Electronic Supporting Information

3,4,5-Trinitro-1-(nitromethyl)-1H-pyrazole (TNNMP): A Perchlorate Free High Energy Density Oxidizer with High Thermal Stability

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1. Crystal Structure Data

Table 1. Crystal data and structure refinement for Compound **2**.

Identification code	shrv442	
Empirical formula	$C_4H_4N_6O_6$	
Formula weight	232.13	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 6.7081(2) Å	α= 90°.
	b = 13.8115(5) Å	β= 99.282(2)°.
	c = 9.3931(3) Å	γ = 90°.
Volume	858.87(5) $Å^3$	
Z	4	
Density (-123°C)	1.795 Mg/m^3	
Density (20°C)	1.763 Mg/m^3	
Absorption coefficient	1.502 mm^{-1}	
F(000)	472	
Crystal size	0.364 x 0.247 x 0.053 mm^3	
Theta range for data collection	5.748 to 74.471°.	
Index ranges	-6<=h<=8, -16<=k<=15, -11<=l<=8	
Reflections collected	5110	
Independent reflections	1592 [R_{int} = 0.0292]	
Completeness to theta = 67.679°	93.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7538 and 0.6215	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1592 / 0 / 146	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	R_1 = 0.0333, wR_2 = 0.0835	
R indices (all data)	R_1 = 0.0364, wR_2 = 0.0859	
Extinction coefficient	0.0148(11)	
Largest diff. peak and hole	0.273 and -0.248 $e.Å^{-3}$	
CCDC No	1536560	

Table 2. Bond lengths [Å] and angles [°] for Compound **2.**

O(1)-N(3)	1.2203(17)	O(2)-N(3)	1.2163(17)
N(3)-C(4)	1.5108(19)	C(4)-N(5)	1.4283(18)
C(4)-H(4B)	0.9900	C(4)-H(4A)	0.9900
N(5)-N(16)	1.3315(17)	N(5)-C(6)	1.3778(17)
C(6)-C(10)	1.393(2)	C(6)-N(7)	1.4007(18)
N(7)-O(8)	1.2320(17)	N(7)-O(9)	1.2391(16)
C(10)-N(11)	1.3352(18)	C(10)-C(12)	1.4152(19)
N(11)-H(11A)	0.8800	N(11)-H(11B)	0.8800
C(12)-N(16)	1.3230(19)	C(12)-N(13)	1.4321(19)
N(13)-O(15)	1.2255(17)	N(13)-O(14)	1.2345(17)

O(2)-N(3)-O(1)	125.64(13)	O(2)-N(3)-C(4)	119.37(12)
O(1)-N(3)-C(4)	114.99(12)	N(5)-C(4)-N(3)	110.92(11)
N(5)-C(4)-H(4B)	109.5	N(3)-C(4)-H(4B)	109.5
N(5)-C(4)-H(4A)	109.5	N(3)-C(4)-H(4A)	109.5
H(4B)-C(4)-H(4A)	108.0	N(16)-N(5)-C(6)	111.09(12)
N(16)-N(5)-C(4)	118.56(11)	C(6)-N(5)-C(4)	130.30(12)
N(5)-C(6)-C(10)	108.70(12)	N(5)-C(6)-N(7)	123.66(13)
C(10)-C(6)-N(7)	127.62(13)	O(8)-N(7)-O(9)	124.35(13)
O(8)-N(7)-C(6)	119.53(12)	O(9)-N(7)-C(6)	116.13(13)
N(11)-C(10)-C(6)	129.23(14)	N(11)-C(10)-C(12)	129.95(14)
C(6)-C(10)-C(12)	100.82(12)	C(10)-N(11)-H(11A)	120.0
C(10)-N(11)-H(11B)	120.0	H(11A)-N(11)-H(11B)	120.0
N(16)-C(12)-C(10)	114.62(13)	N(16)-C(12)-N(13)	119.21(13)
C(10)-C(12)-N(13)	126.16(13)	O(15)-N(13)-O(14)	124.96(14)
O(15)-N(13)-C(12)	118.54(13)	O(14)-N(13)-C(12)	116.49(13)
C(12)-N(16)-N(5)	104.76(11)		

Table 3. Hydrogen bonds for Compound **2** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(4)-H(4B)...O(1)#1	0.99	2.48	3.1659(18)	126.5
C(4)-H(4A)...O(8)#3	0.99	2.44	3.3899(19)	161.5
N(11)-H(11A)...O(9)	0.88	2.26	2.8084(18)	120.0
N(11)-H(11B)...O(14)	0.88	2.29	2.8356(18)	120.1

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

#4 x-1/2,-y+1/2,z-1/2 #5 -x,-y,-z+2

Table 4. Crystal data and structure refinement for Compound **3**.

Identification code	shrv443	
Empirical formula	$C_4H_2N_6O_8$	
Formula weight	262.12	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 6.0874(2) Å	α= 90°.
	b = 19.3210(8) Å	β= 108.2550(10)°.
	c = 8.3437(3) Å	γ = 90°.
Volume	931.95(6) $Å^3$	
Z	4	
Density (-123°C)	1.868 Mg/m^3	
Density (20°C)	1.843 Mg/m^3	
Absorption coefficient	0.182 mm^{-1}	
F(000)	528	
Crystal size	0.439 x 0.270 x 0.118 mm^3	
Theta range for data collection	2.108 to 30.019°.	
Index ranges	-7<=h<=8, -26<=k<=26, -11<=l<=11	
Reflections collected	10890	
Independent reflections	2647 [R_{int} = 0.0151]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7460 and 0.6910	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2647 / 0 / 163	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R_1 = 0.0325, wR_2 = 0.0825	
R indices (all data)	R_1 = 0.0354, wR_2 = 0.0849	
Largest diff. peak and hole	0.377 and -0.327 $e.Å^{-3}$	
CCDC No	1536561	

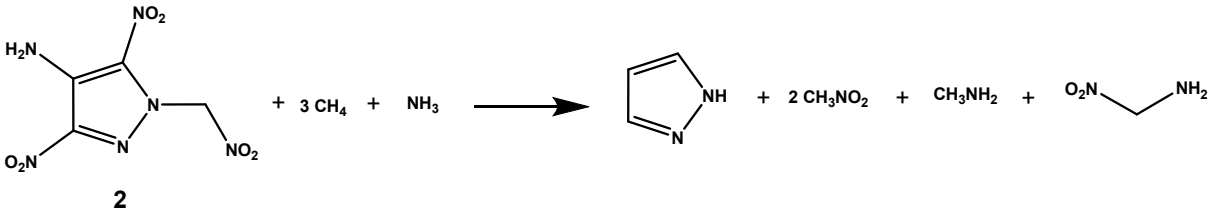
Table 5. Bond lengths [Å] and angles [°] for Compound **3**.

O(1)-N(3)	1.2167(11)	O(2)-N(3)	1.2142(12)
N(3)-C(4)	1.5118(12)	C(4)-N(5)	1.4401(11)
C(4)-H(2)	0.9900	C(4)-H(3)	0.9900
N(5)-N(18)	1.3415(11)	N(5)-C(6)	1.3606(11)
C(6)-C(10)	1.3713(12)	C(6)-N(7)	1.4406(12)

N(7)-O(8)	1.2203(12)	N(7)-O(9)	1.2251(11)
C(10)-C(14)	1.3950(12)	C(10)-N(11)	1.4574(11)
N(11)-O(13)	1.2120(13)	N(11)-O(12)	1.2120(13)
C(14)-N(18)	1.3206(11)	C(14)-N(15)	1.4460(12)
N(15)-O(17)	1.2197(12)	N(15)-O(16)	1.2282(11)

O(2)-N(3)-O(1)	125.75(9)	O(2)-N(3)-C(4)	119.05(8)
O(1)-N(3)-C(4)	115.19(8)	N(5)-C(4)-N(3)	110.32(7)
N(5)-C(4)-H(2)	109.6	N(3)-C(4)-H(2)	109.6
N(5)-C(4)-H(3)	109.6	N(3)-C(4)-H(3)	109.6
H(2)-C(4)-H(3)	108.1	N(18)-N(5)-C(6)	111.44(7)
N(18)-N(5)-C(4)	117.81(8)	C(6)-N(5)-C(4)	130.75(8)
N(5)-C(6)-C(10)	107.45(8)	N(5)-C(6)-N(7)	124.30(8)
C(10)-C(6)-N(7)	128.24(8)	O(8)-N(7)-O(9)	126.33(9)
O(8)-N(7)-C(6)	118.00(8)	O(9)-N(7)-C(6)	115.66(8)
C(6)-C(10)-C(14)	103.57(8)	C(6)-C(10)-N(11)	127.21(8)
C(14)-C(10)-N(11)	129.17(8)	O(13)-N(11)-O(12)	126.50(10)
O(13)-N(11)-C(10)	116.01(9)	O(12)-N(11)-C(10)	117.48(9)
N(18)-C(14)-C(10)	112.86(8)	N(18)-C(14)-N(15)	120.12(8)
C(10)-C(14)-N(15)	127.02(8)	O(17)-N(15)-O(16)	126.48(9)
O(17)-N(15)-C(14)	118.30(8)	O(16)-N(15)-C(14)	115.22(8)
C(14)-N(18)-N(5)	104.68(7)		

2. Isodesmic Reaction



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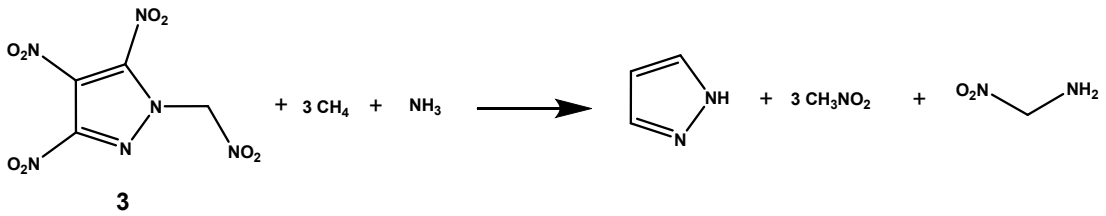

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3. NMR spectra

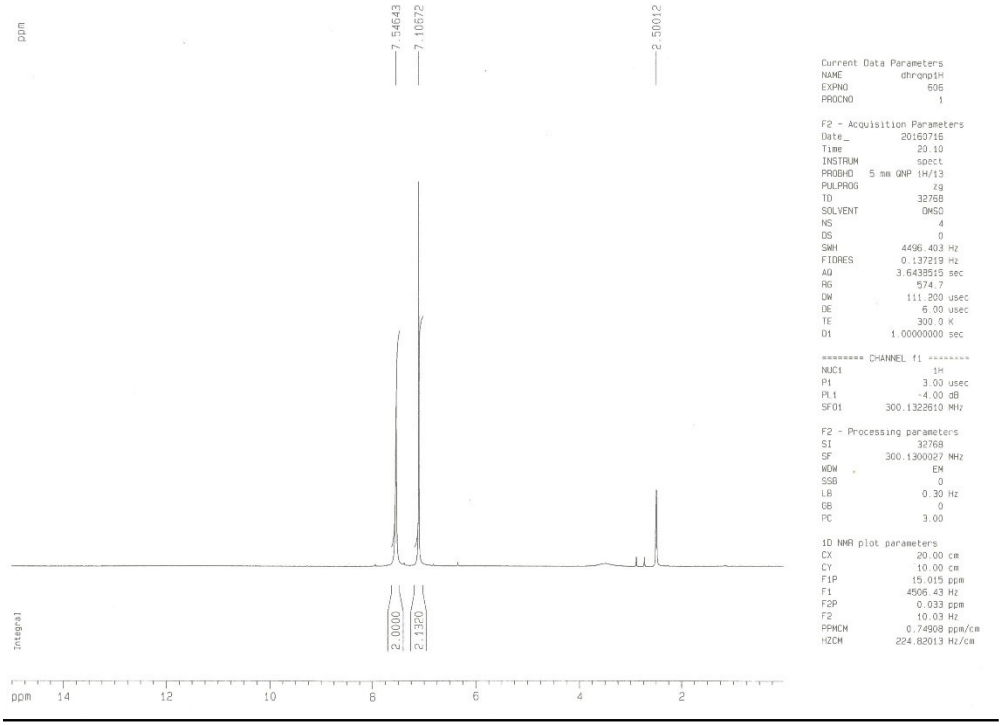

Fig S1: ^{1}H NMR Spectrum of compound **2**

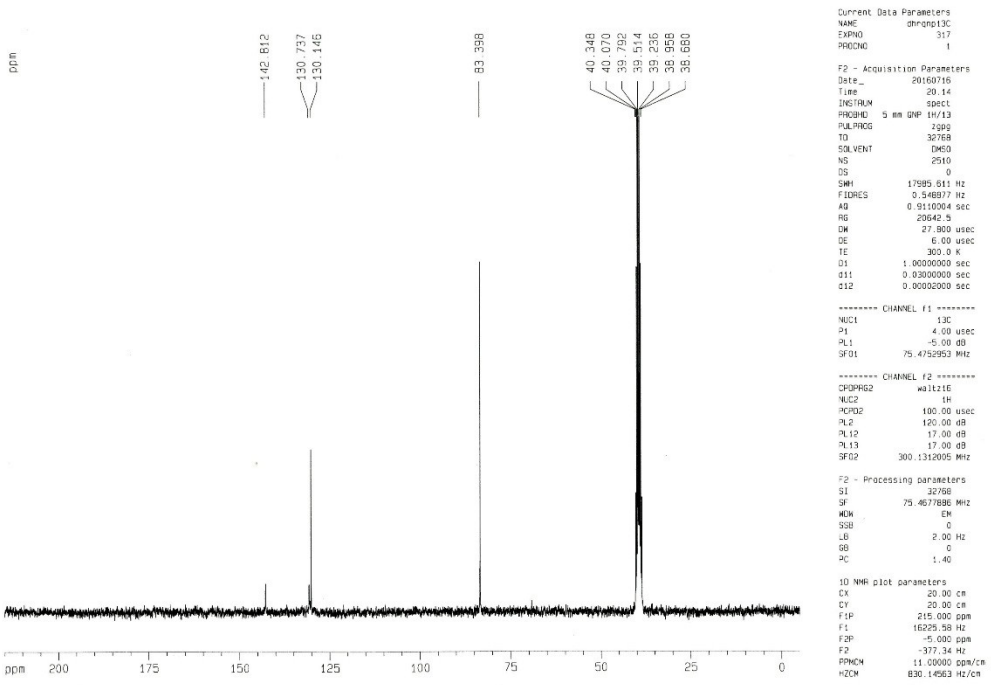

Fig S2: $^{13}C\{^{1}H\}$ NMR Spectrum of compound **2**

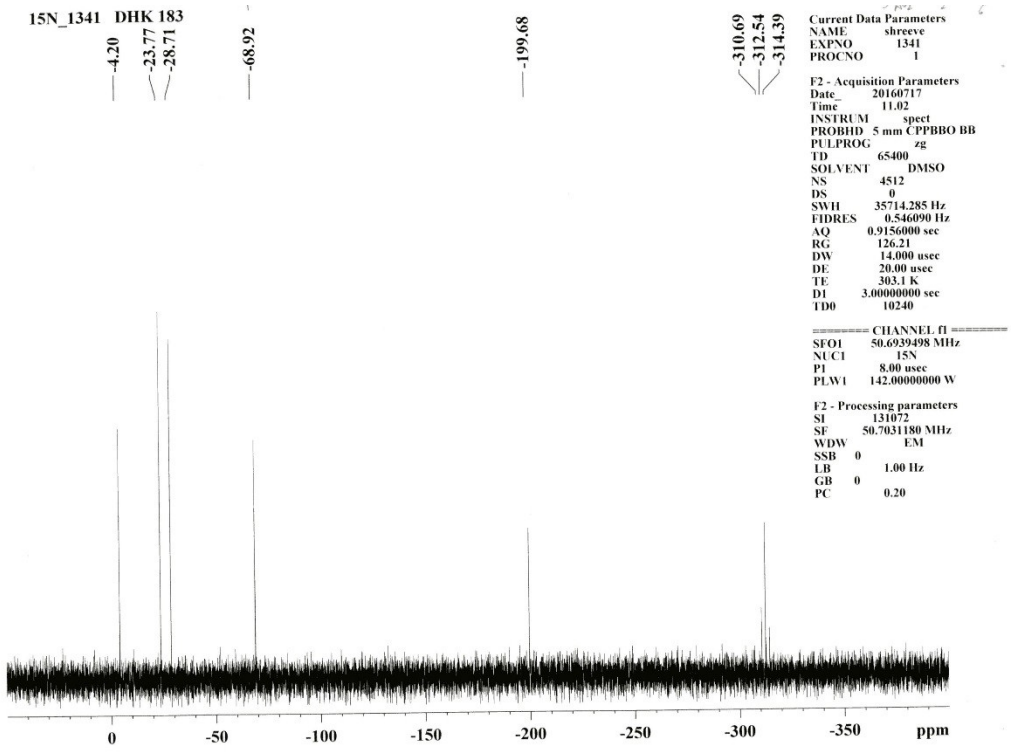

Fig S3: ^{15}N NMR Spectrum of compound **2**

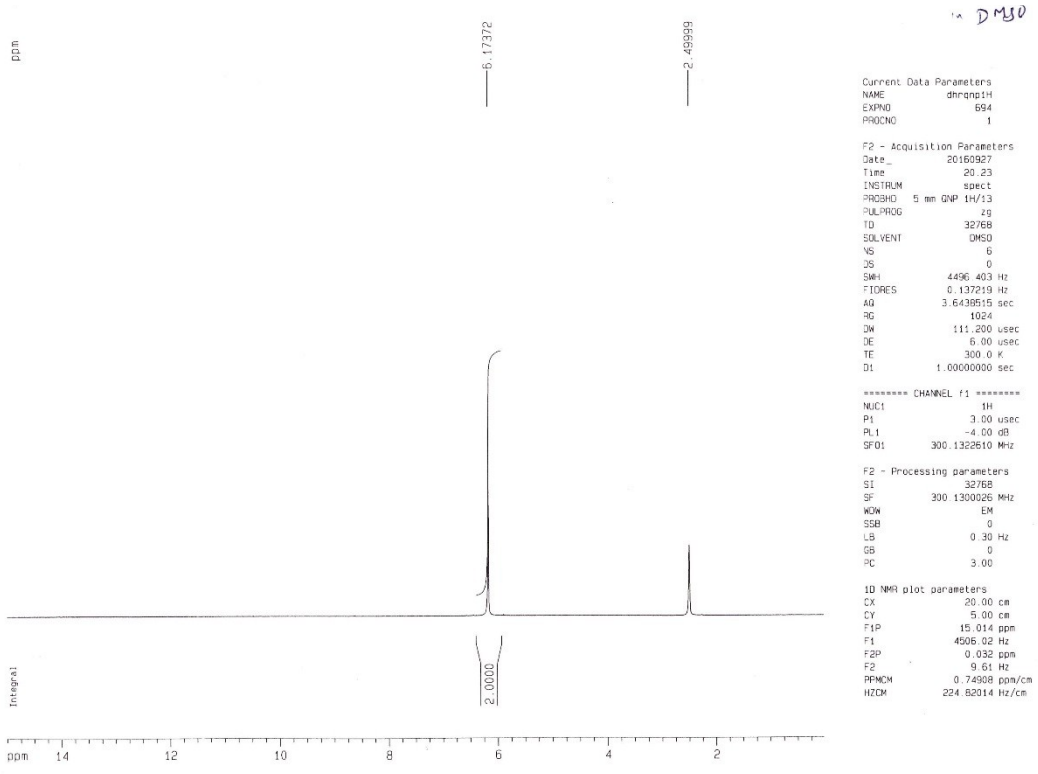

Fig S4: ^{1}H NMR Spectrum of **3 (TNNMP)**

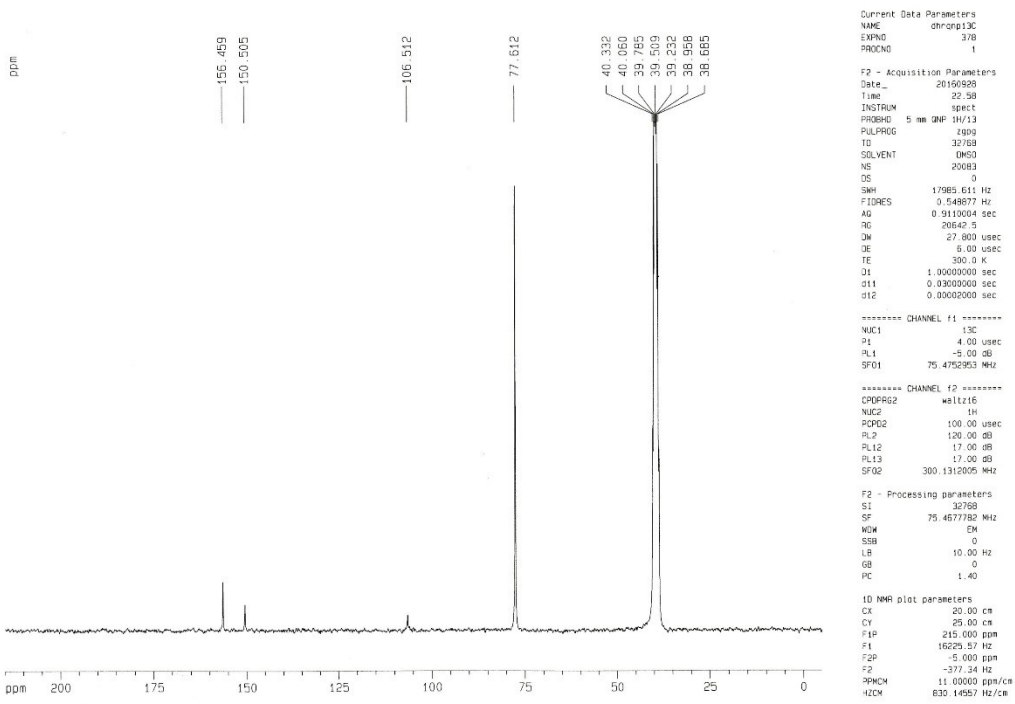

Fig S5: $^{13}C\{^{1}H\}$ NMR Spectrum of **3 (**TNNMP)

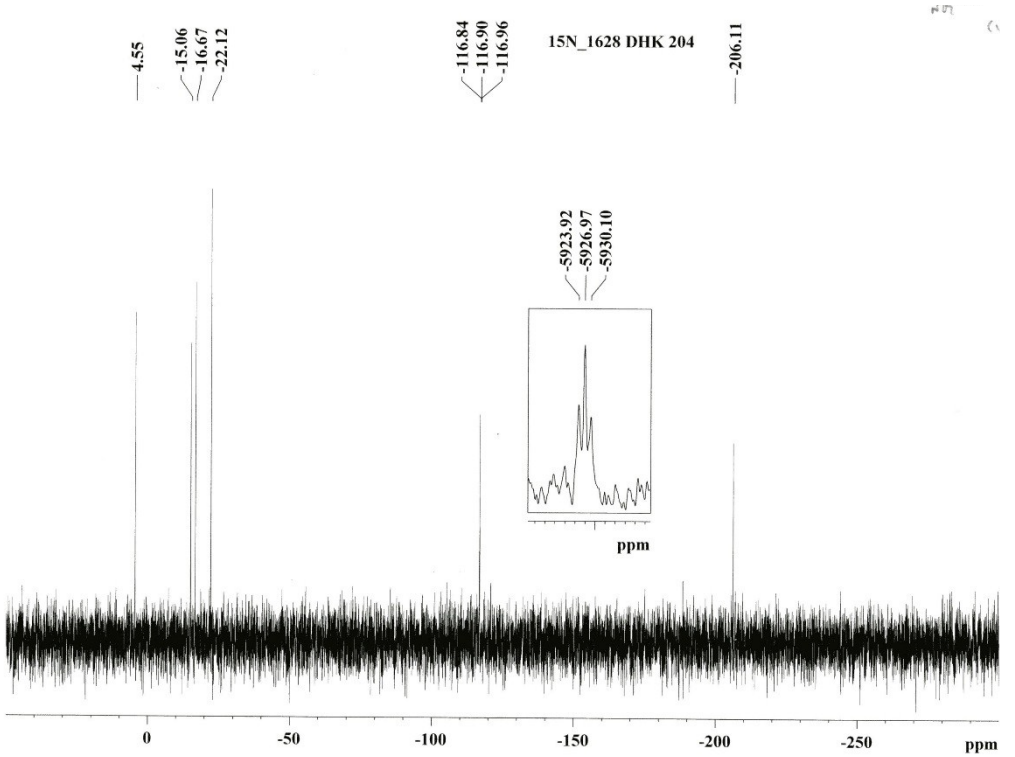

Fig S6: ^{15}N NMR Spectrum of **4 (**TTX)