample: NHNO2T-1CH2-NHNO2Triz 2NH4-3
Size: 0.7000 mg
Method: Ramp

DSC

File: C:...\NHNO2T-1CH2-NHNO2Triz 2NH4-3.001
Operator: TYX
Run Date: 13-Apr-2016 09:44
Instrument: DSC Q20 V24.11 Build 124