Supporting Information

Facile Synthesis of Bicyclic Heat-Resistant Energetic Materials via A C-N Coupling Strategy

Xiu'e Jiang[a,b], Mingren Fan[a,b], Ruihui Wang[a,b], Yi Wang[a,b]*, Qinghua Zhang[a,b]*

[a] National Key Laboratory of Solid Propulsion, Northwestern Polytechnical University, Shanxi Xi'an, 710065, China

[b] School of Astronautics, Northwestern Polytechnical University, Shanxi Xi'an, 710065, China

*Corresponding author. E-mail address: ywang0521@nwpu.edu.cn (Yi Wang), qinghuazhang@nwpu.edu.cn (Qinghua Zhang)

Table of content

1. Experimental

1.1 Safety Precaution

Caution! Compounds reported in this work are highly explosive compounds, thus appropriate safety precaution are necessary. Proper protective measures (face shield, ear protection, body armor, Kevlar gloves, and earthed equipment) should be used at all times. Additionally, the small-scale experiment and real time monitoring is indispensable

1.2 General methods

All reagents were obtained from commercial resources were used as received. The samples were characterized by ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) using a Bruker Advance 400 spectrometer with d_6-DMSO (D.99.9%+0.03%TMS) as the solvent, and tetramethylsilane (TMS) was used as the internal reference standard (δ: 0.00). The samples were characterized by ^{15}N NMR (600 MHz) spectroscopy using a Bruker Advance 400 spectrometer with d_2-H_2SO_4 (D.99.5%, 98% in D_2O) as the solvent and nitromethane (CH_3NO_2) as an external standard (δ: 0.00). The DSC measurements were carried out on a Netzsch STA449F5 simultaneous thermal analyser at a heating rate of 10 °C min^{-1}, respectively. IR spectra was recorded by a Bruker Tensor II FTIR spectrometer. Elemental analysis was performed on a Elementar-UNICUBE elemental analyzer. Density data were determined using a AccuPyc II 1345 automatic gas displacement true density meter. Mass spectra were recorded on a Thermo Scientific-Q Exactive mass spectrometer with electrospray ionization (ESI). Impact and friction sensitivity measurements were launched using a standard BAM Fall hammer and a BAM friction tester.

1.3 Method of compound preparation

Synthesis of 3,5-diamino-1-(4,6-diamino-5-nitropyrimidin-4-yl)-4-nitro-1*H*-pyrazole (NPX-05): 3,5-diamino-4-nitropyrazole[1] (1.43 g, 0.01 mol) was dissolved in 50 mL DMF, and then 2-chloro-5-nitro-4,6-pyrimidinediamine (1.90 g, 0.01 mol) was added, and reacted at 110 ℃ for 9 h. Adding 500 mL water in above DMF solution, a large amount of precipitates was formed. After filtration and washing with plenty of water, the yellow solid was dried to 2.56 g (yield: 86.5 %). ^{1}H NMR (DMSO-d_6, 400 MHz, δ): 9.52, 8.94, 8.75, 8.27, 6.21; ^{13}C NMR (DMSO-d_6, 100 MHz, δ): 159.88, 155.97, 149.83, 149.19, 109.76, 109.00. ^{15}N NMR (H_2SO_4-d_2, 600 MHz, δ): -22.60, -23.95, -27.49, -28.49, -240.43, -258.72, -259.60, -292.78, -293.52, -314.57. IR (ATR) v: 3393, 3221, 3255, 3155, 2106, 1622, 1525, 1357, 1276, 1157, 1107, 975,

893, 833, 775, 590 cm^{-1}. Anal. calcd for $C_7H_8N_{10}O_4$: C 28.38, H 2.72, N 47.29. Found: C 28.59, H 2.58, N 47.35. ESI-HRMS: m/z Calcd for $[C_7H_8N_{10}O_4+H]^+$: 297.0808. Found: 297.0804.

Synthesis of 3,5-diamino-1-(2,4-diamino-1,3,5-triazin-6-yl)-4-nitro-1*H*-pyrazole (NPX-06): 3,5-diamino-4-nitropyrazole (1.43 g, 0.01 mol) was dissolved in 50 mL DMF, and then 6-chloro-1,3,5-triazine-2,4-diamine (1.45 g, 0.01 mol) was added, and reacted at 110 ℃ for 9 h. Adding 500 mL water in above DMF solution, a large amount of precipitates was formed. After filtration and washing with plenty of water, the yellow solid was dried to 2.14 g (yield: 84.9 %). ^{1}H NMR (DMSO-d_6, 400 MHz, δ): 9.54 (broad), 8.28 (broad), 7.31, 7.03, 6.24; ^{13}C NMR (DMSO-d_6, 100 MHz, δ): 167.09, 163.38, 149.65, 149.15, 108.97. ^{15}N NMR (H_2SO_4-d_2, 600 MHz, δ): -24.46, -209.03, -220.53, -230.59, -256.32, -266.23, -285.13, -288.18, -291.05, -310.30. IR (ATR) *v*: 3539, 3462, 3406, 3363, 3201, 1629, 1571, 1533, 1481, 1350, 1244, 1159, 1097, 1045, 985, 927, 790, 775, 590 cm^{-1}. Anal. calcd for $C_6H_8N_{10}O_2$: C 28.58, H 3.20, N 55.54. Found: C 28.73, H 2.99, N 55.37. ESI-HRMS: m/z Calcd for $[C_6H_8N_{10}O_2+H]^+$: 253.0910. Found: 253.0905.

Synthesis of 3,5-diamino-1-(2,4-diamino-3,5-dinitro-pyridin-6-yl)-4-nitro-1*H*- pyrazole (NPX-07): 3,5-diamino-4-nitropyrazole (1.43 g, 0.01 mol) was dissolved in 50 mL DMF, and then 6-chloro-3,5-dinitropyridine-2,4-diamine[2] (2.33 g, 0.01 mol) was added, and reacted at 110 ℃ for 9 h. The precipitate was collected by filtration to give **NPX-07** (3.04 g, 89.4 %) as yellow solid. ^{1}H NMR (DMSO-d_6, 400 MHz, δ): 10.26, 10.22, 9.34, 9.24, 8.75, 8.57, 7.95, 7.88; ^{13}C NMR (DMSO-d_6, 100 MHz, δ): 156.45, 155.18, 153.99, 152.52, 151.97, 148.39, 114.04, 110.59. IR (ATR) *v*: 3342, 3190, 2798, 2171, 2042, 1766, 1687, 1643, 1533, 1417, 1282, 1247, 1112, 1043, 991, 862, 804, 746, 626 cm^{-1}. Anal. calcd for $C_8H_8N_{10}O_6$: C 28.24, H 2.37, N 41.17. Found: C 28.42, H 2.49, N 41.29. ESI-HRMS: m/z Calcd for $[C_8H_8N_{10}O_6+H]^+$: 341.0707. Found: 341.0703.

Synthesis of 3,5-diamino-1-(4,6-diamino-5-nitropyrimidin-4-yl)-1*H*-1,2,4-triazole (NPX-08): 3,5-diamino-1,2,4-triazole (0.99 g, 0.01 mol) was dissolved in 30 mL DMF, and then 2-chloro-5-nitro-4,6-pyrimidinediamine (1.90 g, 0.01 mol) was added, and reacted at 110 ℃ for 8 h. The precipitate was filtered off, washed with water and dried in air to yield yellow solid (2.12 g, 84.8 %). ^{1}H NMR (DMSO-d_6, 400 MHz, δ): 8.84, 8.68, 7.82, 7.02; ^{13}C NMR (DMSO-d_6, 100 MHz, δ): 161.62, 160.04, 157.20, 154.61, 109.33. ^{15}N NMR (H_2SO_4-d_2, 600

MHz, δ): -21.98, -23.43, -27.78, -34.59, -259.70, -263.97, -282.74, -303.16, -315.85, -326.18. IR (ATR) *v*: 3408, 3346, 3255, 3074, 1691, 1587, 1523, 1415, 1242, 1159, 1014, 873, 827, 775, 672, 607 cm^{-1}. Anal. calcd for $C_6H_8N_{10}O_2$: C 28.58, H 3.20, N 55.54. Found: C 28.27, H 2.96, N 55.41. ESI-HRMS: m/z Calcd for $[C_6H_8N_{10}O_2+H]^+$: 253.0910. Found: 253.0901.

Synthesis of 3,5-diamino-1-(2,4-diamino-1,3,5-triazin-6-yl)-1*H*-1,2,4-triazole (NPX-09): 3,5-diamino-1,2,4-triazole (0.99 g, 0.01 mol) was dissolved in 30 mL DMF, and then 6-chloro-1,3,5-triazine-2,4-diamine (1.45 g, 0.01 mol) was added, and reacted at 110 ℃ for 8 h. The precipitate was filtered off, washed with water and dried in air to yield white solid (1.86 g, 89.4 %). ^{1}H NMR (DMSO-d_6, 400 MHz, δ): 9.54, 8.32, 7.46, 7.16, 6.27 (broad); ^{13}C NMR (DMSO-d_6, 100 MHz, δ): 162.78, 156.45, 151.79, 148.23, 111.28. IR (ATR) *v*: 3338, 3298, 3236, 2106, 1606, 1529, 1408, 1247, 1174, 1022, 881, 781, 680 cm^{-1}. Anal. calcd for $C_5H_8N_{10}$: C 28.85, H 3.87, N 67.28. Found: C 28.74, H 3.69, N 67.38. ESI-HRMS: m/z Calcd for $[C_5H_8N_{10}+H]^+$: 209.1012. Found: 209.1003.

2. Computational Details

Computations were carried out by using the Gaussian09 suite of programs.[3] The elementary geometric optimization and the frequency analysis were performed at the level of Becke three Lee-Yan-Parr (B3LYP) Functionals[4,5] with 6-31+G** basis set.[3]All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. Then, the single-point energies of optimized structures were accessed under the level of MP2/6-311++G**. The predictions of heats of formation (HOF) were implemented via designed isodesmic reactions. The isodesmic reaction processes, i.e., the number of each kind of formal bond is conserved, are used with application of the bond separation reaction (BSR) rules. The molecule is broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF of these compounds are in **Scheme S1**.

The change of enthalpy for the reactions at 298 K can be expressed as:

$$\Delta H_{298} = \sum \Delta_f H_P - \sum \Delta_f H_R \quad (1)$$

Where $\Delta_f H_R$ and $\Delta_f H_P$ are the HOF of reactants and products at 298 K, respectively, and ΔH_{298} can be calculated using the following expression:

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

Where E_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 thermal correction from 0 to 298 K. The $\Delta(PV)$ value in eq (2) is the *PV* work term. It equals ΔnRT for the reactions of ideal gas. For the isodesmic reactions, $\Delta n = 0$, so $\Delta(PV) = 0$. On the left side of Eq. (1), apart from target compound, all the others are called reference compounds. The HOF of reference compounds are available either from the experiments[6-8] or from the high level computing like G4(MP2)-6x[9].

For ionic energetic compounds, the HOF can be simplified by eq 3:

$$\Delta H_f^0(\text{salt},298\text{ K}) = \Delta H_f^0(\text{cation},298\text{ K}) + \Delta H_f^0(\text{anion},298\text{ K}) - \Delta H_L \quad (3)$$

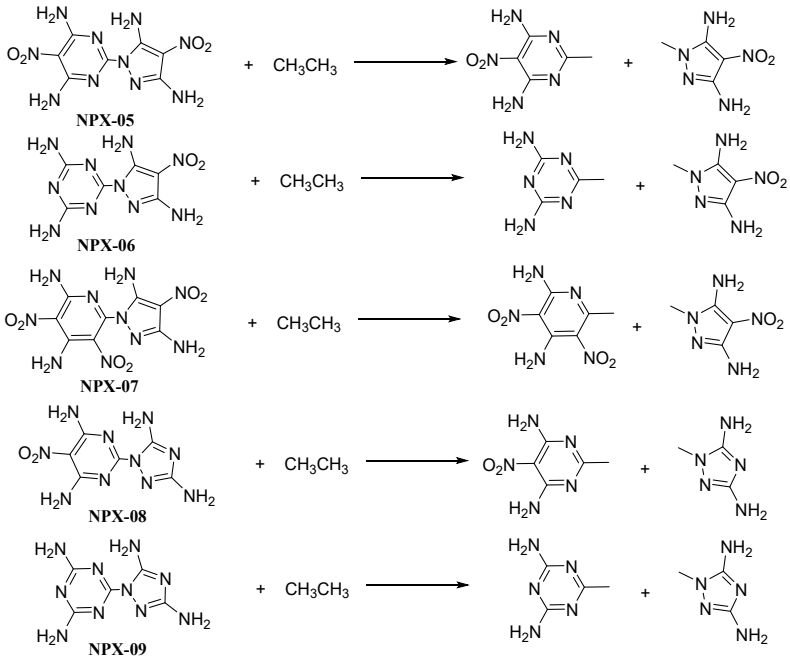
where ΔH_L is the lattice energy of the salts that can be predicted by the formula suggested by Jenkins et al. as：

$$\Delta H_L = U_{POT} + [\,p(nM/2 - 2) + q(nX/2 - 2)]RT \quad (4)$$

where nM and nX depend on the nature of the ions Mp+ and Xq−, respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy UPOT (kJ mol^{-1}) is as follows:

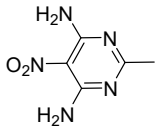
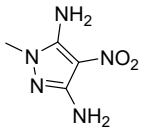
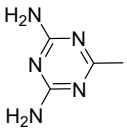
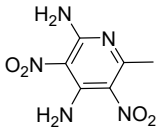
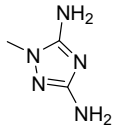
$$U_{POT}\ (\text{kJ mol}^{-1}) = \gamma\,(\rho_m/M_m)^{1/3} + \delta \quad (5)$$

where ρ (g cm^{-3}) is the density and M (g mol^{-1}) is the chemical formula mass of the ionic material. For 1:1 (charge ratio) salts, the coefficients γ and δ are 1981.2 kJ mol^{-1}·cm and 103.8 kJ mol^{-1}, respectively.[10]



Scheme S1. Isodemic reaction for computing the HOF

Table S1 Thermodynamic Data of Fragments for Homodesmotic Reactions

Compound	H^a (298 K, a.u.)	ZPE (a.u.)	ΔH_T (a.u.)	H^b (298 K, a.u.)	H^c (298 K, a.u.)	ΔH_f (kJ mol^{-1})
CH_3CH_3	-79.5716336	0.074609	0.004458472	-79.49363304	-79.66303958	-83.3
	-617.4365523	0.140917	0.010970599	-617.2866798	-618.1593456	45.9
	-579.3882533	0.135184	0.011594443	-579.243408	-580.0602697	131.5
	-429.3767768	0.125575	0.010415176	-429.2425823	-429.884971	74.7
	-805.4927314	0.155631	0.013847324	-805.3254786	-806.4279612	32.3
	-391.3266591	0.121314	0.009052781	-391.1980271	-391.7838909	165.5
NPX-05	-1117.258288	0.200703	0.019183203	-1117.041272	-	314.2
NPX-06	-929.2000474	0.185954	0.017296578	-928.999456	-	266.6
NPX-07	-1305.314802	0.21487	0.02165443	-1305.08135	-	260.2
NPX-08	-929.1970622	0.186666	0.016618399	-928.9964471	-	293.3
NPX-09	-741.1385052	0.171924	0.014738818	-740.9543009	-	304.7

[a] The enthalpy of the fragments was calculated at the B3LYP/6-31+G** level of theory. [b] The correction to the enthalpy of the fragments calculated at the B3LYP/6-31+G** level of theory.

[c] The enthalpy of the fragments was calculated at the MP2/6-311++G** level of theory.

3. Crystallographic detail

3.1 Crystallographic experimental for NPX-06

Crystalline samples of **NPX-06** suitable for X-ray diffraction analysis were grown by slow solvent evaporation of a DMF/H_2O mixed solvent system. A colourless, block-shaped crystal of **NPX-06** was mounted on the goniometer. Data were collected at 293 K on a multiwire proportional Bruker APEX-II CCD with a fine-focus sealed tube using a graphite as monochromator. The diffractometer was equipped with a low temperature device and used CuK_α radiation (λ = 1.54178 Å). The structure was solved by direct methods using ShelXT and refined by full-matrix least-squares methods against F^2 by XL using Olex2.[11-13] All non-hydrogen atoms were refined with anisotropic displacement parameters. The heteroatom-bound hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms.

3.2 Crystallographic data for NPX-06

Table S2. Crystallographic data and ellipsoid plot for **NPX-06**·2DMF·H_2O

Crystals	**NPX-06**·2DMF·H_2O
CCDC	2370243
Formula	$C_{21}H_{39}N_{23}O_8$
Formula weight	741.75
Temperature	298 K
Crystal system	monoclinic
Space group	$P2_1/n$
ρ/g·cm^{-1}	1.465
a/Å	13.9342(1)
b/Å	14.6464(2)
c/Å	16.6514(2)
α/(°)	90
β/(°)	98.281(1)
γ/(°)	90

Goodness-of-fit on F^2	1.069
R	0.0577
wR_2	0.1300

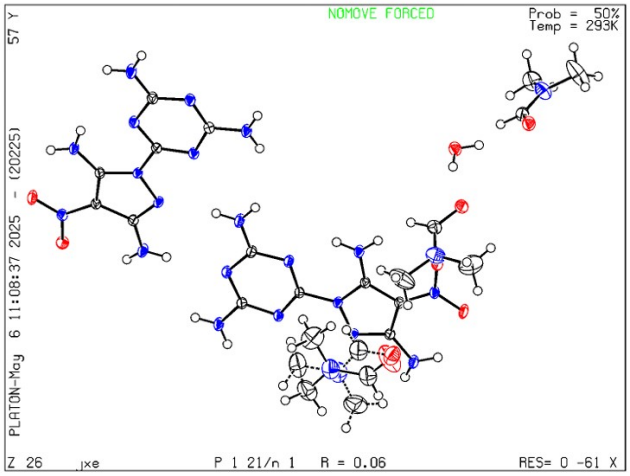


Fig S1. Structure of **NPX-06**·2DMF·H_2O

3.3 Crystallographic experimental for NPX-07

Compound **NPX-07** was crystallized by slow evaporation of a DMF/H_2O mixed solvent system to obtain a crystal sample suitable for testing. A colourless, block-shaped crystal of **NPX-07** was mounted on the goniometer. Data were collected at 298.15 K on a multiwire proportional with a fine-focus sealed tube using a graphite as monochromator. The diffractometer was equipped with a low temperature device and used CuK_α radiation (λ = 1.54178 Å). The structure was solved by direct methods using ShelXT and refined by full-matrix least-squares methods against F^2 by XL using Olex2.[11-13] All non-hydrogen atoms were refined with anisotropic displacement parameters. The heteroatom-bound hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms.

3.4 Crystallographic data for NPX-07

Table S3. Crystallographic data and ellipsoid plot for **NPX-07**·H_2O

Crystals	**NPX-07**·H_2O
CCDC	2370244
Formula	$C_8H_{10}N_{10}O_7$
Formula weight	358.26

Temperature	298 K
Crystal system	monoclinic
Space group	$P2_1/c$
ρ/g·cm^{-1}	1.762
a/Å	5.1692(1)
b/Å	19.0438(4)
c/Å	13.7975(3)
α/(°)	90
β/(°)	96.071(2)
γ/(°)	90
Goodness-of-fit on F^2	1.033
R	0.0415
wR$_2$	0.1206

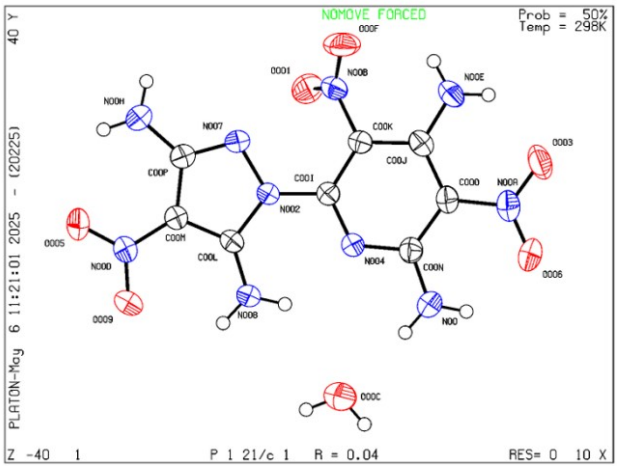


Fig S2. Structure of **NPX-07**·H_2O

3.5 Crystallographic experimental for NPX-09

Compound **NPX-09** were dissolved in 70% perchloric acid at 55 ℃ and slowly cooled to precipitate crystal samples suitable for single crystal diffraction. A colourless, block-shaped crystal of **NPX-09** was mounted on the goniometer. Data were collected from a shock-cooled single crystal at 150 K on a Bruker APEX-II CCD with a fine-focus sealed tube using a graphite as monochromator. The diffractometer was equipped with a low temperature device and used MoK_α radiation (λ = 0.71073 Å). The structure was solved by direct methods using ShelXT and refined by full-matrix least-squares methods against F^2 by XL using Olex2.[11-13] All non-

hydrogen atoms were refined with anisotropic displacement parameters. The heteroatom-bound hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms.

3.6 Crystallographic data for NPX-09

Table S4. Crystallographic data and ellipsoid plot for **NPX-09**·$2HClO_4$

Crystals	**NPX-09**·$2HClO_4$
CCDC	2370245
Formula	$C_5H_{10}Cl_2N_{10}O_8$
Formula weight	409.10
Temperature	150 K
Crystal system	triclinic
Space group	$P_{\bar{1}}$
ρ/g·cm^{-1}	1.984
a/Å	8.2784(7)
b/Å	9.1672(7)
c/Å	9.3028(7)
α/(°)	92.785(3)
β/(°)	90.887(3)
γ/(°)	103.678(3)
Goodness-of-fit on F^2	1.027
R	0.0619
wR_2	0.1453

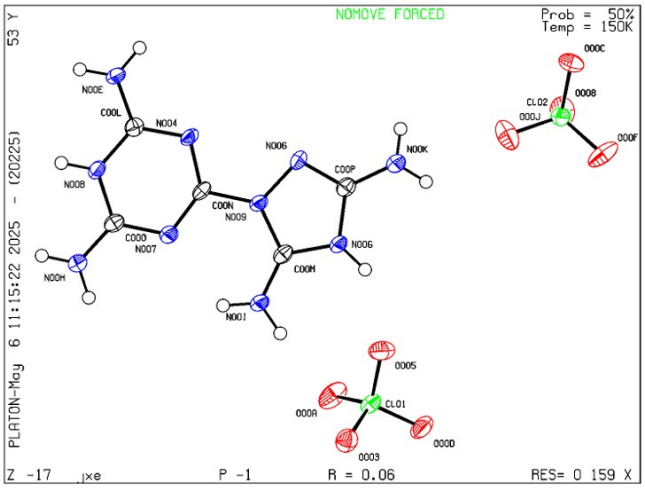


Fig S3. Structure of **NPX-09**·2HClO$_4$

4. ^{1}H NMR, ^{13}C NMR, HRMS and ^{15}N NMR spectra for compounds.

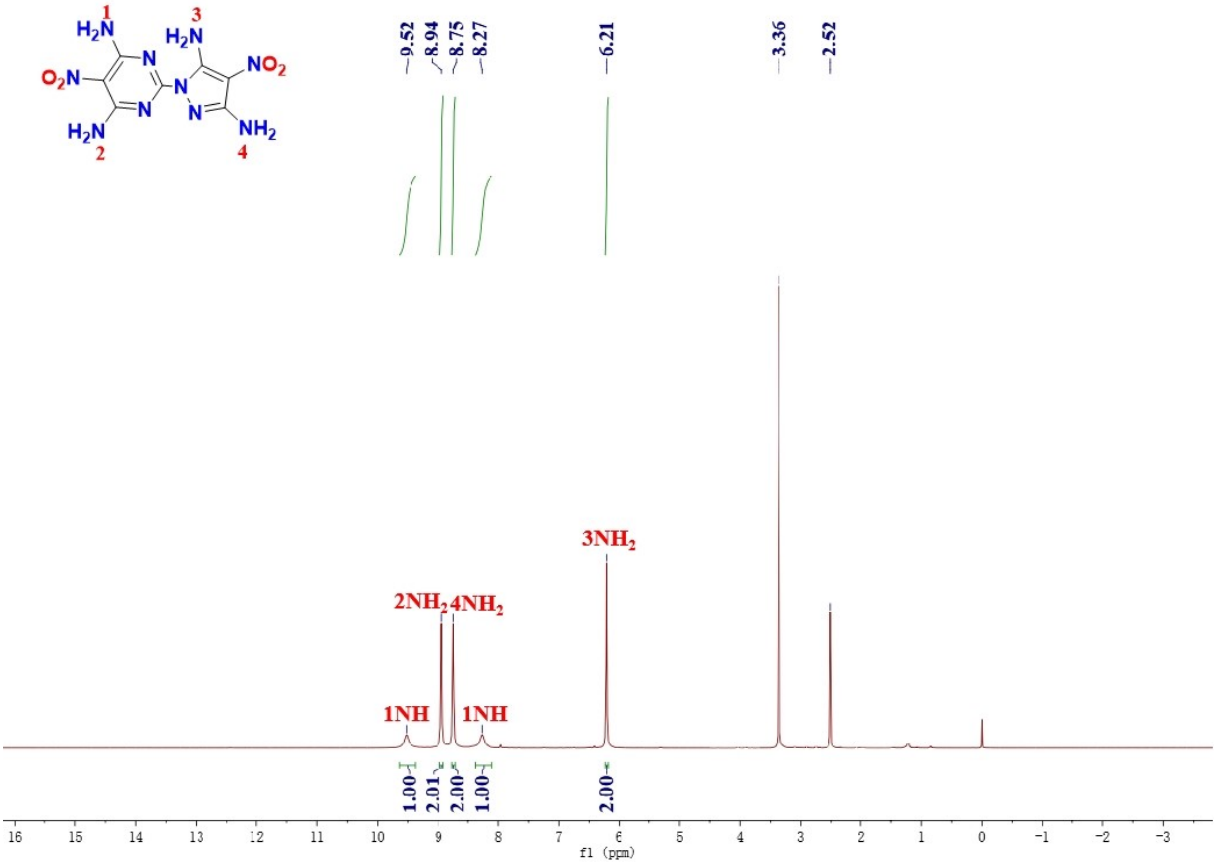


Fig S4. ^{1}H NMR spectrum of **NPX-05** in d_6-DMSO.

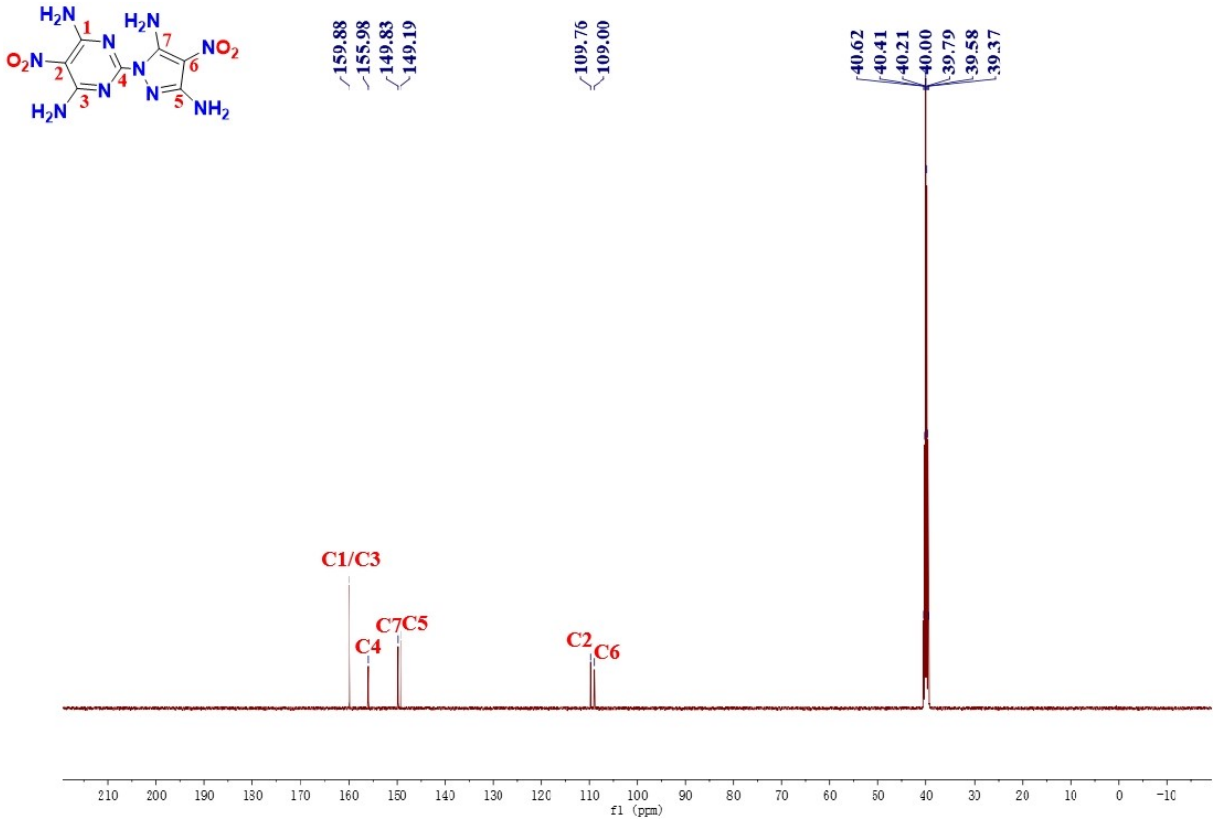


Fig S5. ^{13}C NMR spectrum of **NPX-05** in d_6-DMSO

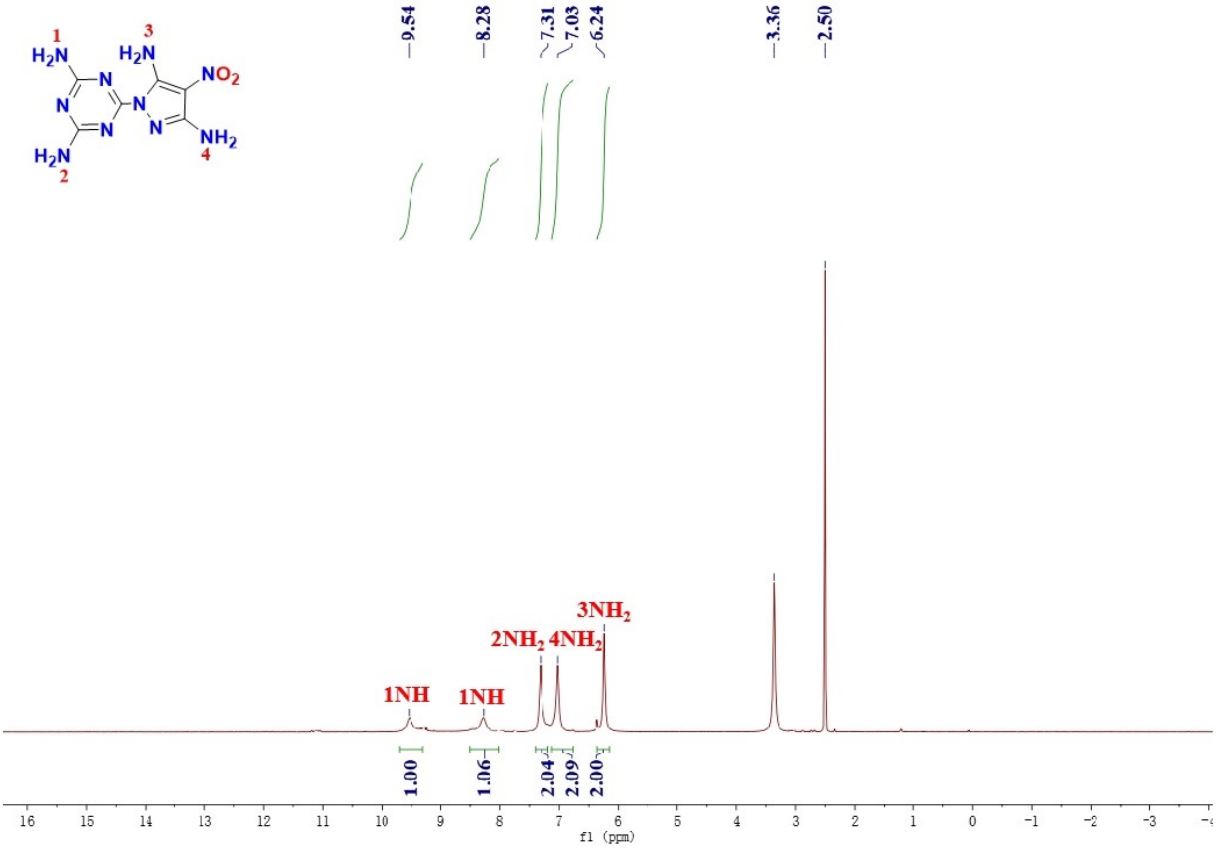


Fig S6. ^{1}H NMR spectrum of **NPX-06** in d_6-DMSO.

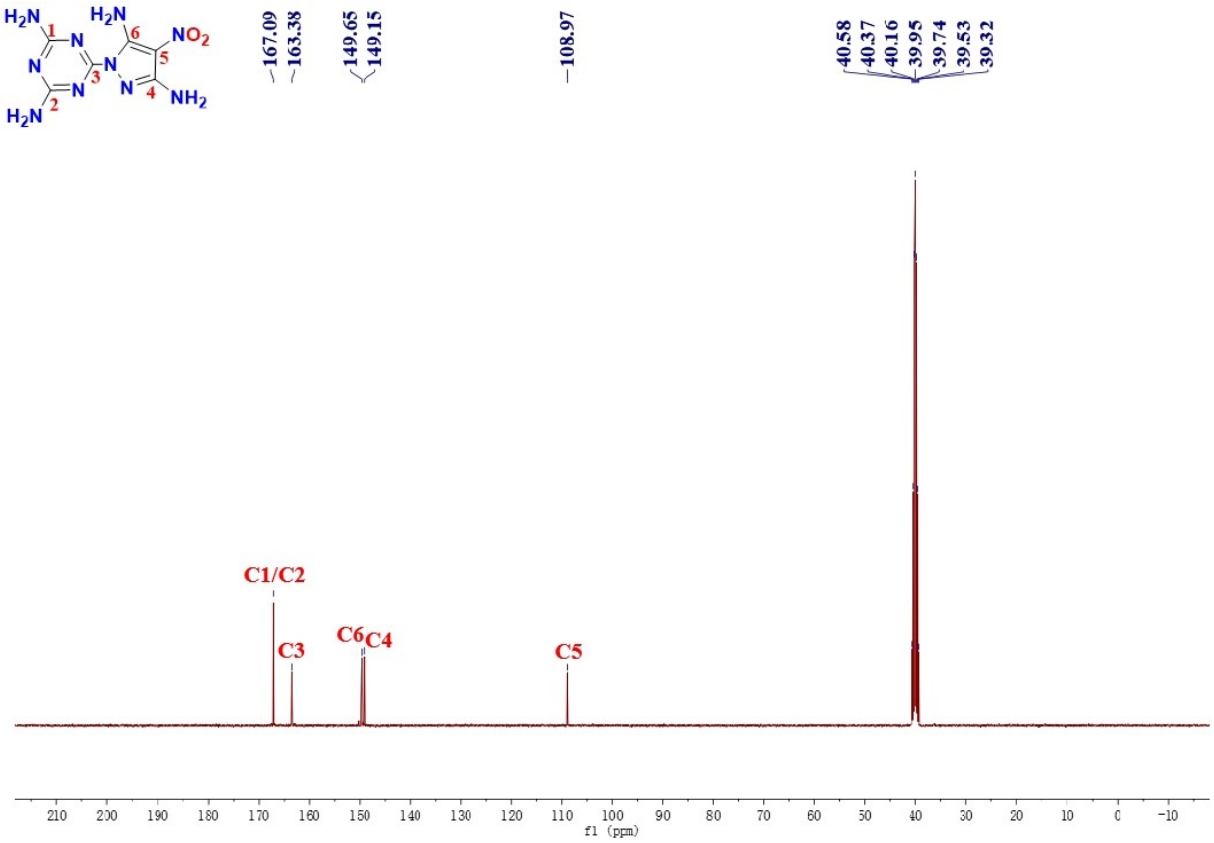


Fig S7. ^{13}C NMR spectrum of **NPX-06** in d_6-DMSO.

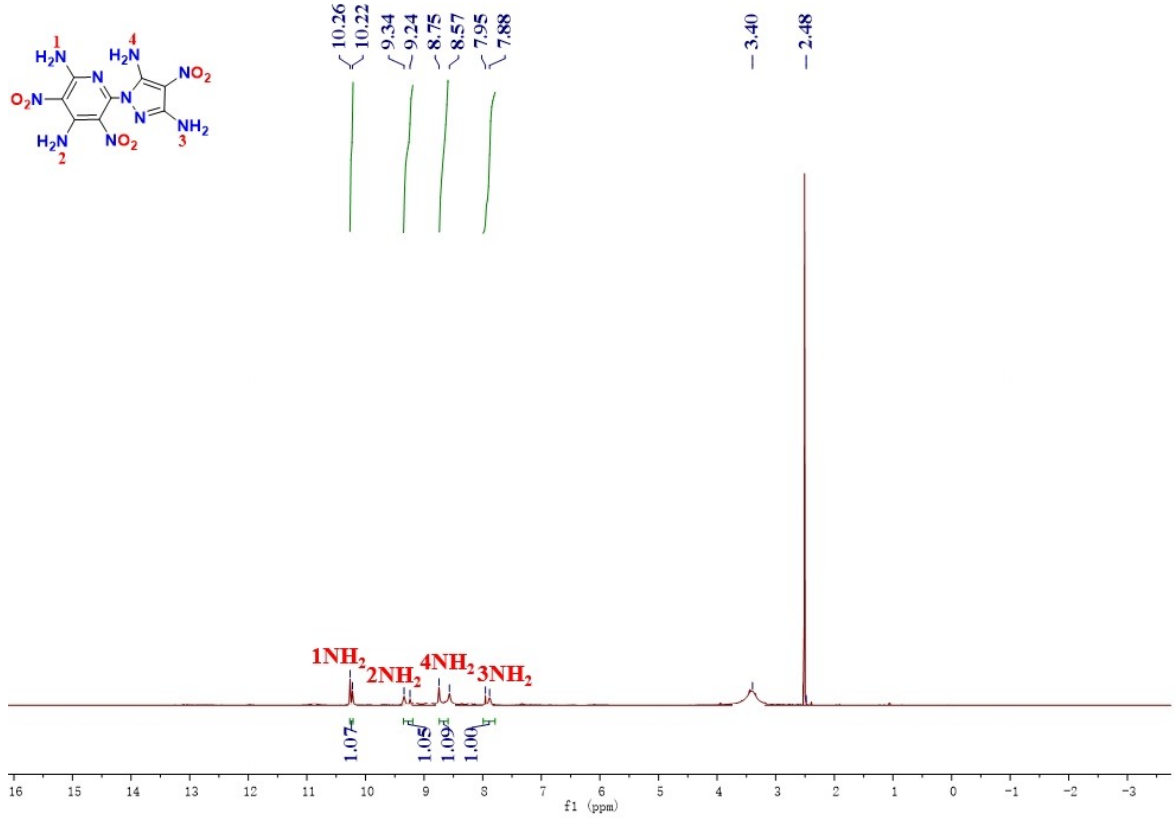


Fig S8. ^{1}H NMR spectrum of **NPX-07** in d_6-DMSO.

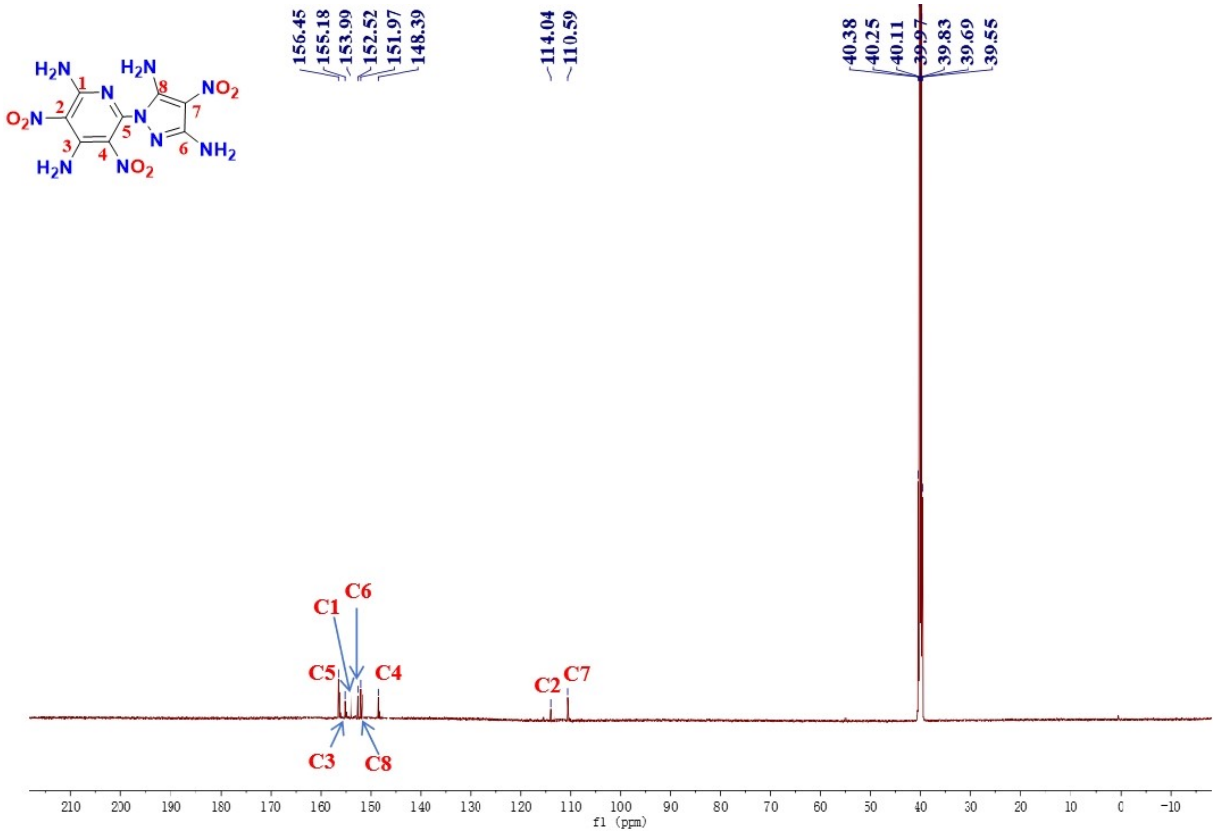


Fig S9. ^{13}C NMR spectrum of **NPX-07** in d_6-DMSO.

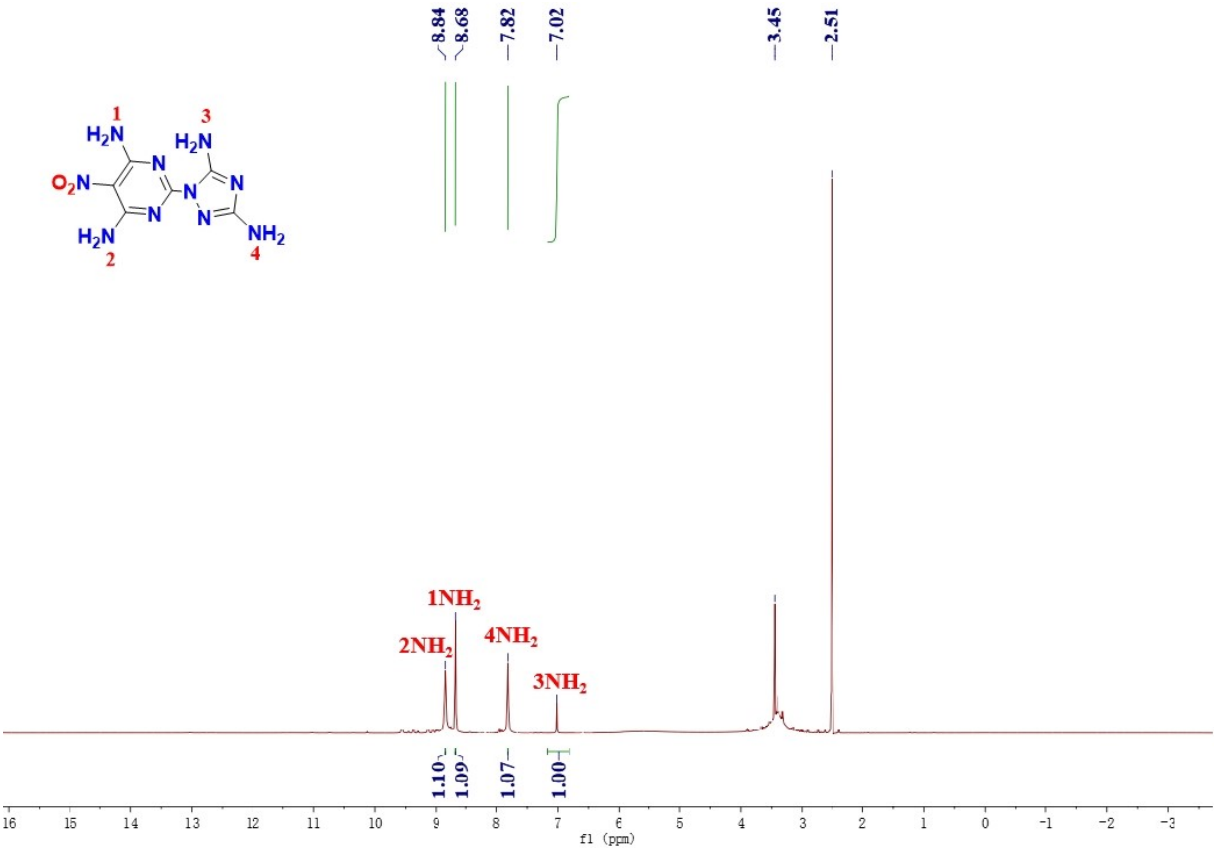


Fig S10. ^{1}H NMR spectrum of **NPX-08** in d_6-DMSO.

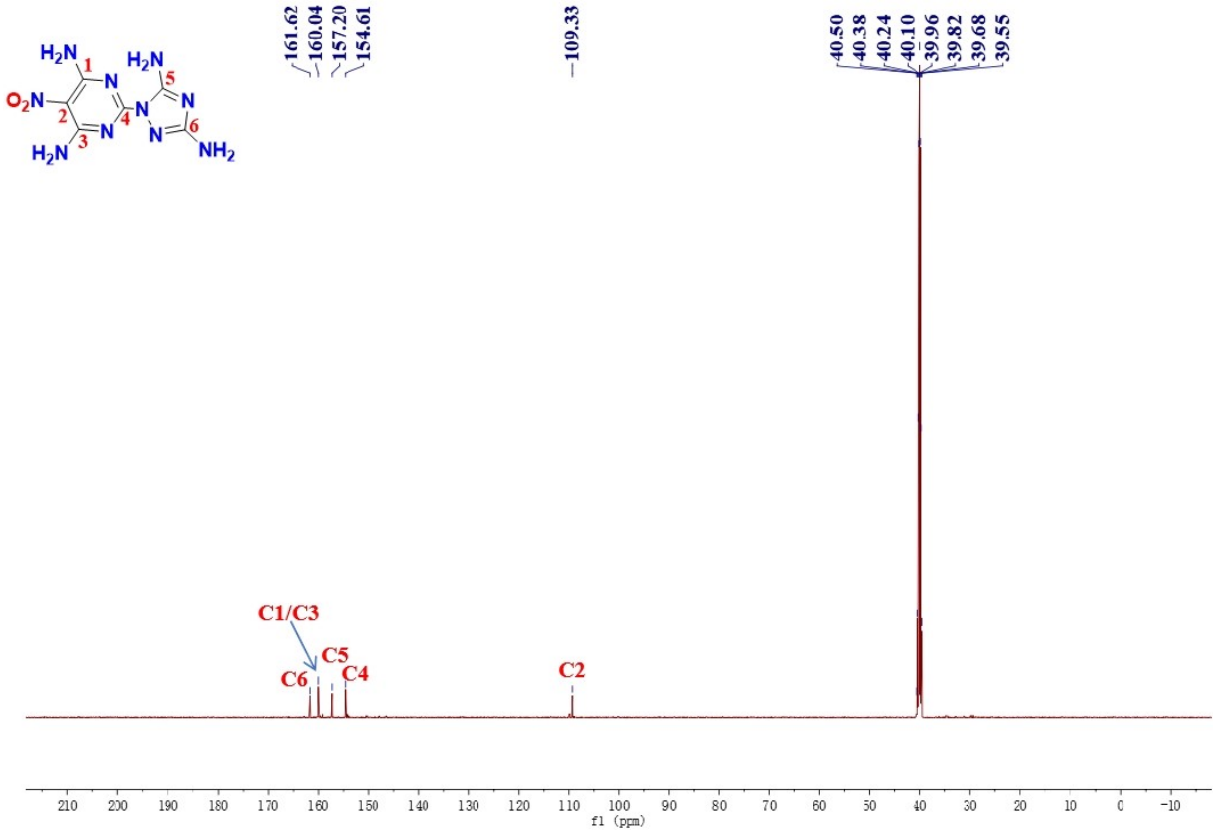


Fig S11. ^{13}C NMR spectrum of **NPX-08** in d_6-DMSO.

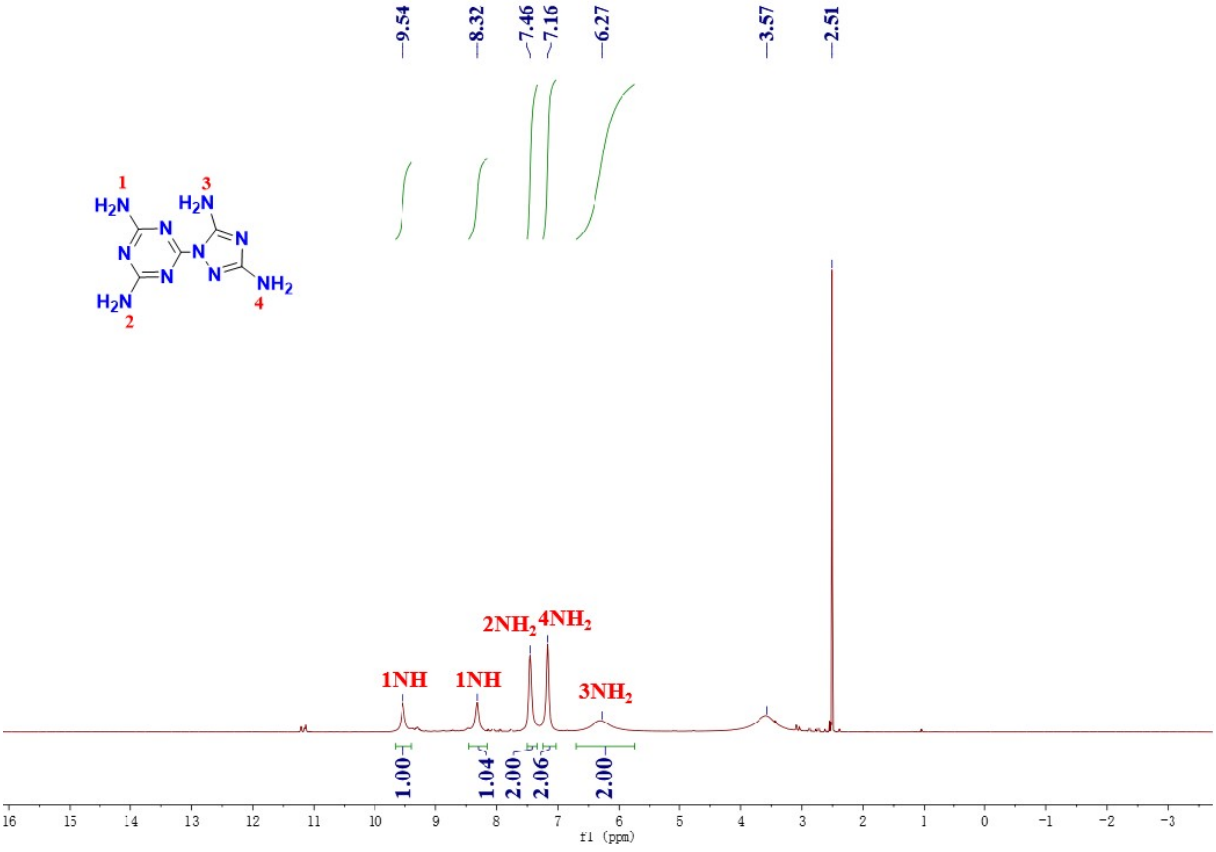


Fig S12. ^{1}H NMR spectrum of **NPX-09** in d_6-DMSO

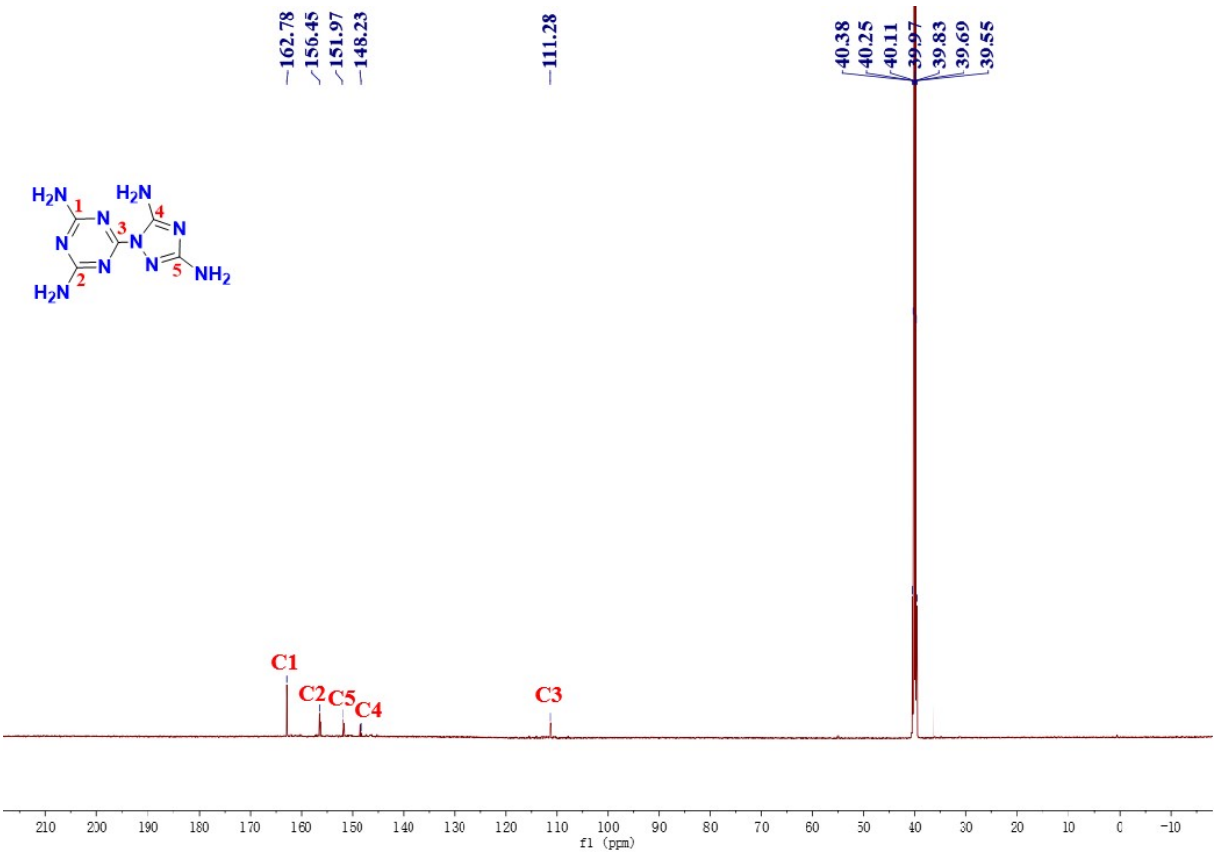


Fig S13. ^{13}C NMR spectrum of **NPX-09** in d_6-DMSO.

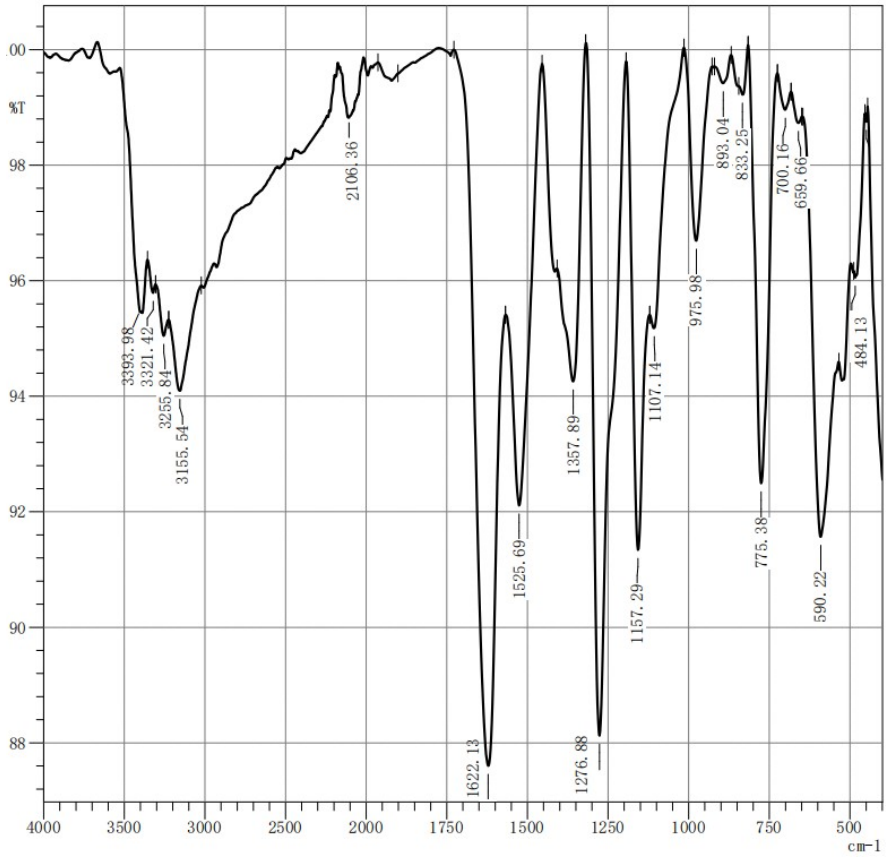


Fig S14. IR spectrum of **NPX-05**

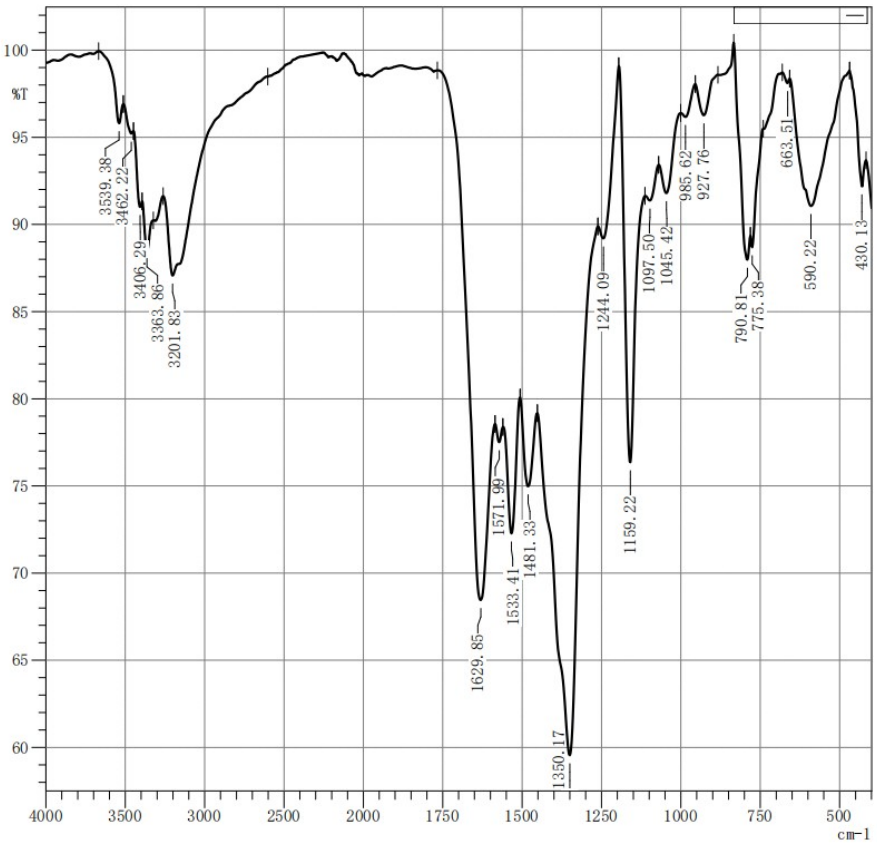


Fig S15. IR spectrum of **NPX-06**

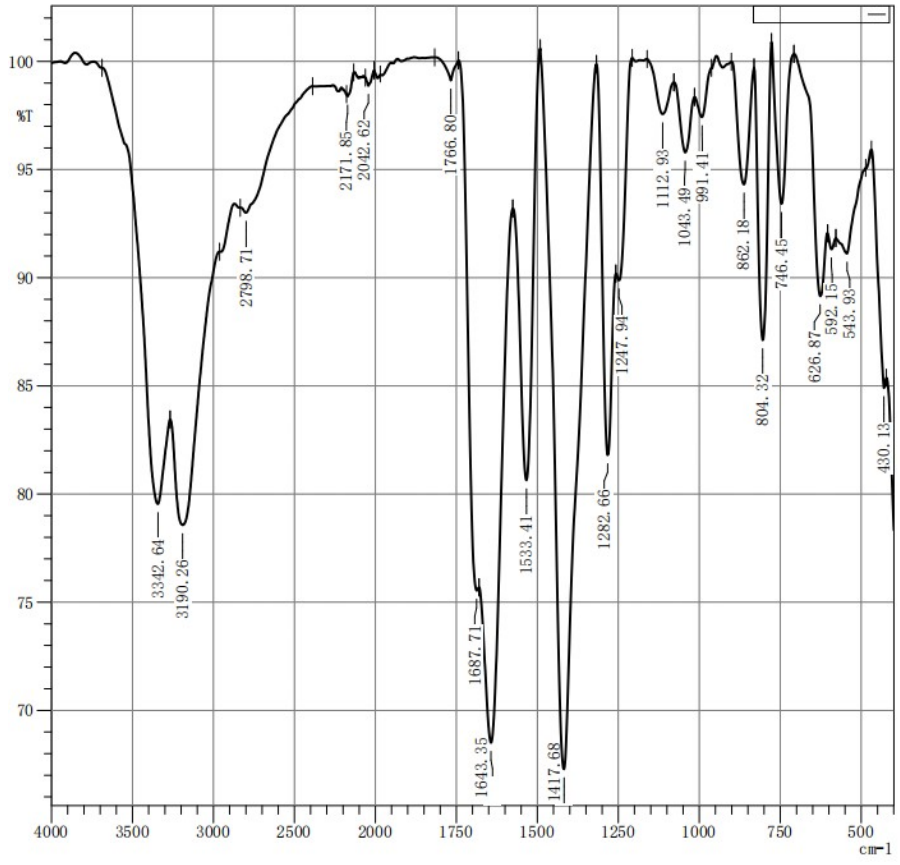


Fig S16. IR spectrum of **NPX-07**

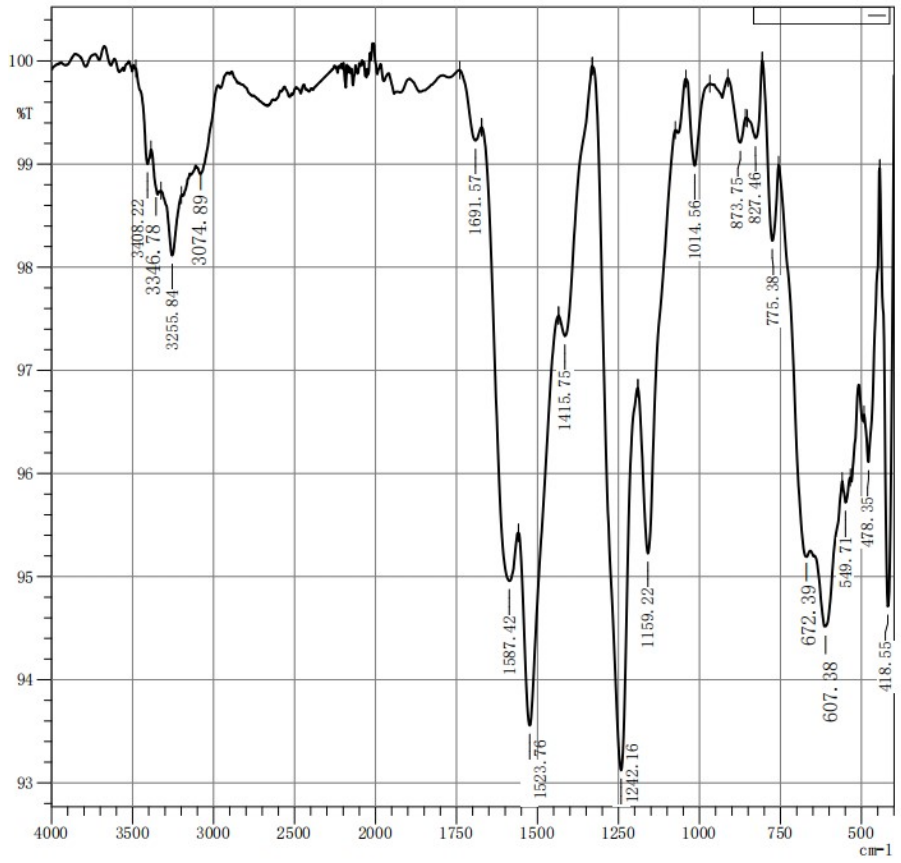


Fig S17. IR spectrum of **NPX-08**

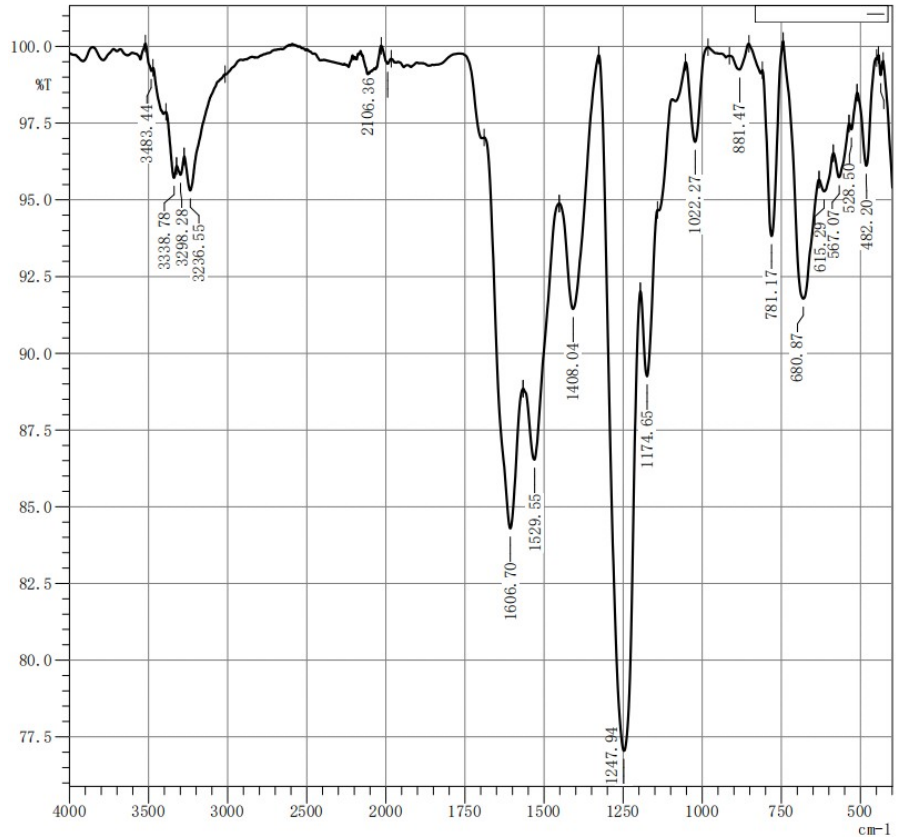


Fig S18. IR spectrum of **NPX-09**

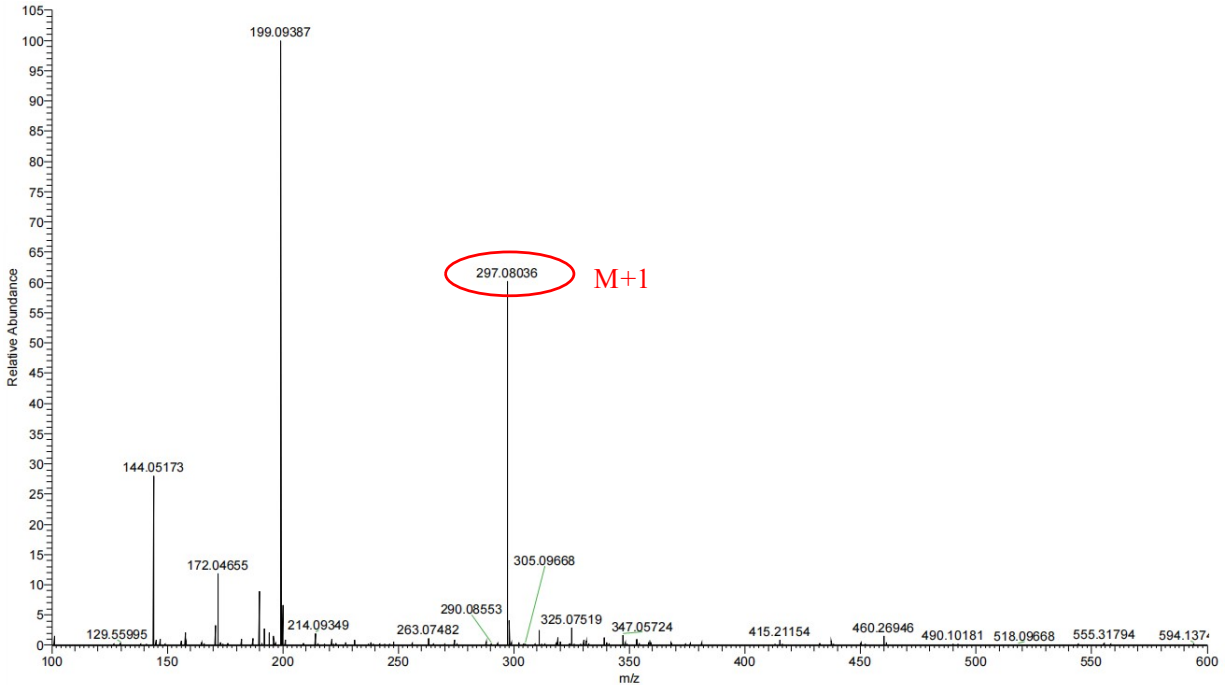


Fig S19. HRMS spectrum of **NPX-05** (ESI, Positive).

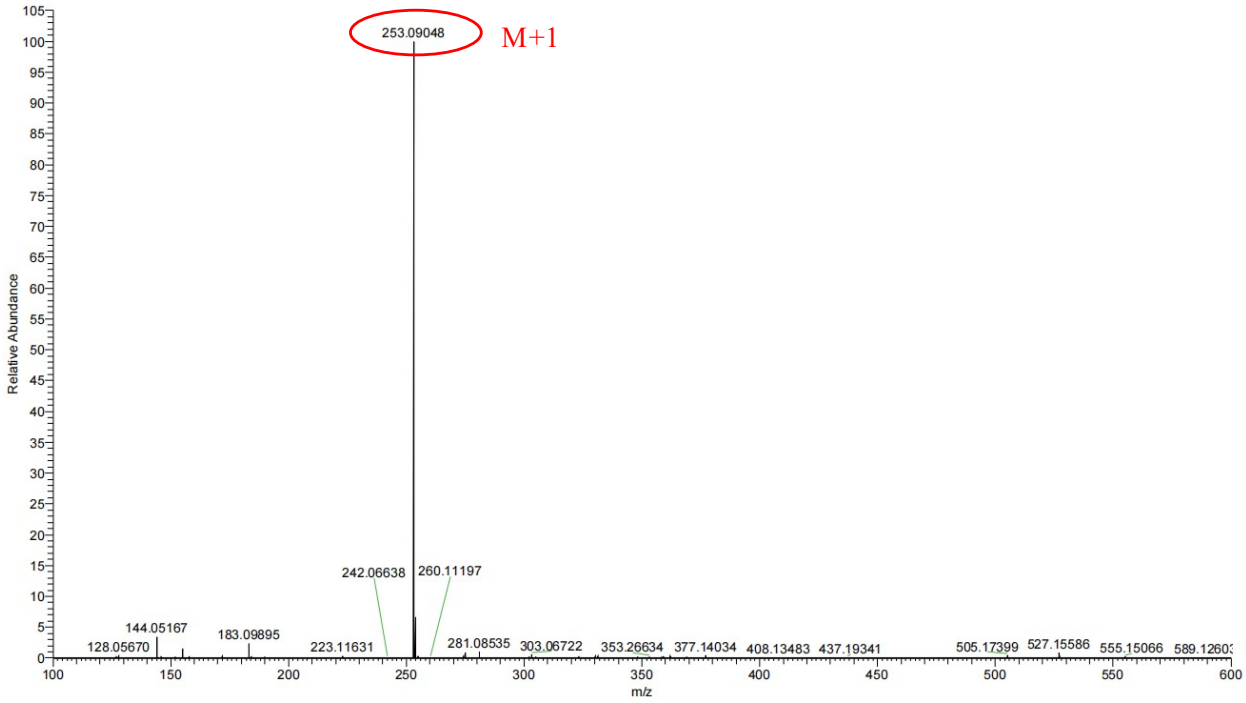


Fig S20. HRMS spectrum of **NPX-06** (ESI, Positive).

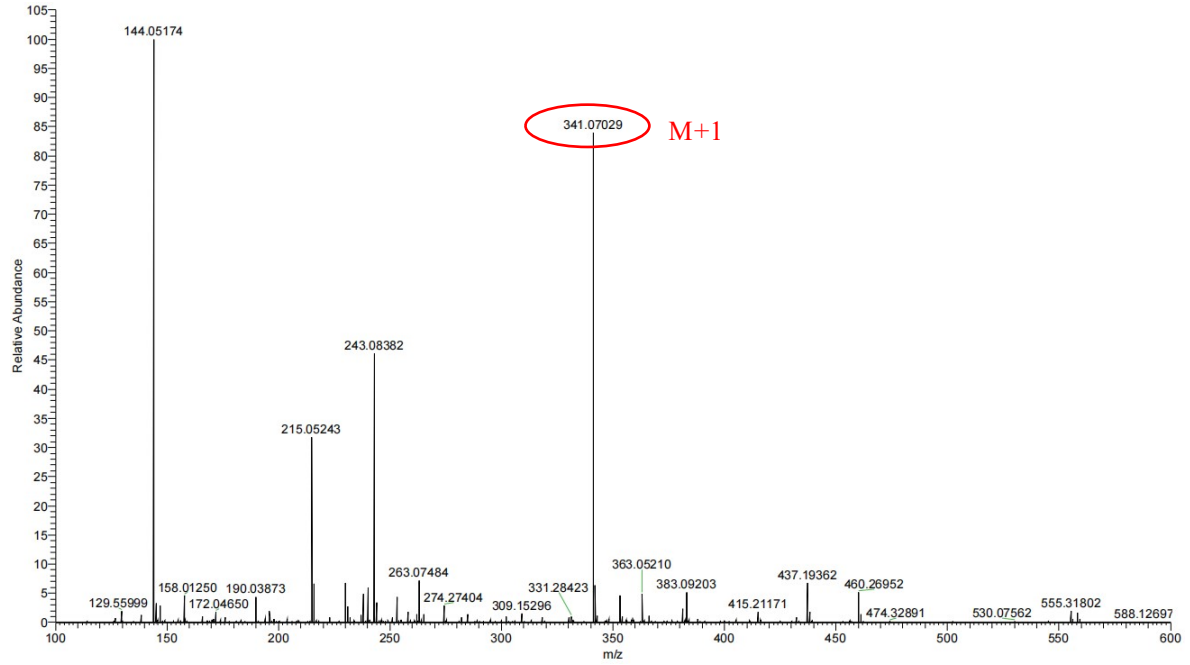


Fig S21. HRMS spectrum of **NPX-07** (ESI, Positive).

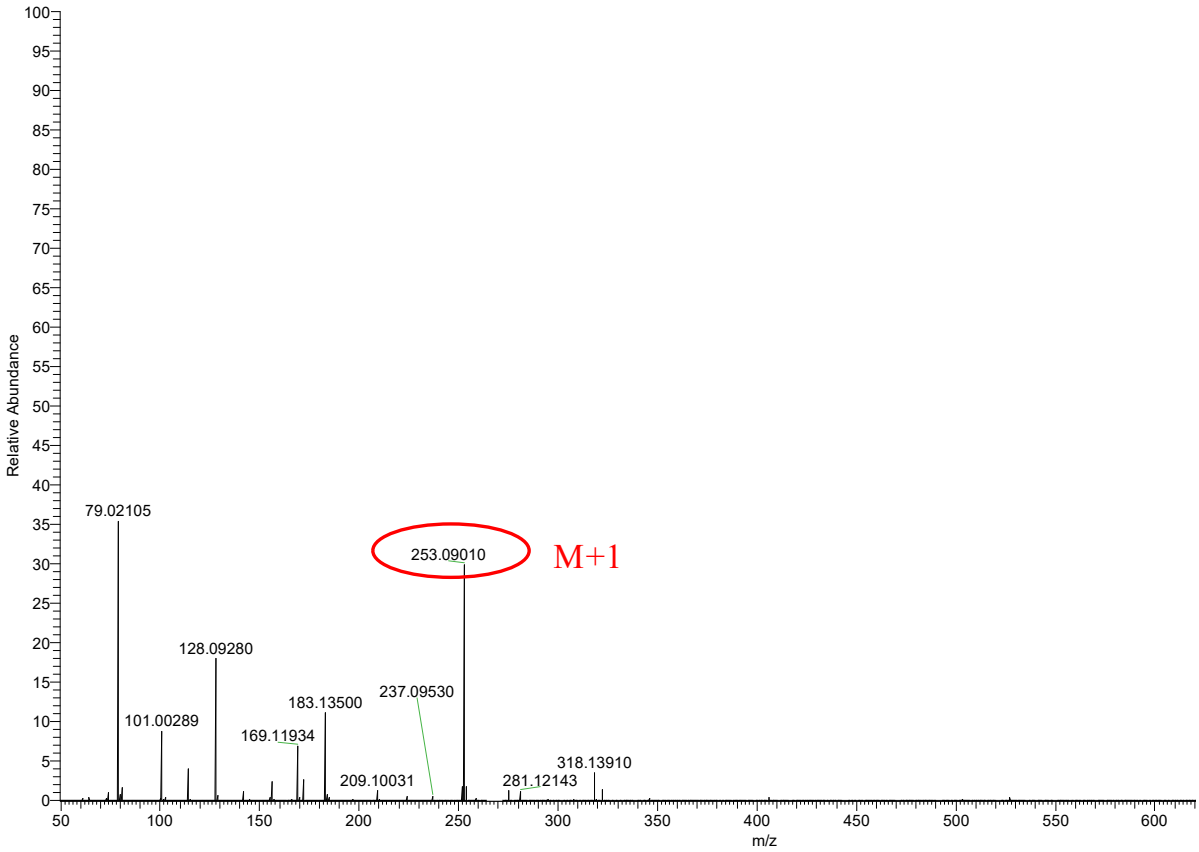


Fig S22. HRMS spectrum of **NPX-08** (ESI, Positive).

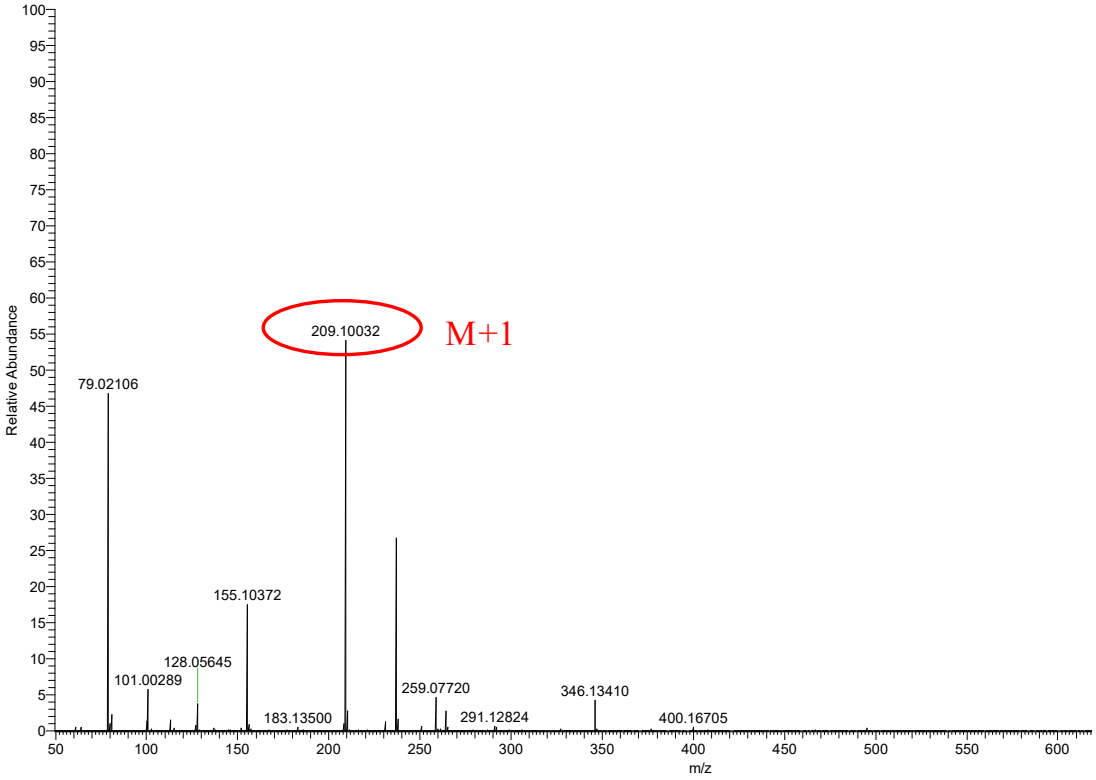


Fig S23. HRMS spectrum of **NPX-09** (ESI, Positive).

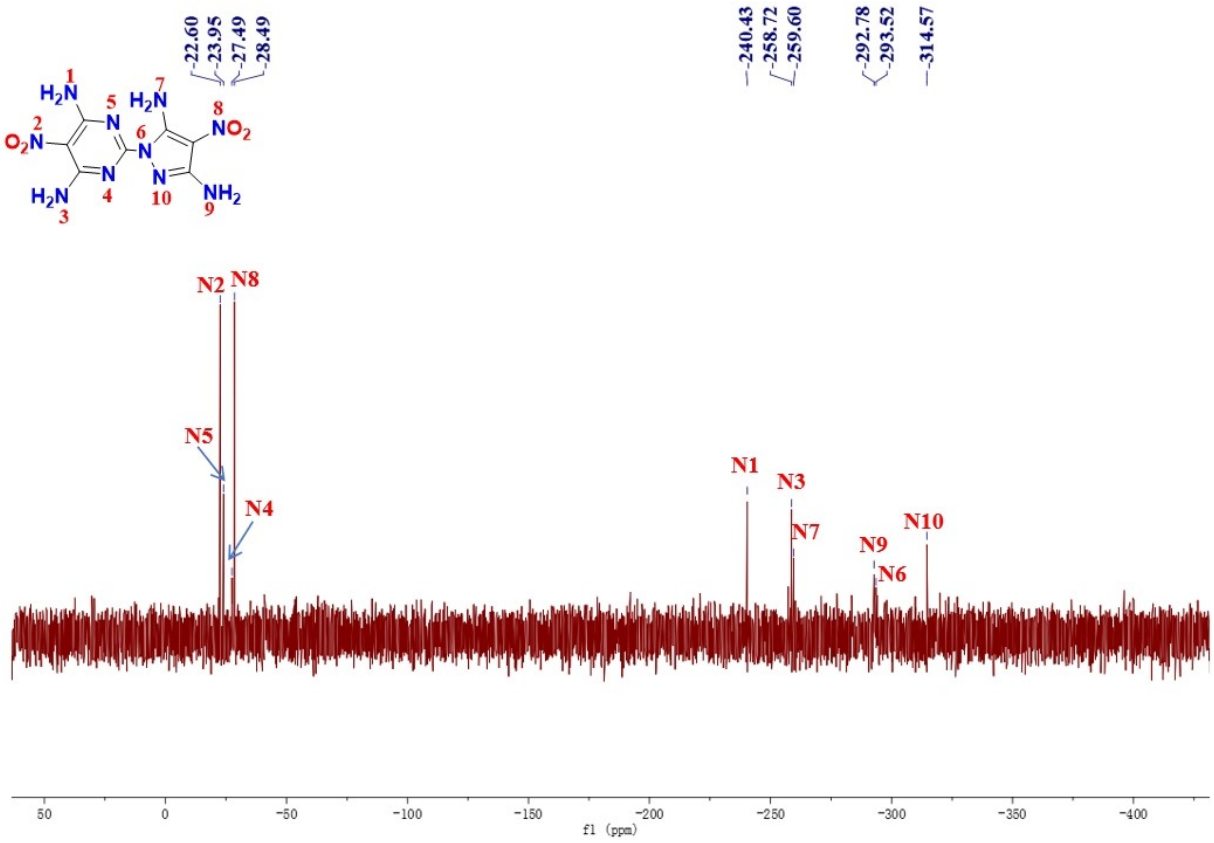


Fig S24. ^{15}N NMR spectrum of **NPX-05** in d_2-H_2SO_4

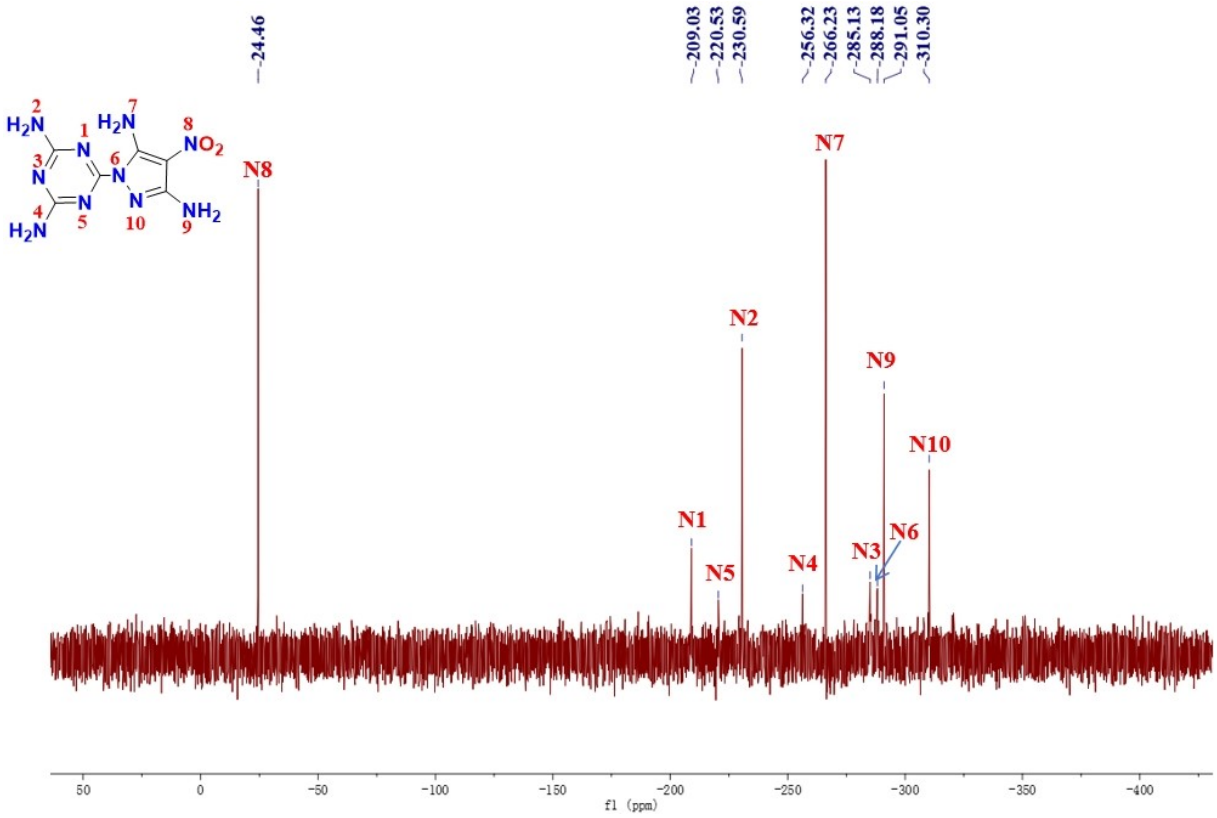


Fig S25. ^{15}N NMR spectrum of **NPX-06** in d_2-H_2SO_4

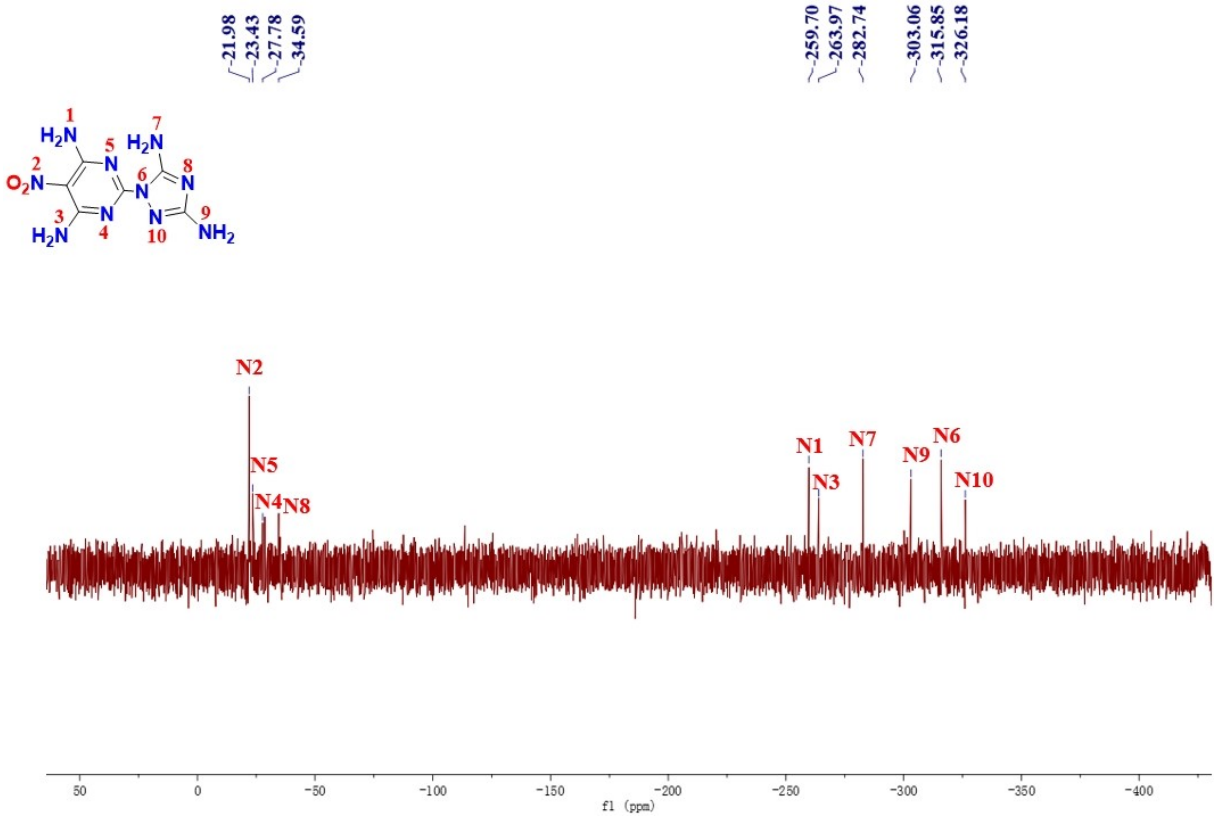


Fig S26. ^{15}N NMR spectrum of **NPX-08** in d_2-H_2SO_4

References

[1] Y. Tang, Y. Liu, G. H. Imler, D. A. Parrish, J. M. Shreev, Org. Lett., 2019, 21, 8, 2610-2614.

[2] R. Lv, L. Jiang, J. Wang, S. Huang, S. Song, L. Wei, Q. Zhang, K. Wang, J. Mater. Chem. A, 2024, 12, 10050-10058.

[3] M. J. Frisch, et al. Gaussian 09, Revision D.01 (Gaussian, Inc., Wallingford CT, 2013).

[4] A. D. Becke. J Phys Chem, 1993, 98, 5648-5652.

[5] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, J. Phys. Chem, 1994, 98, 11623-11627.

[6] a) M. W. Schmidt, M. S. Gordon, J. A. Boatz, J. Phys. Chem. A, 2005, 109, 7285-7295; b) H. Gao, C. Ye, C. M. Piekarski, J. M. Shreeve, J. Phys. Chem. C, 2007, 111, 28, 10718-10731.

[7] M. Jaidann, S. Roy, H. Abou-Rachid, L. Lussier, J. Hazard. Mater., 2010, 176, 165-173.

[8] J. A. Pople. J. S. Binkley, R. Seeger, Int. J. Quantum. Chem, 1976, 10, 1-19.

[9] B. Chan, J. Deng, L. Radom, J. Chem. Theory. Comput, 2011, 7, 112-120.

[10] X. Xu, H. Xiao, X. Ju, X. Gong, W. Zhu, J. Phys. Chem. A, 2006, 110, 5929- 5933; b) G. Wang, X. Gong, Y. Liu, H. Du, X. Xu, H. Xiao, J. Hazard. Mater., 2010, 177, 703-710.

[11] G. M. Sheldrick, Acta Cryst. 2015, A71, 3-8.

[12] G. M. Sheldrick, Acta Cryst. 2015, C71, 3-8.

[13] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Cryst. 2009, 42, 339-341,