Supporting information

The Synthesis and Properties of Azamonocyclic Energetic Materials with Geminal Explosophores

Kaidi Yang[a,b], Fuqiang Bi[a,b], Qi Xue[a], Huan Huo[a], Chao Bai[c], Junlin Zhang[a,b,*] , Bozhou Wang[a,b,*]

[a] Xi'an Modern Chemistry Research Institute, Xi'an 710065, China

[b] State Key Laboratory of Fluorine & Nitrogen Chemicals, Xi'an 710065, China

[c] College of Chemistry & Mateirals Secience, Northwest University, Xi'an 710127, China.

Computer Method

The reaction mechanism of C-Br cleavage calculations were carried out using Gaussian 16 package. The geometry optimizations were performed at the B3LYP/6-31G(d,p) level and frequency analyses were conducted at the same level of theory to obtain the thermal correction and confirm the stationary points to be minima or transition states. The single-point energy calculations were performed at the M062X/6-311+G(d,p) level. The Grimme's empirical dispersion-correction (Grimme-D3) was applied and the SMD solvation model (considering methanol as the solvent) was introduced in all the calculations.

Crystallographic data

The apparatus and conditions of crystal structure determination

A single crystal of TNHP suitable for X-ray diffraction analysis was prepared by slow evaporation of acetone-H_2O solvent at room temperature. A colorless crystal with dimension of 0.30×0.30×0.20 mm was selected for X-ray single crystal diffraction analysis. The diffraction data were collected on a BRUKER SMART Apex Ⅱ CCD X-ray diffractometer equipped with a Mo Kα radiation (λ=0.71073 A) using an ω-θ scan mode at 296(2) K. A total of 4432 reflections were obtained in the range of 1.78≤θ≤26.37, of which 1674 were independent (R_{int} =0.0261) were considered to

be observed and used for the refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELES-97 and SHELXL-97 programs. A full-matrix least-squares refinement gave the final R_1= 0.0371 and ωR_2= 0.0972 ($\omega=1/[\sigma^2(F_0^2) + (0.0270\ P)^2 + 0.0000\ P]$, where $P =(F_0^2+2Fc^2)/3$). The goodness-of-fit on F^2 is 1.036. The largest difference peak and hole were 0.168and -0.178 e/Å^3.

A single crystal of TNHA suitable for X-ray diffraction analysis was prepared by slow evaporation of ethyl acetate solvent at room temperature. A colorless crystal with dimension of 0.15×0.14×0.12 mm was selected for X-ray single crystal diffraction analysis. The diffraction data were collected on a BRUKER SMART Apex Ⅱ CCD X-ray diffractometer equipped with a Mo Kα radiation (λ=0.71073 A) using an ω-θ scan mode at 150(2) K. A total of 5950 reflections were obtained in the range of 3.242°≤θ≤26.422°,of which 1716 were independent (R_{int} =0.0392) were considered to be observed and used for the refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F2 using SHELES-97 and SHELXL-97 programs. A full-matrix least-squares refinement gave the final R1= 0.0280 and ωR2=0.0560($\omega=1/[\sigma^2(F_0^2) + (0.0270\ P)^2 + 0.0000\ P]$, where $P =(F_0^2+2Fc^2)/3$). The goodness-of-fit on F^2 is 1.054. The largest difference peak and hole were 0.145 and -0.144 e/Å^3.

A single crystal of DNNC suitable for X-ray diffraction analysis was prepared by slow evaporation of ethyl acetate solvent at room temperature. A colorless crystal was selected for X-ray single crystal diffraction analysis. The diffraction data were collected on a BRUKER SMART Apex Ⅱ CCD X-ray diffractometer equipped with a Mo Kα radiation (λ=1.54178 A) using an ω-θ scan mode at 150(2) K. A total of 35702 reflections were obtained of which 10000 were independent (R_{int} =0.0450) were considered to be observed and used for the refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELES-97 programs. A full-matrix least-squares refinement gave the final R_1=

0.0582 and ωR_2= 0.1503 (I≥2(I)), where P =(F_0^2+2Fc^2)/3). The goodness-of-fit on F^2 is 1.057.

Table S1. Crystal data and structure refinement parameters for TNHP and TNHA

Compound	TNHP	TNHA	DNNC
Empirical formula	$C_4H_7N_5O_6$	$C_4H_6N_8O_6$	$C_4H_6N_6O_8$
Molar mass (g/mol)	221.15	262.17	266.15
Temperature (K)	296(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	orthorhombic
Space group	*P2(1)/n*	*Cc*	$P2_1\ 2_1\ 2_1$
a (Å)	12.218(18)	13.308	11.0204
b (Å)	6.501(9)	6.3183	15.5390
c (Å)	11.023(17)	12.2565	33.3517
α (◦)	90.00(6)	90	90
β (◦)	110.168(2)	109.22	90
γ (◦)	90.00	90	90
V (Å ^{3})	821.9 (2)	973.15	5711.34
Z	4	4	24
h	-14<= *h* <=15	-15<= *h* <=15	-12<= *h* <=13
k	-8<= *k* <=4	-7<= *k* <=7	-18<= *k* <=18
l	-13<= *l* <=11	-14<= *l* <=14	-39<= *l* <=39
*D*c (g/cm^3)	1.787	1.789	1.857
λ (Å)	0.71073	0.71073	1.54178
F(0 0 0)	456	536	3264.0
θ range (◦)	1.78-26.37	3.242-26.422	2.650-70.199

Measured reflections	4432	6793	35702
Unique data (*R*int)	1674 (0.0261)	1980(0.0392)	10000（0.0450）
*R*1, *wR*2 [$I > 2\sigma(I)$]	0.0371,0.0872	0.0280, 0.0560	0.0582，0.1503
*R*1, *wR*2 (all data)	0.0532, 0.0962	0.0345, 0.0600	0.0628，0.1553
Goodness-of-fit	1.036	1.054	1.057

X-Ray crystal structure

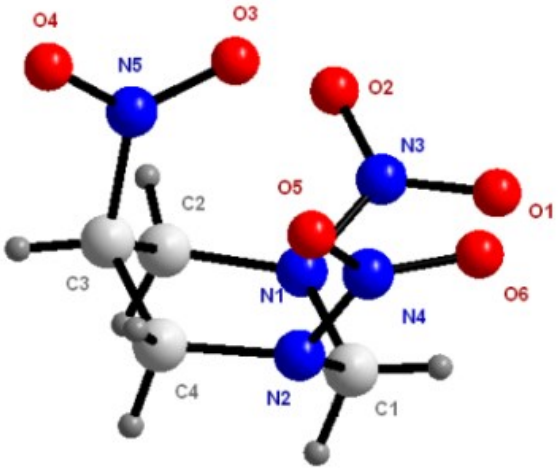

Figure S1. The molecular structure of TNHP

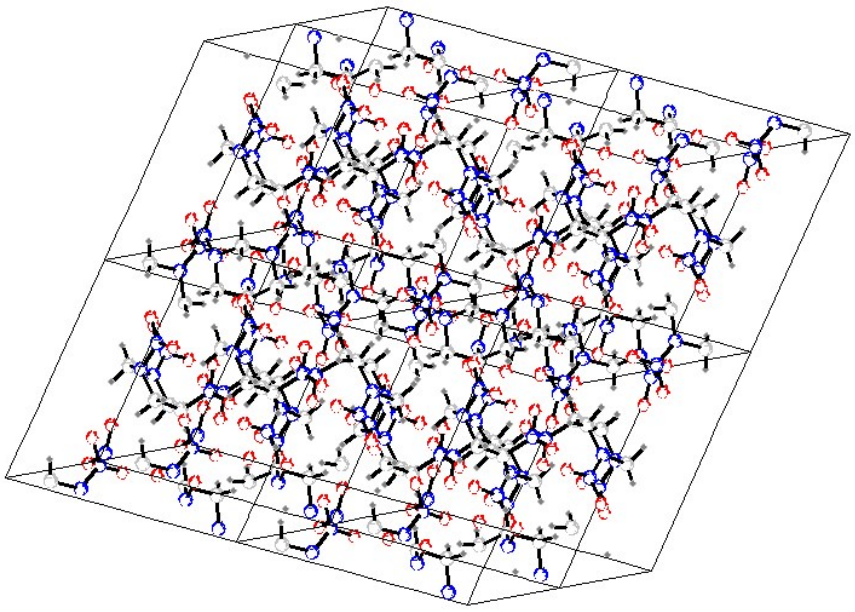

Figure S2. The packing diagram of TNHP

Bond lengths and angles of TNHA, DNNC and TNHP

Table S2. Bond length of TNHA/ Å

C(1)-N(1)	1.456(4)
C(1)-N(2)	1.458(4)
C(1)-H(1)	0.9900
C(2)-N(1)	1.456(4)
C(2)-C(3)	1.542(4)
C(2)-H(2)	0.9900
C(3)-N(5)	1.443(4)
C(3)-C(4)	1.533(4)
C(3)-N(8)	1.544(4)
C(4)-N(2)	1.454
C(4)-H(4)	0.9900
N(1)-N(3)	1.388(4)
N(2)-N(4)	1.377(4)
N(3)-O(2)	1.225(3)
N(4)-O(3)	1.219(3)
N(4)-O(4)	1.227(3)
N(5)-N(6)	1.257(4)
N(6)-N(7)	1.116(4)
N(8)-O(6)	1.211(3)
N(8)-O(5)	1.215(4)

Table S3. Bond angles of TNHA

N(1)-C(1)-N(2)	111.3(2)
N(1)-C(1)-H(1A)	109.4
H(1A)-C(1)-H(1B)	108.0
N(1)-C(2)-C(3)	110.1(2)
N(1)-C(2)-H(2A)	109.6
H(2A)-C(2)-H(2B)	108.1
N(5)-C(3)-C(4)	107.1(2)
N(5)-C(3)-C(2)	114.6(2)
C(4)-C(3)-C(2)	111.4(2)
N(5)-C(3)-N(8)	110.0(2)
C(4)-C(3)-N(8)	107.0(2)
C(2)-C(3)-N(8)	106.5(2)
N(2)-C(4)-C(3)	108.8(2)
N(3)-N(1)-C(1)	117.1(2)
C(4)-N(2)-C(1)	116.2(2)
O(2)-N(3)-O(1)	125.2(3)
O(2)-N(3)-N(1)	117.3(3)
O(3)-N(4)-O(4)	125.0(3)
O(3)-N(4)-N(2)	117.6(2)
N(6)-N(5)-C(3)	115.0(3)
N(7)-N(6)-N(5)	172.1(3)
O(6)-N(8)-O(5)	124.8(3)
O(6)-N(8)-C(3)	118.5(3)
O(5)-N(8)-C(3)	116.7(2)

Table S4. Bond length of DNNC/ Å

C(1)-N(1)	1.459(7)
C(1)-N(2)	1.488(6)
C(1)-H(1)	0.9900
C(2)-N(1)	1.460(6)
C(2)-C(3)	1.533(7)
C(2)-H(2)	0.9900
C(3)-N(5)	1.455(6)
C(3)-C(4)	1.534(7)
C(3)-N(8)	1.443(7)
C(4)-N(2)	1.461(6)
C(4)-H(4)	0.9900
N(1)-N(3)	1.376(6)
N(2)-N(4)	1.363(6)
N(3)-O(2)	1.211(6)
N(4)-O(3)	1.226(6)
N(4)-O(4)	1.216(6)

Table S5. Bond angles of DNNC

N(1)-C(1)-N(2)	119.4(4)
N(1)-C(1)-H(1A)	109.7
H(1A)-C(1)-H(1B)	108.0
N(1)-C(2)-C(3)	106.1(4)
N(1)-C(2)-H(2A)	109.6
H(2A)-C(2)-H(2B)	108.1
N(5)-C(3)-C(4)	109.0(4)

N(5)-C(3)-C(2)	110.7(4)
C(4)-C(3)-C(2)	114.3(4)
N(5)-C(3)-N(8)	104.1(4)
C(4)-C(3)-N(8)	111.6(4)
C(2)-C(3)-N(8)	110.1(4)
N(2)-C(4)-C(3)	111.0(2)
O(2)-N(3)-N(1)	116.8(5)
O(3)-N(4)-O(4)	125.5(5)
O(3)-N(4)-N(2)	116.7(5)
N(6)-N(5)-C(3)	110.1(4)
N(7)-N(6)-N(5)	172.1(3)
O(6)-N(8)-O(5)	125.5(6)
O(6)-N(8)-C(3)	117.7(5)
O(5)-N(8)-C(3)	113.7(5)

Table S6. Bond lengths of TNHP/ Å

C(1)-N(1)	1.452(2)
C(1)-N(2)	1.453(2)
C(2)-N(1)	1.454(2)
C(2)-C(3)	1.517(2)
C(3)-N(5)	1.505(2)
C(3)-C(4)	1.521(3)
C(4)-N(2)	1.459(2)
N(1)-N(3)	1.356(2)
N(2)-N(4)	1.400(2)

N(3)-O(2)	1.2221(19)
N(3)-O(1)	1.2235(19)
N(4)-O(6)	1.208(2)
N(4)-O(5)	1.214(2)
N(5)-O(4)	1.2110(19)
N(5)-O(3)	1.2186(19)

Table S7. Bond angles of TNHP

N(1)-C(1)-N(2)	110.98(14)
N(1)-C(2)-C(3)	111.89(14)
N(5)-C(3)-C(2)	111.54(15)
N(5)-C(3)-C(4)	109.05(15)
C(2)-C(3)-C(4)	112.02(15)
N(2)-C(4)-C(3)	112.72(14)
N(3)-N(1)-C(1)	119.89(14)
N(3)-N(1)-C(2)	119.44(15)
C(1)-N(1)-C(2)	118.08(14)
N(4)-N(2)-C(1)	116.04(14)
N(4)-N(2)-C(4)	116.07(14)
C(1)-N(2)-C(4)	114.48(14)
O(2)-N(3)-O(1)	124.13(16)
O(2)-N(3)-N(1)	118.12(15)
O(6)-N(4)-N(2)	117.26(15)
O(5)-N(4)-N(2)	116.82(16)
O(4)-N(5)-O(3)	124.56(17)

O(4)-N(5)-C(3)	117.61(16)

DSC-TG traces of TNBrP and TNHP

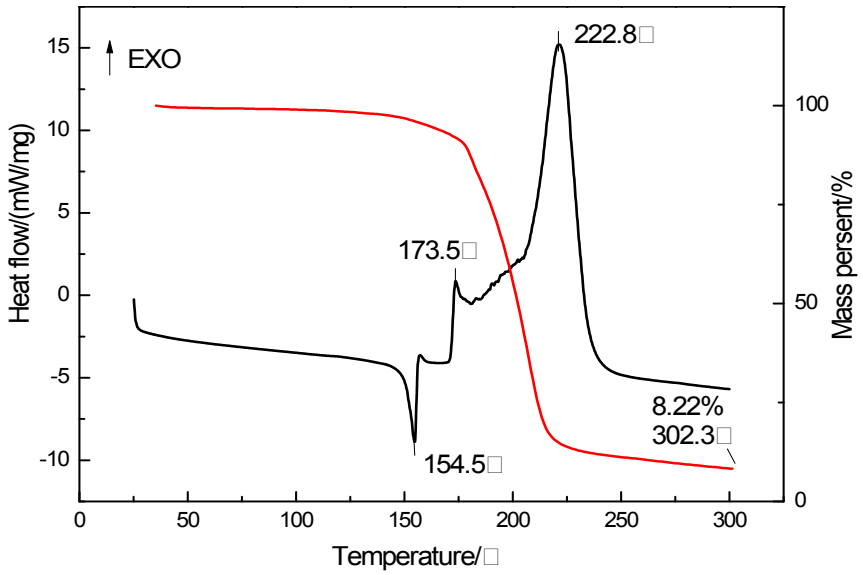

Figure S3. DSC-TG curves of TNBrP

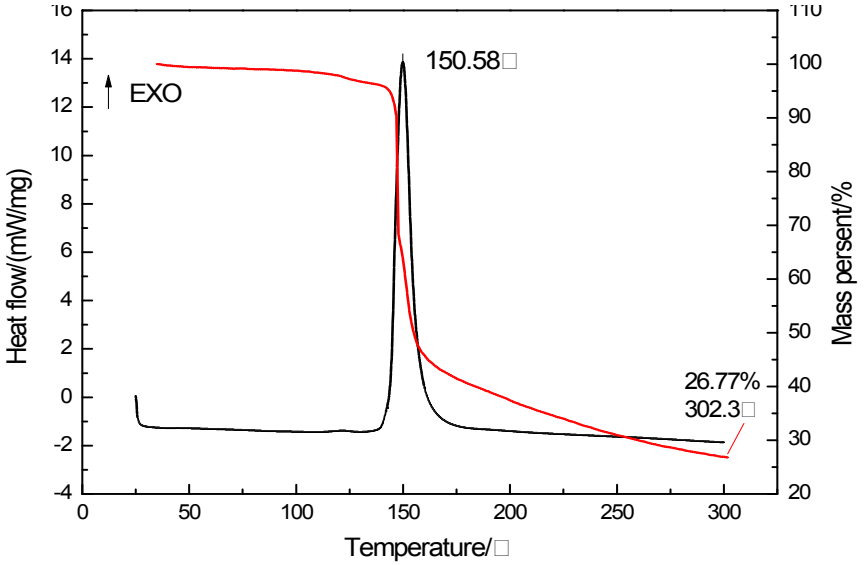

Figure S4. DSC-TG curves of TNHP

NMR spectra

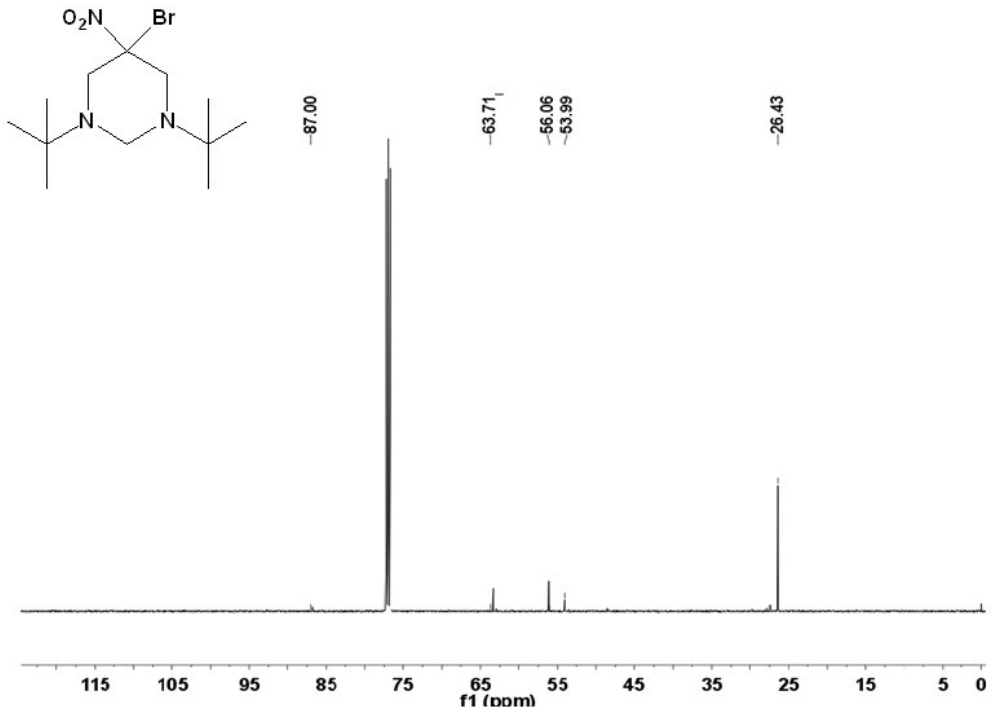

Figure S5. ^{13}C NMR of DBBrP (*d*-$CDCl_3$)

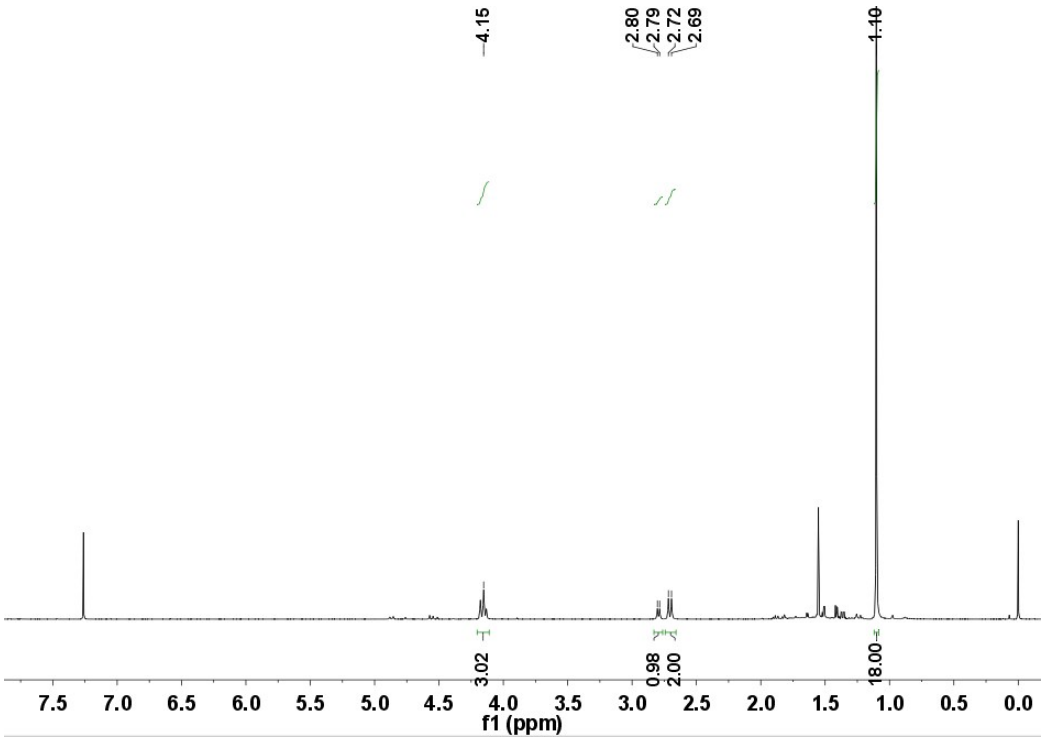

Figure S6. ^{1}H NMR of DBBrP (*d*-$CDCl_3$)

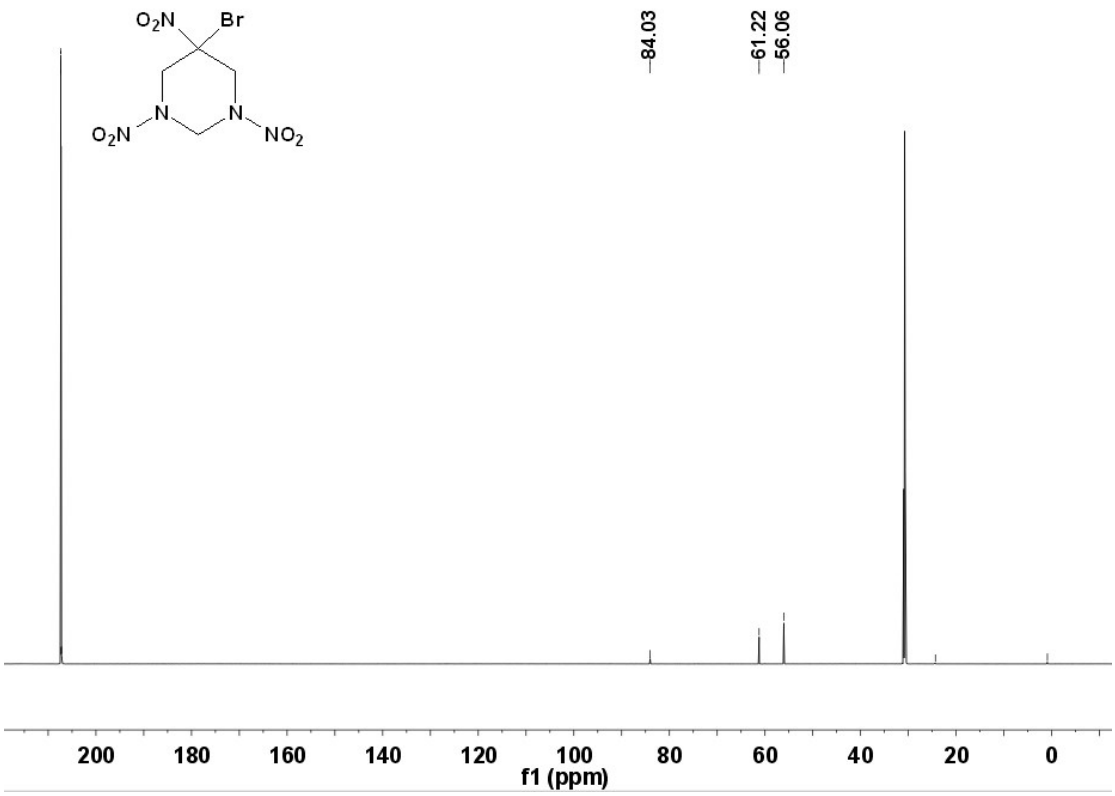

Figure S7. ^{13}C NMR of TNBrP (*d*-acetone)

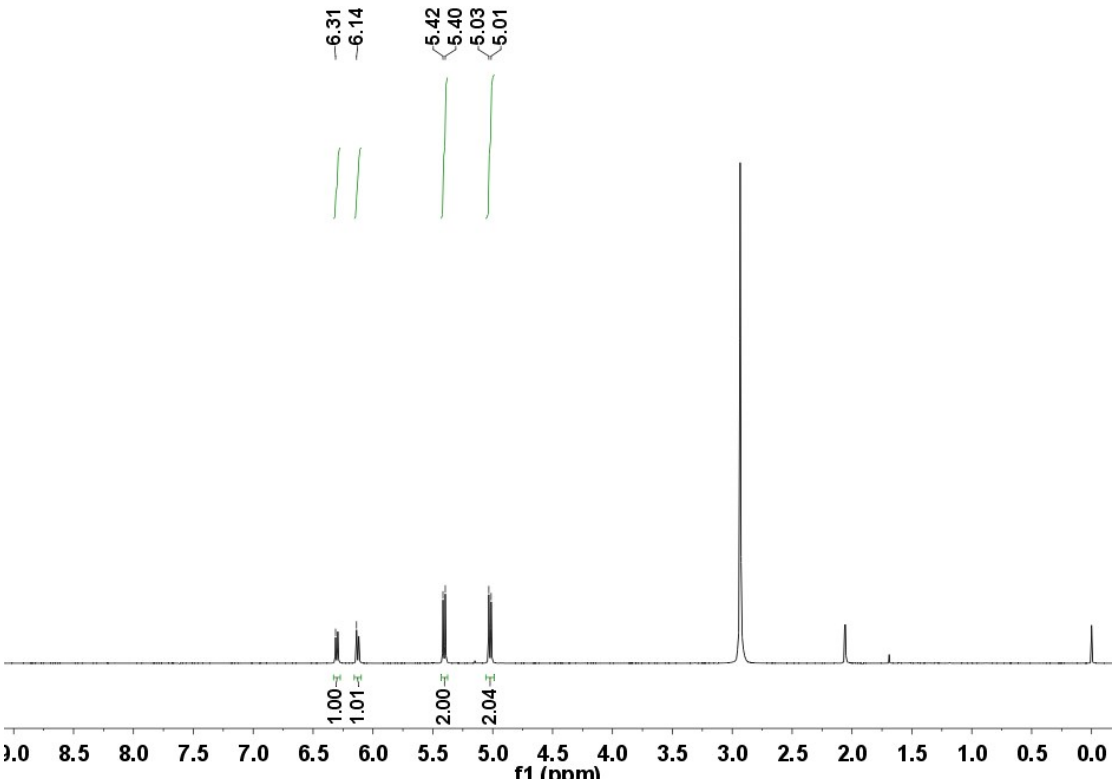

Figure S8. ^{1}H NMR of TNBrP (*d*-acetone)

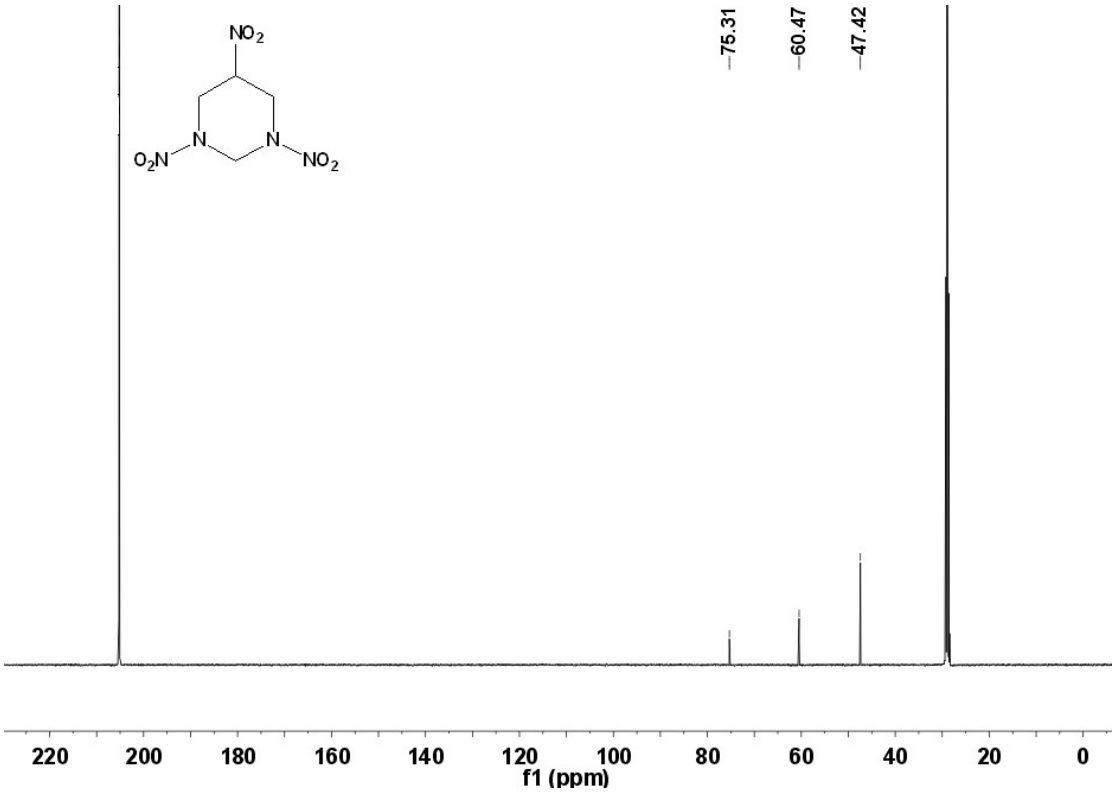

Figure S9. ^{13}C NMR of TNHP (*d*-acetone)

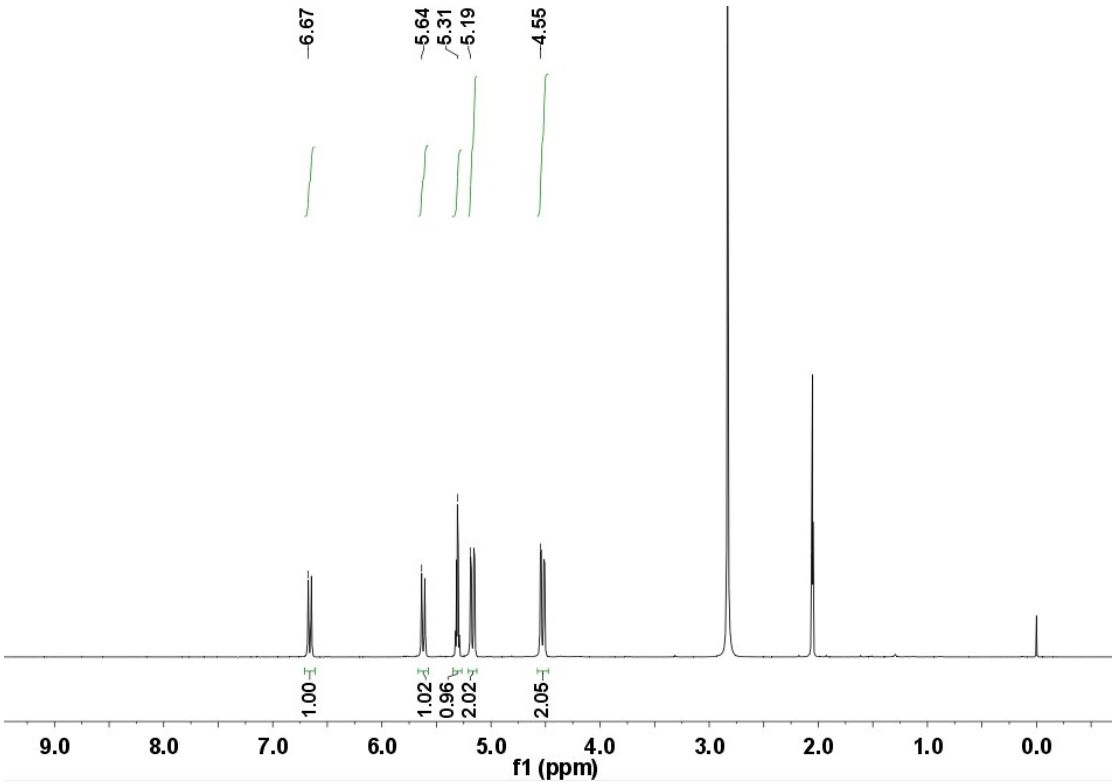

Figure S10. ^{1}H NMR of TNHP (*d*-acetone)

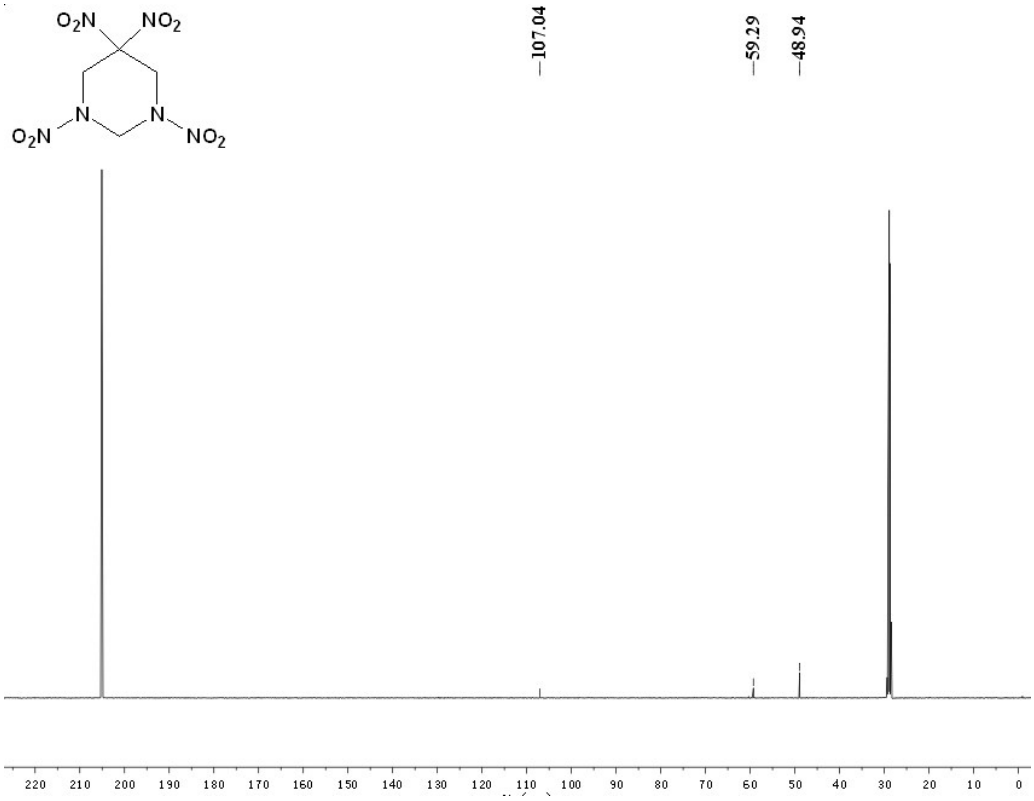

Figure S11. ^{13}C NMR of DNNC (*d*-acetone)

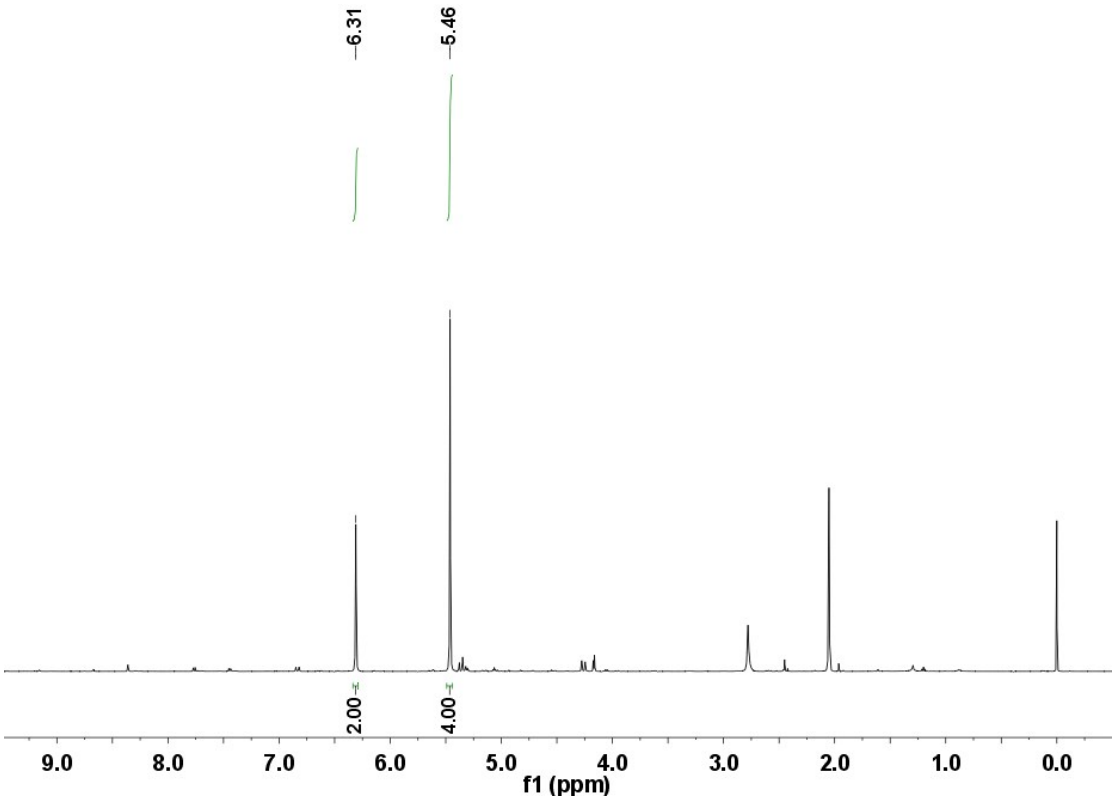

Figure S12.^{1}H NMR of DNNC (*d*-acetone)

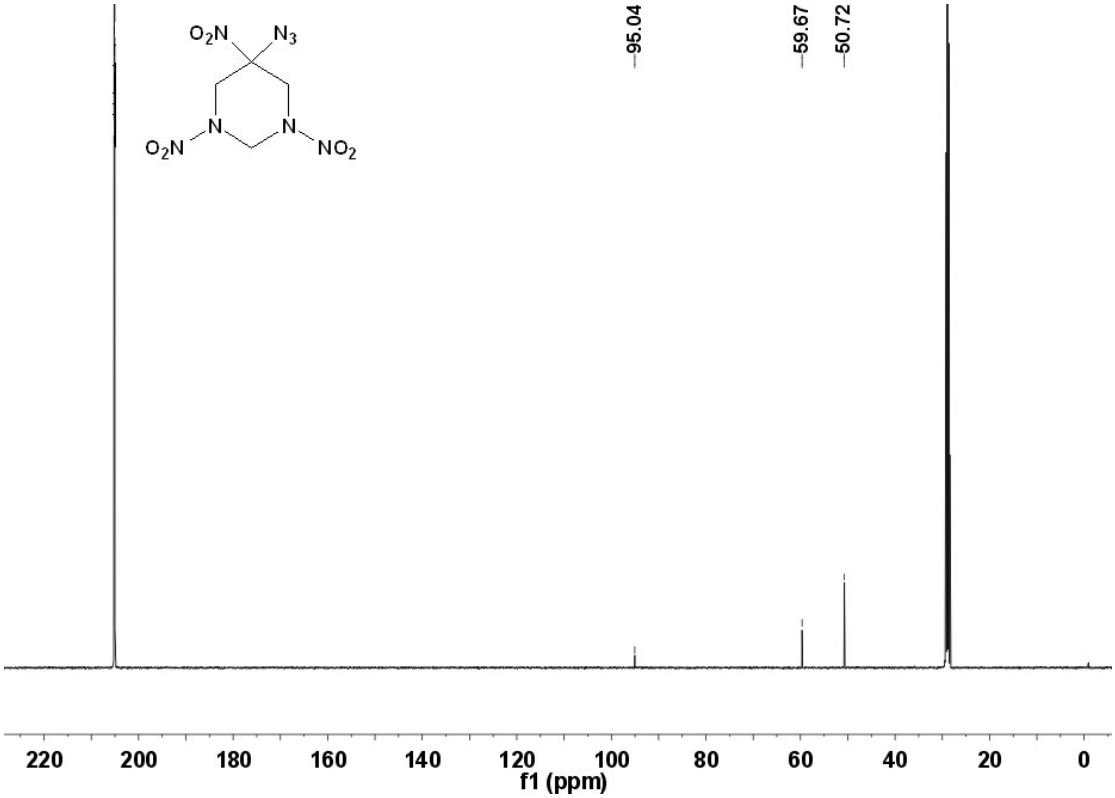

Figure S13. ^{13}C NMR of TNHA (*d*-acetone)

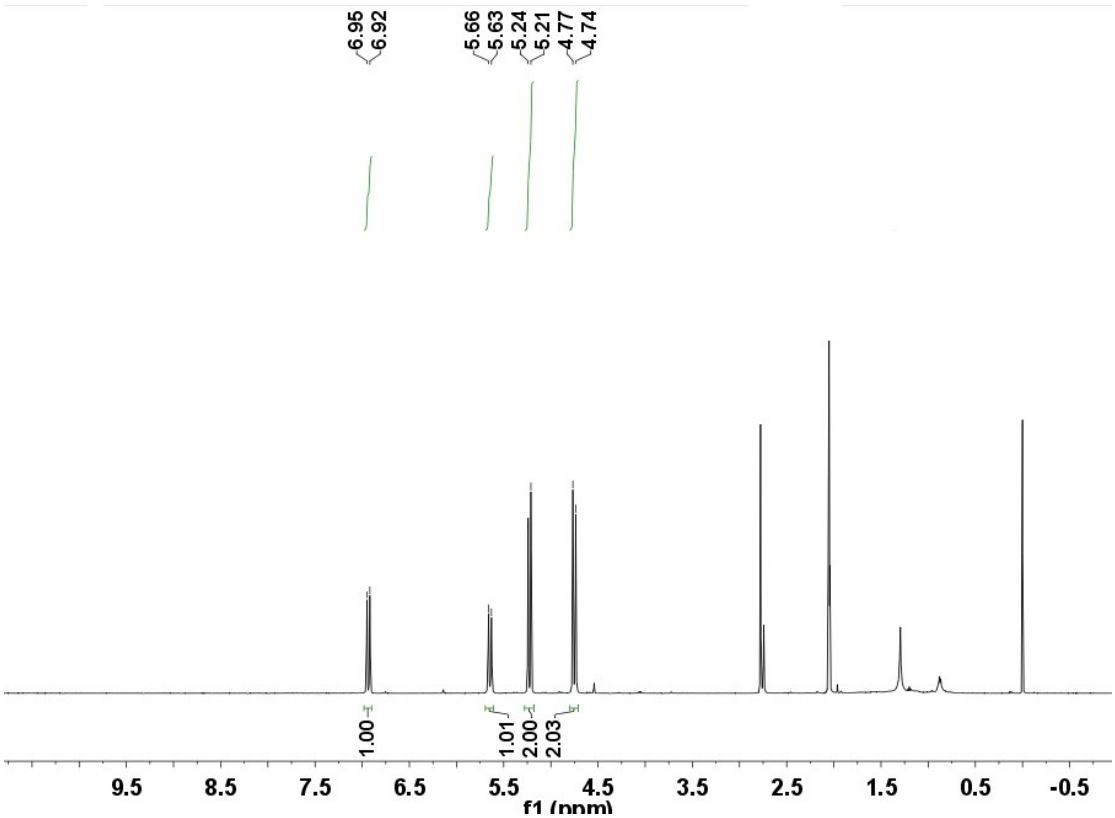

Figure S14. ^{1}H NMR of TNHA (*d*-acetone)

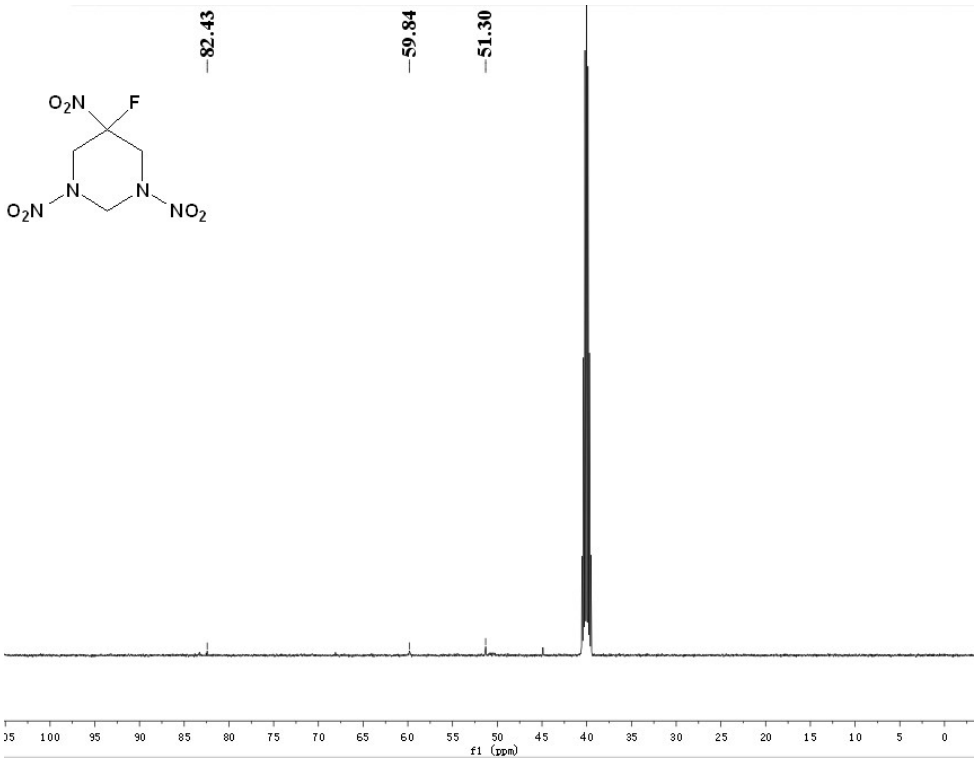

Figure S15. ^{13}C NMR of TNHF (*d*-DMSO)

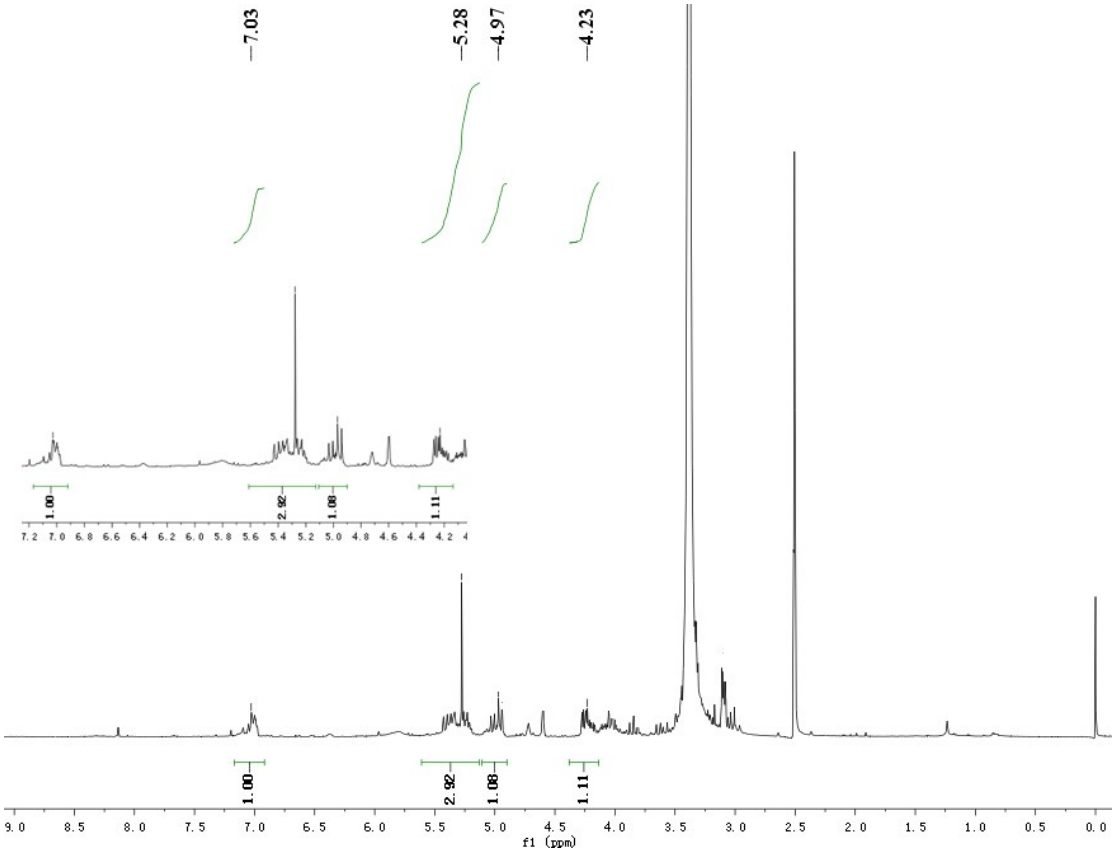

Figure S16. ^{1}H NMR of TNHF (*d*-DMSO)

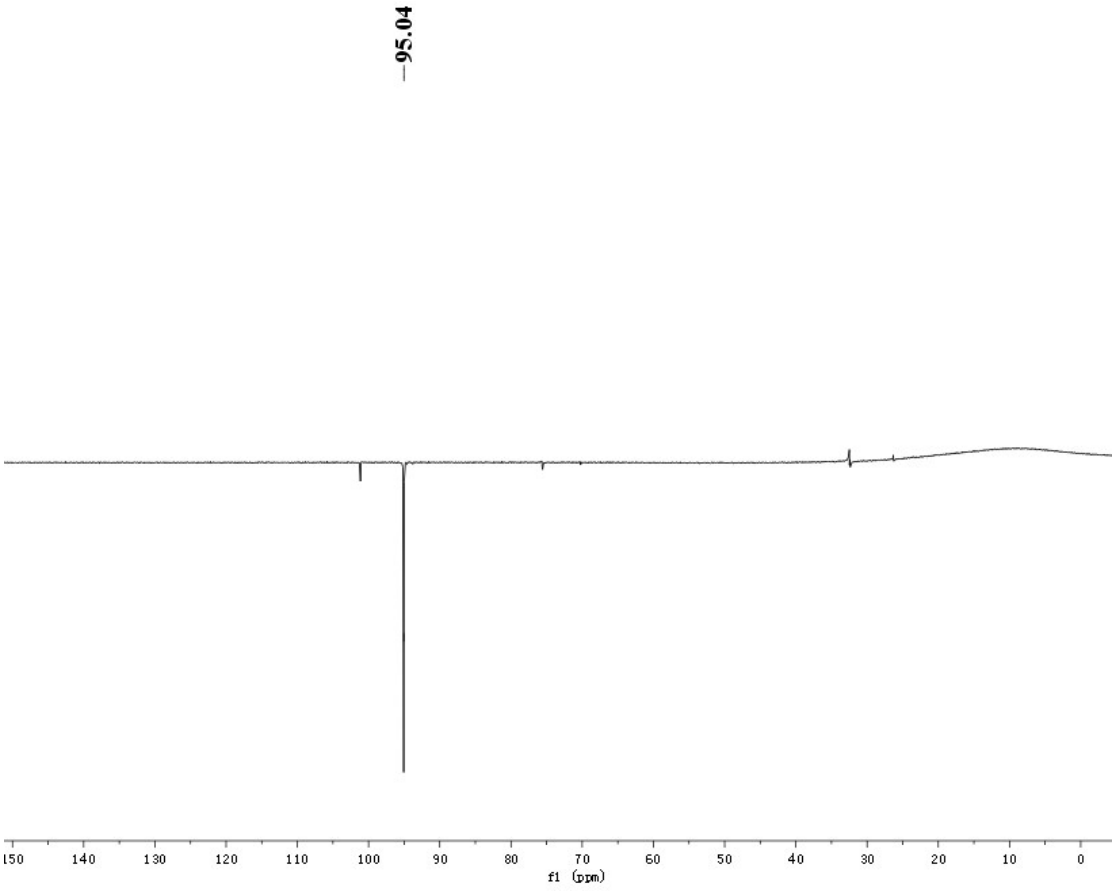

Figure S17. ^{19}F NMR of TNHF (*d*-DMSO)

IR Spectra

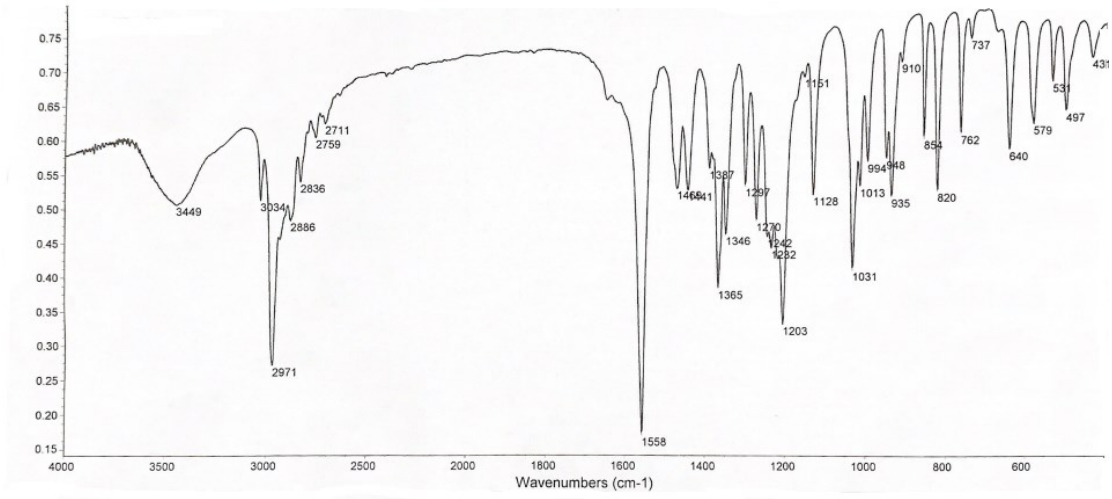

Figure S18. IR spectra of DBBrP

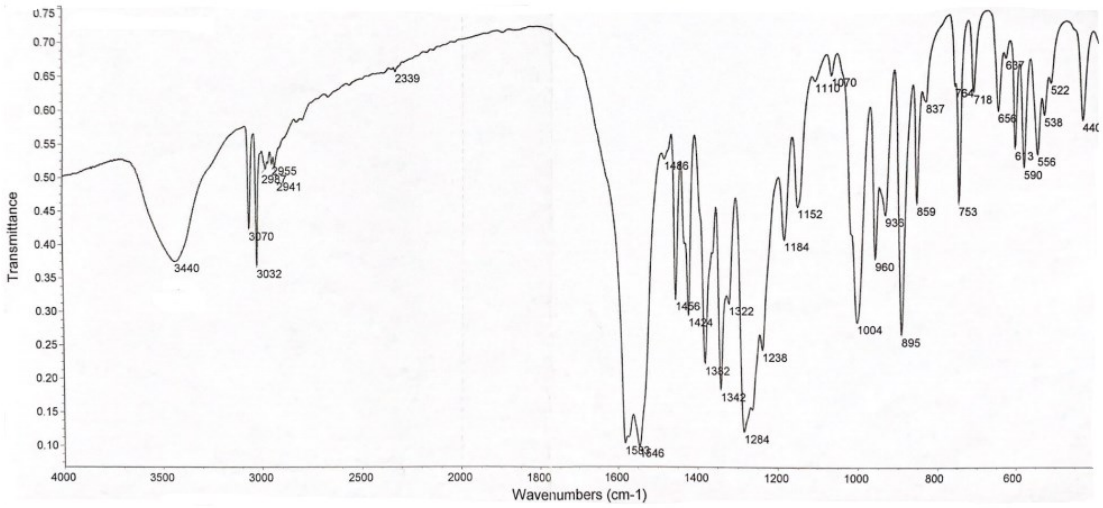

Figure S19. IR spectra of TNBrP

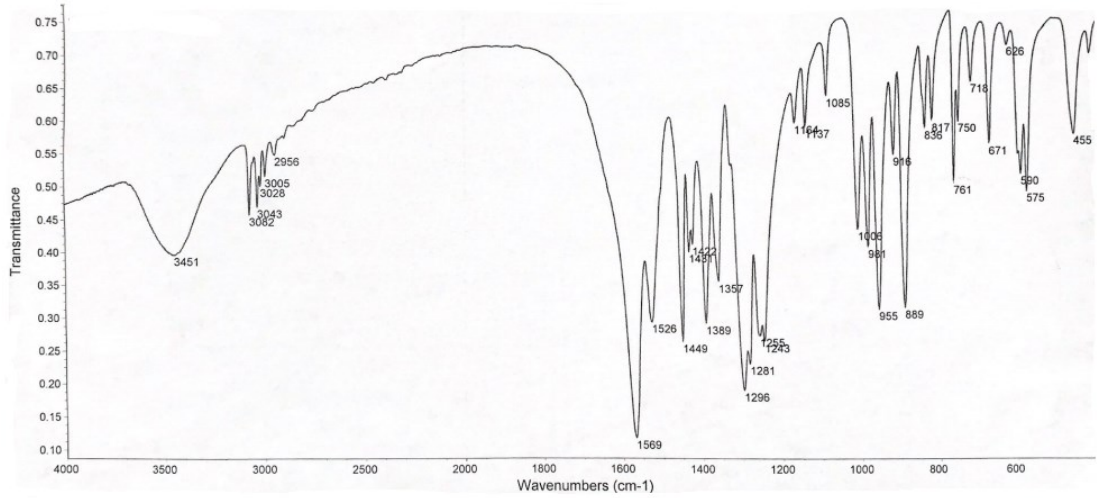

Figure S20. IR spectra of TNHP

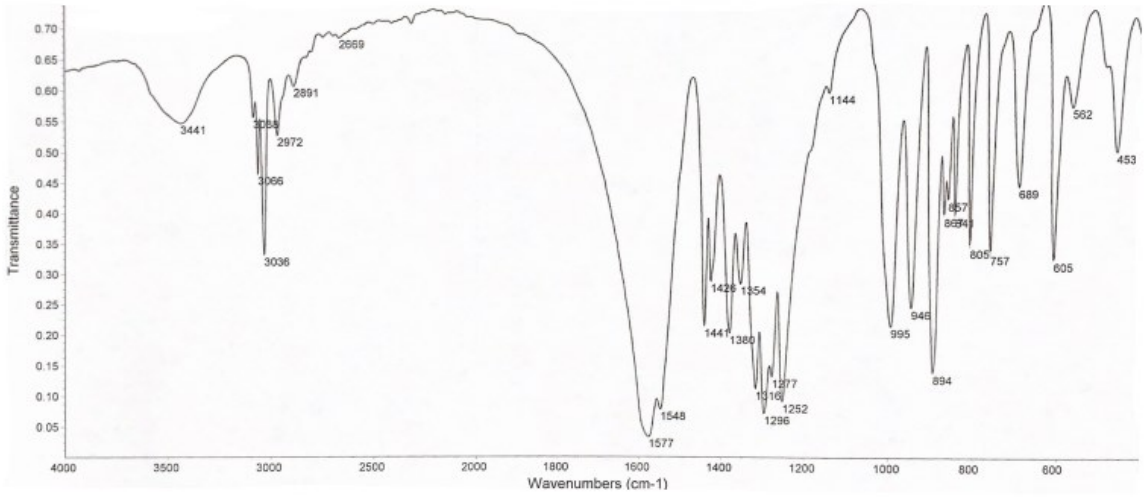

Figure S21. IR spectra of DNNC

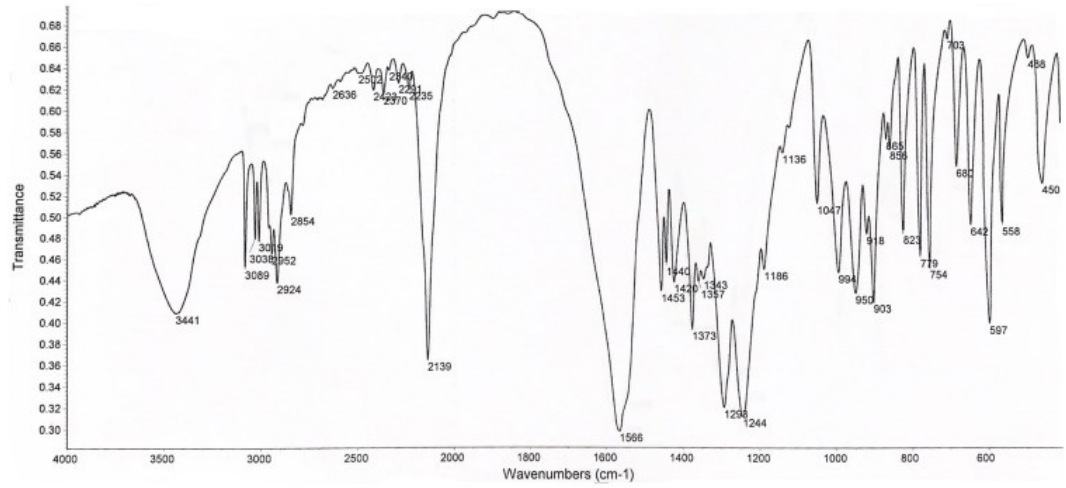

Figure S22. IR spectra of TNHA

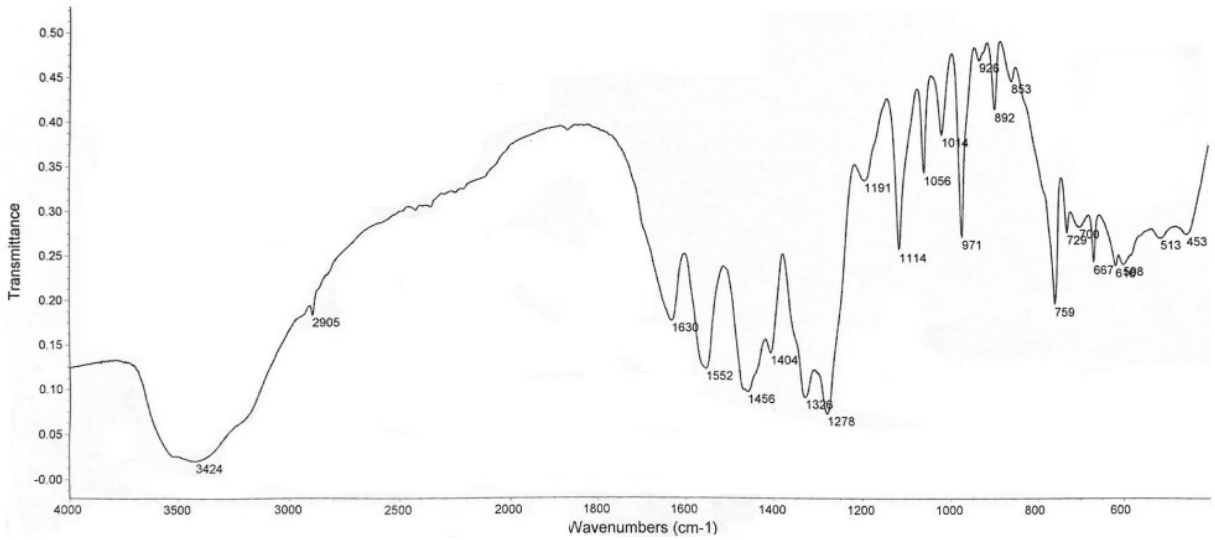

Figure S23. IR spectra of TNK

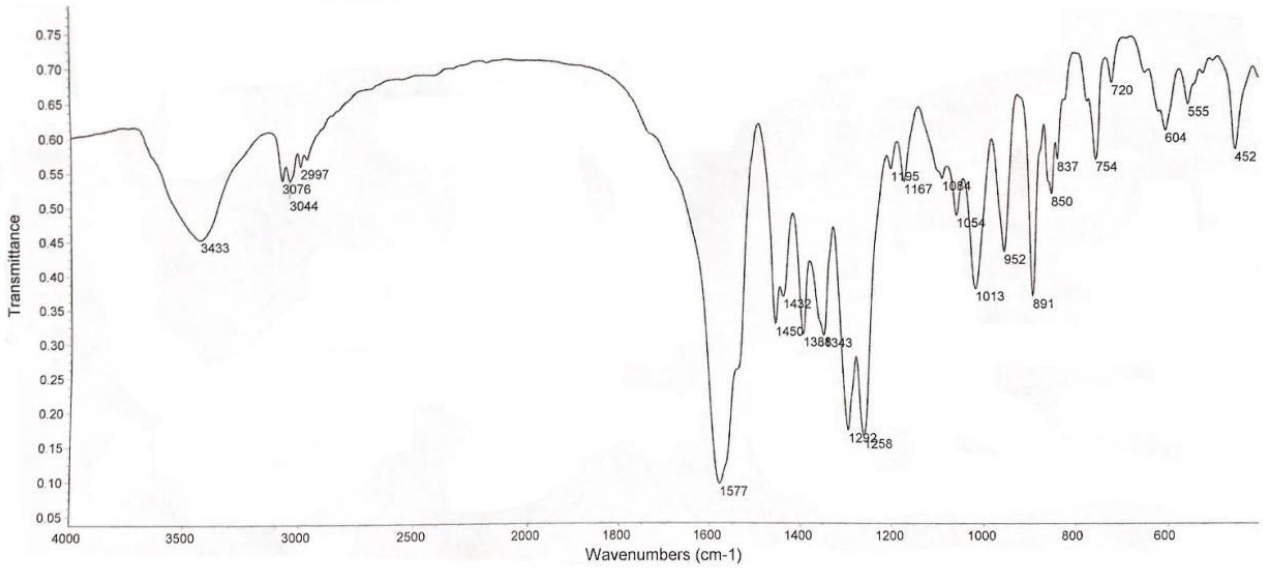

Figure S24. IR spectra of TNHF