Supporting Information

Combination of 5-Amino-4-nitro-1,2-dihydro-3H-pyrazol-3-one and Azine Frameworks for Insensitive Heat-resistant Energetic Materials

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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. X-ray single-crystal diffraction data were collected on a Rigaku XtaLAB synergy R/S diffractometer with Mo-Kα radiation (λ=0.71073 Å). The Bruker Advance 400 NMR spectrometer was used at 400 MHz and 100 MHz respectively, with d_6-DMSO as the solvent, the ^{1}H NMR and ^{13}C NMR spectra of the samples were tested. The DSC measurements were carried out on a Netzsch STA449F5 simultaneous thermal analyser at a heating rate of 10 °C min^{-1}, respectively.The TGA measurements were carried out on a Netzsch-STA2500 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 III automatic gas displacement true density meter. Impact and friction sensitivity measurements were launched using a standard BAM Fall hammer and a BAM friction tester. The heat of formation of compound was calculated by Gaussian09 (RevD.01) program[1]. The standard detonation properties were calculated by EXPLO5 (version 6.02) software[2].

1.3 Synthetic Procedures

5-Amino-1-(4,6-diamino-5-nitropyrimidin-2-yl)-4-nitro-1,2-dihydro-3*H*-pyrazol-3-one (NPX-10): 5-amino-4-nitro-1,2-dihydro-3*H*-pyrazol-3-one (1.44 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 120 ℃ for 9 h. After filtration and washing with plenty of water, the yellow solid was dried to 2.67 g (yield: 89.9 %). ^{1}H NMR (DMSO-d_6, 400 MHz, δ): 9.58, 8.80, 8.57, 7.96; ^{13}C NMR (DMSO-d_6, 100 MHz, δ):

162.79, 159.69, 157.24, 154.75, 150.55, 109.81, 107.26. IR (ATR) *v*: 3585, 3420, 3386, 3306, 3141, 2943, 2815, 1610, 1551, 1430, 1357, 1272, 1231, 1176, 1155, 979, 792, 770, 798, 554 cm^{-1}. Anal. calcd for $C_7H_7N_9O_5$: C 28.29, H 2.37, N 42.42. Found: C 28.43, H 2.52, N 42.31.

5-Amino-1-(4,6-diamino-1,3,5-triazin-2-yl)-4-nitro-1,2-dihydro-3*H*-pyrazol-3-one (NPX-11): 5-amino-4-nitro-1,2-dihydro-3*H*-pyrazol-3-one (1.44 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 120 ℃ for 9 h. After filtration and washing with plenty of water, the beige solid was dried to 2.23 g (yield: 88.1 %). ^{1}H NMR (DMSO-d_6, 400 MHz, δ): 9.64, 8.59, 8.39, 7.10; ^{13}C NMR (DMSO-d_6, 100 MHz, δ): 165.80, 161.27, 149.75, 149.31, 106.08. IR (ATR) *v*: 3466, 3420, 3334, 3190, 1707, 1649, 1539, 1474, 1362, 1198, 1154, 1121, 989, 796, 775, 730, 687, 627, 481 cm^{-1}. Anal. calcd for $C_6H_7N_9O_3$: C 28.46, H 2.79, N 49.79. Found: C 28.35, H 2.63, N 49.65.

1,1'-(1,2,4,5-Tetrazine-3,6-diyl)bis(5-amino-4-nitro-1,2-dihydro-3*H*-pyrazol-3-one) (NPX-12): 5-amino-4-nitro-1,2-dihydro-3*H*-pyrazol-3-one (2.88 g, 0.02 mol) was dissolved in 30 mL DMF, and then 3,6-dichloro-1,2,4,5-tetrazine (1.51 g, 0.01 mol) was added, and reacted at 120 ℃ for 8 h. The precipitate was filtered off, washed with water and dried in air to yield red solid (2.98 g, 81.4 %). ^{1}H NMR (DMSO-d_6, 400 MHz, δ): 8.21, 8.11, 8.00; ^{13}C NMR (DMSO-d_6, 100 MHz, δ): 162.92, 159.21, 152.07, 106.46. IR (ATR) *v*: 3415, 3285, 3253, 2938, 2544, 1638, 1580, 1465, 1409, 1354, 1166, 1112, 1121, 1032, 958, 861, 812, 765, 550 cm^{-1}. Anal. calcd for $C_8H_6N_{12}O_6$: C 26.24, H 1.65, N 45.90. Found: C 26.38, H 1.52, N 45.81.

6-Amino-4-(5-amino-3-hydroxy-4-nitro-1*H*-pyrazol-1-yl)-1,3,5-triazin-2(1*H*)-one (NPX-13): 5-amino-4-nitro-1,2-dihydro-3*H*-pyrazol-3-one (1.44 g, 0.01 mol) was dissolved in 30 mL DMF, and then 2-amino-4,6-dichlorotriazine (1.65 g, 0.01 mol) was added, and reacted at 120 ℃ for 8 h. The precipitate was filtered off, washed with water and dried in air to yield intermediate (beige solid) (2.37 g, 87.1 %). 0.5 g the intermediate was dispersed in 2 mL 70% perchloric acid ($HClO_4$), heated at 60 ℃ and dissolved, cooled and filtered to obtain white solid. Then, white solid was dispersed in water, and adjusted pH to 8 with $NaHCO_3$, stirred and reacted for 30 min to obtain

precipitation, filtered and washed to obtain yellow solid (0.31 g, 66.4 %). ^{1}H NMR (DMSO-d_6, 400 MHz, δ): 11.35, 8.39, 7.95, 7.23; ^{13}C NMR (DMSO-d_6, 100 MHz, δ): 166.01, 164.92, 162.79, 150.40, 109.00, 107.59. IR (ATR) v: 3667, 3409, 3234, 2986, 2901, 1669, 1609, 1548, 1457, 1366, 1286, 1231, 1162, 1075, 913, 794, 771, 703, 604, 519, 446 cm^{-1}. Anal. calcd for $C_6H_6N_8O_4$: C 28.35, H 2.38, N 44.09. Found: C 28.46, H 2.26, N 44.21.

1,1'-(6-Amino-1,3,5-triazine-2,4-diyl)bis(5-amino-4-nitro-1,2-dihydro-3*H*-pyrazol-3-one) (NPX-14): 5-amino-4-nitro-1,2-dihydro-3*H*-pyrazol-3-one (2.88 g, 0.02 mol) was dissolved in 30 mL DMF, and then 2-amino-4,6-dichlorotriazine (1.65 g, 0.01 mol) was added, and reacted at 120 ℃ for 48 h. The precipitate was filtered off, washed with water and dried in air to yield white solid (3.25 g, 85.5 %). ^{1}H NMR (DMSO-d_6, 400 MHz, δ): 9.28, 9.11, 8.40, 7.96; ^{13}C NMR (DMSO-d_6, 100 MHz, δ): 162.79, 158.14, 156.26, 150.31, 107.44. IR (ATR) v: 3490, 3415, 3383, 3317, 3275, 3246, 3152, 2935, 1711, 1654, 1567, 1516, 1472, 1426, 1354, 1271,1235, 1199, 1158, 1142, 1109, 1089, 905, 799, 777, 755, 692, 665, 600, 512, 441 cm^{-1}. Anal. calcd for $C_9H_8N_{12}O_6$: C 28.43, H 2.12, N 44.20. Found: C 28.32, H 2.23, N 44.33.

2. Crystallographic detail

2.1 Preparation of crystal samples

Compound **NPX-10** was slowly volatilized in DMF to obtain a crystal sample suitable for testing. However, it was difficult to obtain single crystal samples of **NPX-11** after many attempts. Compounds **NPX-12~NPX-14** were dissolved in 70% perchloric acid at 55 ℃ and slowly cooled to precipitate crystal samples suitable for single crystal diffraction.

2.2 Crystallographic data

Table S1. Crystallographic data and ellipsoid plot for **NPX-10**·DMF·H_2O

Crystals	**NPX-10**·DMF·H_2O
CCDC	2390031
Formula	$C_{11}H_{16}N_9O_7$
Formula weight	386.33
Temperature	293 K
Crystal system	monoclinic

Space group	$P2_1/c$
ρ/g·cm^{-1}	1.488
a/Å	16.6318(4)
b/Å	14.9763(3)
c/Å	6.9855(2)
α/(°)	90
β/(°)	94.907(2)
γ/(°)	90
Goodness-of-fit on F^2	1.055
R	0.0492
wR$_2$	0.1375

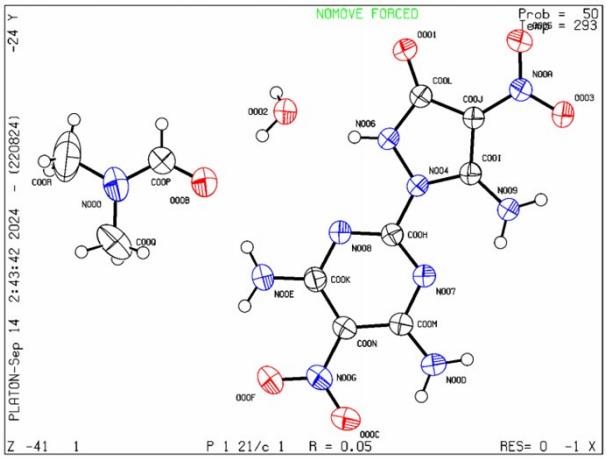


Table S2 The torsion angles of compound **NPX-10**·DMF·H_2O

Parameter	Bond angles (°)	Parameter	Bond angles (°)
C00H-N004-N006-C00L	179.56(12)	C00I-N004-N006-C00L	1.02(16)
N006-N004-C00H-N008	3.39(19)	C00I-N004-C00H-N007	0.9(2)
N006-N004-C00I-N009	178.63(13)	N006-N004-C00I-C00J	-0.99(15)
C00H-N004-C00I-C00J	-179.35(13)	N004-N006-C00L-O001	179.77(13)
C00M-N007-C00H-N004	-178.96(12)	C00M-N007-C00H-N008	0.2(2)
C00H-N007-C00M-C00N	0.3(2)	C00K-N008-C00H-N004	179.58(12)
C00H-N008-C00K-N00E	178.09(13)	C00H-N008-C00K-C00N	-1.5(2)
O003-N00A-C00J-C00L	-178.41(14)	O005-N00A-C00J-C00I	-179.40(14)
O00C-N00G-C00N-C00K	-177.80(14)	O00C-N00G-C00N-C00M	-1.7(2)
O00F-N00G-C00N-C00M	178.12(16)	N004-C00I-C00J-N00A	-178.21(13)
N009-C00I-C00J-N00A	2.2(2)	N009-C00I-C00J-C00L	-178.95(15)
N00A-C00J-C00L-N006	178.77(14)	C00I-C00J-C00L-O001	179.57(15)
N008-C00K-C00N-N00G	178.22(14)	N008-C00K-C00N-C00M	2.0(2)
N00E-C00K-C00N-C00M	-177.56(14)	N007-C00M-C00N-N00G	-177.61(13)
N00D-C00M-C00N-N00G	1.7(2)	N00D-C00M-C00N-C00K	177.93(14)
C00H-N004-N006-H006	0	C00I-N004-N006-H006	-179

N006-N004-C00H-N007	-177.29(12)	C00K-N008-C00H-N007	0.4(2)
C00I-N004-C00H-N008	-178.42(13)	O003-N00A-C00J-C00I	0.2(2)
C00H-N004-C00I-N009	0.3(2)	O005-N00A-C00J-C00L	2.0(2)
N004-N006-C00L-C00J	-0.58(16)	O00F-N00G-C00N-C00K	2.0(2)
C00H-N007-C00M-N00D	-179.05(13)	N004-C00I-C00J-C00L	0.65(16)

Table S3 Hydrogen bonds of compound **NPX-10**·DMF·H_2O

D-H…A	d(D-H)/ Å	d(H…A)/ Å	d(D…A)/ Å	<(DHA)/ °
O002-H00M···O00B	0.85	1.89	2.729(2)	171
O002-H00N···O001	0.85	2.03	2.8683(17)	171
N006-H006···O002	0.86	1.88	2.7058(18)	162
N009-H00A···N007	0.86	2.1	2.711(2)	127
N009-H00A···O001	0.86	2.48	3.1670(17)	138'
N009-H00B···O003	0.86	2.22	2.767(2)	121
N009-H00B···O002	0.86	2.24	2.9585(18)	141'
N00D-H00C···O001	0.86	2.12	2.9301(18)	156
N00D-H00D···O00C	0.86	1.99	2.609(2)	128
N00E-H00E···O00B	0.86	1.98	2.833(2)	171
N00E-H00F···O00F	0.86	1.98	2.602(2)	129

Table S4. Crystallographic data and ellipsoid plot for **NPX-12**·$HClO_4$·$2H_2O$

Crystals	**NPX-12**·$HClO_4$·$2H_2O$
CCDC	2390032
Formula	$C_{48}H_{60}Cl_4N_{72}O_{62}$
Formula weight	2779.48
Temperature	150 K
Crystal system	triclinic
Space group	$P\bar{1}$
ρ/g·cm^{-1}	1.957
a/Å	10.5731(5)
b/Å	16.0518(8)
c/Å	16.8857(13)
α/(°)	118.314(2)
β/(°)	108.221(2)
γ/(°)	90.012(2)
Goodness-of-fit on F^2	1.027
R	0.0872
wR_2	0.2735

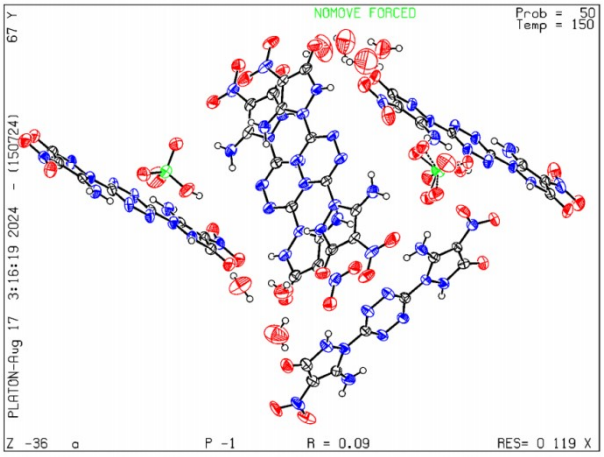


Table S5 The torsion angles of compound **NPX-12**·$HClO_4$·$2H_2O$

Parameter	Bond angles (°)	Parameter	Bond angles (°)
O5-N1-C2-C1	-4.7(10)	O5-N1-C2-C3	171.2(6)
O6-N1-C2-C3	-8.0(10)	C3-N3-N4-C1	3.1(7)
N4-N3-C3-N2	178.7(6)	N4-N3-C3-C2	-0.9(7)
C4-N3-C3-C2	179.9(7)	N4-N3-C4-N5	-178.4(6)
C3-N3-C4-N5	0.8(11)	C3-N3-C4-N7	-178.6(6)
N3-N4-C1-C2	-3.8(7)	C4-N5-N6-C5	-1.0(9)
N6-N5-C4-N7	-1.0(10)	N5-N6-C5-N8	1.9(10)
C4-N7-N8-C5	-1.3(9)	N8-N7-C4-N3	-178.4(6)
N7-N8-C5-N6	-0.6(10)	N7-N8-C5-N9	-178.3(6)
C6-N9-N10-C8	-3.8(8)	N10-N9-C5-N6	-0.1(9)
C6-N9-C5-N6	179.1(7)	C6-N9-C5-N8	-2.9(11)
N10-N9-C6-C7	1.1(8)	C5-N9-C6-N11	0.9(12)
N9-N10-C8-O3	-176.9(7)	N9-N10-C8-C7	4.8(8)
O1-N12-C7-C8	5.4(12)	O2-N12-C7-C6	7.1(12)
O4-C1-C2-N1	0.2(13)	O4-C1-C2-C3	-176.3(8)
N4-C1-C2-C3	3.4(8)	N1-C2-C3-N2	2.5(12)
C1-C2-C3-N2	178.9(7)	C1-C2-C3-N3	-1.6(7)
N9-C6-C7-C8	2.0(8)	N11-C6-C7-N12	1.1(13)
N12-C7-C8-O3	-0.5(14)	N12-C7-C8-N10	177.6(7)
C6-C7-C8-N10	-4.3(9)	O6-N1-C2-C1	176.1(6)

Table S6 Hydrogen bonds of compound **NPX-12**·$HClO_4$·$2H_2O$

D-H…A	d(D-H)/ Å	d(H…A)/ Å	d(D…A)/ Å	<(DHA)/ °
N2-H2A···N5	0.88	2.18	2.795(9)	127
N2-H2B···O23	0.88	2.2	3.035(8)	157'
N4-H4···O12	0.88	2.14	3.025(9)	179
O8-H8···O2	0.89(18)	1.89(19)	2.690(11)	149(16)
N10-H10···O14	0.88	2.04	2.916(9)	175
N11-H11A···N8	0.88	2.18	2.788(9)	126

N11-H11B···O2	0.88	2.24	2.799(9)	121
N11-H11B···O8	0.88	2.22	3.052(10)	157'
N13-H13A···N18	0.88	2.17	2.791(8)	127
N13-H13B···O7	0.88	2.22	3.063(10)	159
N16-H16···O17	0.88	2.13	3.006(9)	177
N20-H20A···N23	0.88	2.17	2.784(10)	127
N20-H20B···O10	0.88	2.15	2.999(10)	161
O27-H27D···O3	0.87	1.86	2.598(11)	142
O29-H29B···O16	0.87	1.95	2.642(12)	136

Table S7. Crystallographic data and ellipsoid plot for **NPX-13**·$HClO_4$

Crystals	**NPX-13**·$HClO_4$
CCDC	2390033
Formula	$C_6H_7ClN_8O_8$
Formula weight	354.65
Temperature	298 K
Crystal system	monoclinic
Space group	$P2_1/c$
ρ/g·cm^{-1}	1.958
a/Å	8.0018(2)
b/Å	17.4218(4)
c/Å	9.2060(3)
α/(°)	90
β/(°)	110.350(3)
γ/(°)	90
Goodness-of-fit on F^2	1.055
R	0.0518
wR_2	0.1452

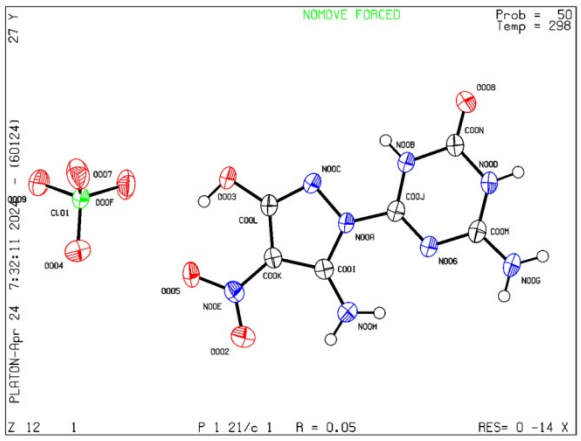


Table S8 The torsion angles of compound **NPX-13**·$HClO_4$

Parameter	Bond angles	Parameter	Bond angles (°)

	(°)		
C00M-N006-C00J-N00A	-179.5(2)	O002-N00E-C00K-C00L	179.6(3)
C00J-N006-C00M-N00G	-179.5(3)	N00A-C00I-C00K-N00E	-175.9(3)
N00C-N00A-C00I-N00H	177.6(3)	N00H-C00I-C00K-C00L	-178.2(3)
C00J-N00A-C00I-C00K	-176.3(3)	C00I-C00K-C00L-O003	179.6(3)
C00I-N00A-C00J-N006	-7.1(4)	C00J-N006-C00M-N00D	0.6(4)
C00N-N00B-C00J-N00A	-178.8(3)	C00J-N00A-N00C-C00L	177.0(2)
N00A-N00C-C00L-O003	179.5(2)	C00J-N00A-C00I-N00H	2.8(5)
C00N-N00D-C00M-N00G	176.3(3)	N00C-N00A-C00J-N00B	-2.1(4)
O002-N00E-C00K-C00I	-4.4(4)	C00N-N00B-C00J-N006	0.8(4)
O005-N00E-C00K-C00L	-1.1(4)	C00J-N00B-C00N-N00D	-3.6(4)
N00H-C00I-C00K-N00E	5.1(5)	C00N-N00D-C00M-N006	-3.8(4)
N00E-C00K-C00L-N00C	176.8(3)	C00M-N00D-C00N-N00B	5.1(4)
C00M-N006-C00J-N00B	0.8(4)	O005-N00E-C00K-C00I	175.0(3)
C00I-N00A-N00C-C00L	1.5(3)	N00A-C00I-C00K-C00L	0.8(3)
N00C-N00A-C00I-C00K	-1.4(3)	N00E-C00K-C00L-O003	-3.7(5)
C00J-N00B-C00N-O008	176.6(3)	C00I-C00K-C00L-N00C	0.1(3)
N00A-N00C-C00L-C00K	-0.9(3)	N00C-N00A-C00J-N006	178.2(2)
C00M-N00D-C00N-O008	-175.1(3)	C00I-N00A-C00J-N00B	172.6(3)

Table S9 Hydrogen bonds of compound **NPX-13**·$HClO_4$

D-H…A	d(D-H)/ Å	d(H…A)/ Å	d(D…A)/ Å	<(DHA)/ °
N00G-H00A···O007	0.86	2.43	3.111(4)	137
N00G-H00C···O004	0.86	2.13	2.953(3)	161
N00H-H00E···N006	0.86	2.23	2.814(4)	125
N00H-H00F···O008	0.86	2.48	3.245(3)	148'
O003-H003···O005	0.90(5)	2.00(5)	2.775(3)	145(5)
O003-H003···O00F	0.90(5)	2.16(5)	2.749(4)	123(4)'
N00B-H00B···O009	0.81(3)	2.08(3)	2.844(4)	157(3)'
N00D-H00D···O007	0.83(5)	2.48(5)	3.091(4)	132(5)

Table S10. Crystallographic data and ellipsoid plot for **NPX-14**·$HClO_4$

Crystals	**NPX-14**·$HClO_4$
CCDC	2390034
Formula	$C_9H_9ClN_{12}O_{9.97}$
Formula weight	480.22
Temperature	302 K
Crystal system	monoclinic
Space group	*C*/*c*
ρ/g·cm^{-1}	1.901
a/Å	15.6357(6)
b/Å	5.8232(3)
c/Å	18.7157(9)

α/(°)	90
β/(°)	100.011(2)
γ/(°)	90
Goodness-of-fit on F^2	1.104
R	0.0436
wR_2	0.1334

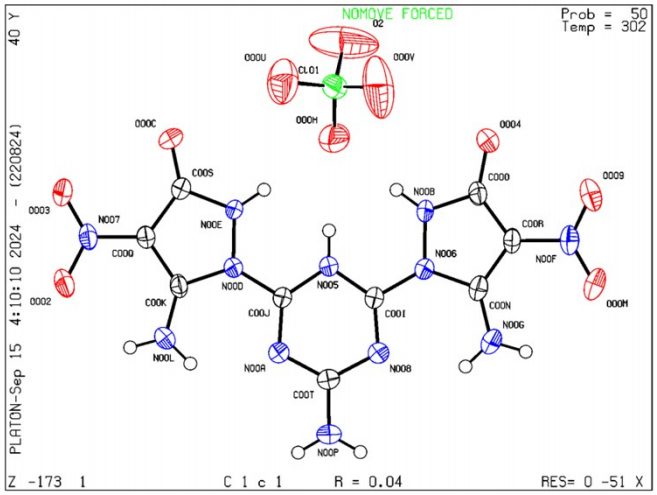


Table S11 The torsion angles of compound **NPX-14**·$HClO_4$

Parameter	Bond angles (°)	Parameter	Bond angles (°)
C00J-N005-C00I-N006	-179.6(2)	C00J-N005-C00I-N008	0.5(4)
C00I-N005-C00J-N00D	-179.9(2)	C00I-N006-N00B-C00O	170.7(2)
N00B-N006-C00I-N005	1.1(4)	N00B-N006-C00I-N008	-178.9(2)
C00N-N006-C00I-N008	-7.8(4)	N00B-N006-C00N-N00G	-179.0(3)
C00I-N006-C00N-N00G	9.1(5)	C00I-N006-C00N-C00R	-170.6(3)
O002-N007-C00Q-C00S	-177.0(3)	O003-N007-C00Q-C00K	176.4(3)
C00T-N008-C00I-N005	-0.1(4)	C00T-N008-C00I-N006	180.0(2)
C00I-N008-C00T-N00P	-179.6(3)	C00T-N00A-C00J-N005	1.0(4)
C00J-N00A-C00T-N008	-0.5(4)	C00J-N00A-C00T-N00P	179.2(3)
N006-N00B-C00O-C00R	2.0(3)	C00J-N00D-N00E-C00S	180.0(3)
N00E-N00D-C00J-N005	1.6(4)	N00E-N00D-C00J-N00A	-177.4(3)
C00K-N00D-C00J-N00A	0.5(4)	N00E-N00D-C00K-N00L	178.7(3)
C00J-N00D-C00K-N00L	0.6(5)	C00J-N00D-C00K-C00Q	-179.7(3)
N00D-N00E-C00S-C00Q	-1.0(3)	O009-N00F-C00R-C00N	-165.7(3)
O00M-N00F-C00R-C00N	10.8(5)	O00M-N00F-C00R-C00O	-176.9(3)
N00D-C00K-C00Q-C00S	1.1(3)	N00L-C00K-C00Q-N007	3.5(5)
N006-C00N-C00R-N00F	173.2(3)	N006-C00N-C00R-C00O	-0.2(3)
N00G-C00N-C00R-C00O	-179.8(3)	O004-C00O-C00R-N00F	5.8(5)
N00B-C00O-C00R-N00F	-174.5(3)	N00B-C00O-C00R-C00N	-1.1(3)
N007-C00Q-C00S-N00E	177.0(3)	C00K-C00Q-C00S-O00C	-179.5(4)

Table S12 Hydrogen bonds of compound **NPX-14**·$HClO_4$

D-H…A	d(D-H)/ Å	d(H…A)/ Å	d(D…A)/ Å	<(DHA)/ °
N005-H005···O00H	0.86	2.25	3.108(4)	172
N00B-H00B···O00H	0.86	1.95	2.811(4)	177
N00E-H00E···O00H	0.86	2.12	2.976(4)	174
N00G-H00A···N008	0.86	2.11	2.716(4)	127
N00G-H00A···O003	0.86	2.59	3.243(4)	134'
N00G-H00C···O00C	0.86	1.97	2.688(4)	140'
N00L-H00D···N00A	0.86	2.14	2.752(4)	128
N00L-H00D···O00V	0.86	2.25	2.931(7)	136'
N00L-H00F···O002	0.86	2.2	2.745(4)	121
N00L-H00F···O009	0.86	2.44	3.045(4)	128'
N00P-H00G···O2	0.86	2.49	3.304(8)	158
N00P-H00G···O00V	0.86	2.52	3.282(6)	149'
N00P-H00H···O009	0.86	2.51	3.069(4)	123
N00P-H00H···O003	0.86	2.54	3.363(4)	162'

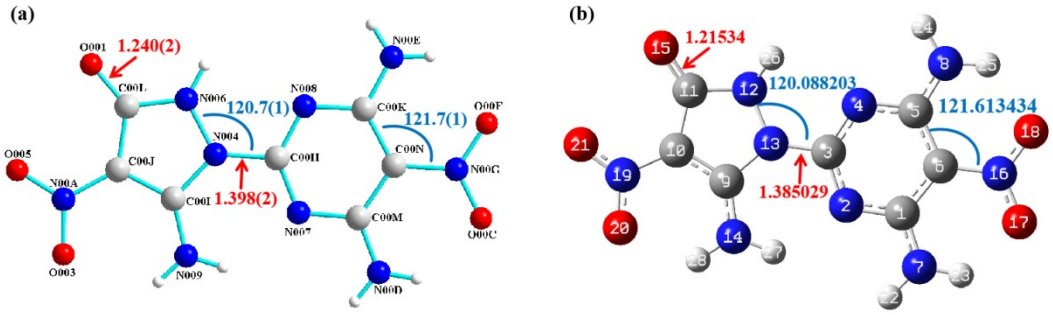


Fig S1. Molecular structure of **NPX-10**. (a) crystal structure; (b)geometrically optimized structure.

Table S13 Bond lengths of crystal **NPX-10**

Bond	Lengths	Bond	Lengths	Bond	Lengths
O001-C00L	1.240(2)	N009-C00I	1.318(2)	N007-C00M	1.351(2)
O003-N00A	1.237(2)	N00E-C00K	1.325(2)	N008-C00H	1.320(2)
N004-N006	1.395(2)	O00F-N00G	1.244(2)	N008-C00K	1.346(2)
N004-C00H	1.398(2)	N00G-C00N	1.408(2)	O00C-N00G	1.235(2)
N004-C00I	1.372(2)	C00I-C00J	1.407(2)	C00M-C00N	1.430(2)
O005-N00A	1.232(2)	C00J-C00L	1.441(2)	N00A-C00J	1.389(2)
N00D-C00M	1.314(2)	C00K-C00N	1.431(2)	N007-C00H	1.320(2)
N006-C00L	1.353(2)				

Table S14 Bond lengths of **NPX-10** based on structure optimization

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
1	2	1.348801	9	13	1.384323
1	6	1.437251	9	14	1.330259

1	7	1.339755	10	11	1.459908
2	3	1.337477	10	19	1.408292
3	4	1.329066	11	12	1.421075
3	13	1.385029	11	15	1.21534
4	5	1.347628	12	13	1.408876
5	6	1.437434	16	17	1.247601
5	8	1.337875	16	18	1.246673
6	16	1.420536	19	20	1.259138
9	10	1.400366	19	21	1.228447

Table S15 Bond angles of crystal **NPX-10**

Bond	Angles	Bond	Angles
N006-N004-C00H	120.7(1)	N008-C00K-N00E	115.6(1)
N006-N004-C00I	109.0(1)	N008-C00K-C00N	120.7(1)
C00H-N004-C00I	130.2(1)	N00E-C00K-C00N	123.7(1)
N004-N006-C00L	110.7(1)	O001-C00L-N006	123.7(1)
C00H-N007-C00M	116.3(1)	O001-C00L-C00J	131.3(1)
C00H-N008-C00K	115.3(1)	N006-C00L-C00J	105.0(1)
O003-N00A-O005	121.8(1)	N007-C00M-N00D	115.4(1)
O003-N00A-C00J	118.6(1)	N007-C00M-C00N	119.6(1)
O005-N00A-C00J	119.5(1)	N00D-C00M-C00N	125.1(1)
O00C-N00G-O00F	119.6(2)	N00G-C00N-C00K	121.7(1)
O00C-N00G-C00N	120.5(1)	N00G-C00N-C00M	120.7(1)
O00F-N00G-C00N	119.9(2)	C00K-C00N-C00M	117.5(1)
N004-C00H-N007	114.8(1)	N00A-C00J-C00L	126.7(1)
N004-C00H-N008	114.8(1)	C00I-C00J-C00L	109.2(1)
N007-C00H-N008	130.5(1)	N009-C00I-C00J	130.2(1)
N004-C00I-N009	123.7(1)	N00A-C00J-C00I	124.1(1)
N004-C00I-C00J	106.1(1)		

Table S16 Bond angles of **NPX-10** based on structure optimization

Atom 1	Atom 2	Atom 3	Angles	Atom 1	Atom 2	Atom 3	Angles
1	2	3	116.689941	9	10	11	109.40921
1	6	5	116.686279	9	10	19	123.591423
1	6	16	121.700287	9	13	12	108.804985
2	1	6	120.714111	10	9	13	107.672768
2	1	7	115.953644	10	9	14	129.266403
2	3	4	128.270798	10	11	12	103.830498
2	3	13	117.026772	10	11	15	133.435669
3	4	5	117.05365	10	19	20	117.039604
3	13	9	130.913177	10	19	21	119.365288
3	13	12	120.088203	11	10	19	126.990074
4	3	13	114.687683	11	12	13	109.183334

4	5	6	120.577621	12	11	15	122.72892
4	5	8	115.603279	13	9	14	123.055428
5	6	16	121.613434	17	16	18	121.104378
6	1	7	123.332092	20	19	21	123.595024
6	5	8	123.818733	6	16	18	119.370323
6	16	17	119.525299				

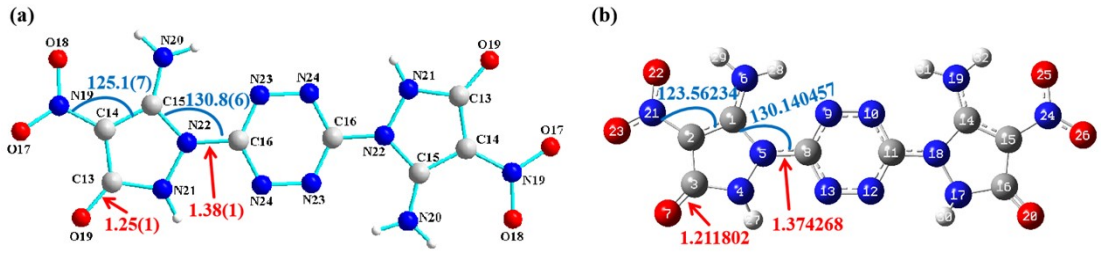


Fig S2. Molecular structure of **NPX-12**. (a) crystal structure; (b)geometrically optimized structure.

Table S17 Bond lengths of crystal **NPX-12**

Bond	Lengths	Bond	Lengths	Bond	Lengths
O18-N19	1.24(1)	N21-C13	1.37(1)	N23-N24	1.33(1)
O19-C13	1.25(1)	N22-N21	1.39(1)	N24-C16	1.342(9)
N19-C14	1.38(1)	N22-C16	1.38(1)	C14-C13	1.41(1)
O17-N19	1.24(1)	N22-C15	1.376(9)	C15-C14	1.41(1)
N20-C15	1.31(1)	N23-C16	1.33(1)	C16-N24	1.342(9)

Table S18 Bond lengths of **NPX-12** based on structure optimization

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
1	2	1.397237	8	9	1.345446	15	24	1.411768
1	5	1.388877	8	13	1.35498	16	17	1.431356
1	6	1.331147	9	10	1.313241	16	20	1.211803
2	3	1.458274	10	11	1.345452	17	18	1.414606
2	21	1.411782	11	12	1.354977	21	22	1.257464
3	4	1.431354	11	18	1.374245	21	23	1.226516
3	7	1.211802	12	13	1.303457	24	25	1.257461
4	5	1.41465	14	15	1.397233	24	26	1.226521
5	8	1.374268	14	18	1.388883	15	16	1.45828
14	19	1.331148						

Table S19 Bond angles of crystal **NPX-12**

Bond	Angles	Bond	Angles
O18-N19-O17	122.1(7)	N22-C15-N20	123.8(7)
O18-N19-C14	118.2(7)	N22-C15-C14	105.7(7)
O18-N19-O17	122.1(7)	N23-N24-C16	115.9(6)
O17-N19-C14	119.7(7)	N23-C16-N24	127.0(7)

O19-C13-N21	122.9(7)	N23-C16-N22	117.5(6)
O19-C13-C14	131.1(8)	N24-N23-C16	117.1(6)
N19-C14-C15	125.1(7)	N24-C16-N23	127.0(7)
N19-C14-C13	125.4(7)	N24-C16-N22	115.5(6)
N20-C15-C14	130.5(7)	C15-C14-C13	109.4(7)
N21-N22-C16	119.7(6)	C15-C14-C13	109.4(7)
N21-N22-C15	109.5(6)	C16-N22-C15	130.8(6)
N21-C13-C14	106.0(7)	C16-N22-C15	130.8(6)
N22-N21-C13	109.1(6)	C16-N24-N23	115.9(6)
N22-C16-N24	115.5(6)		

Table S20 Bond angles of **NPX-12** based on structure optimization

Atom 1	Atom 2	Atom 3	Angles	Atom 1	Atom 2	Atom 3	Angles
1	2	3	109.689438	10	11	12	124.806976
1	2	21	123.56234	10	11	18	119.143135
1	5	4	109.126122	11	12	13	117.60218
1	5	8	130.140457	11	18	14	130.143845
2	1	5	107.535759	11	18	17	119.521584
2	1	6	129.210617	12	11	18	116.02742
2	3	4	104.105019	14	15	16	109.688377
2	3	7	133.60321	14	15	24	123.560951
2	21	22	116.891205	14	18	17	109.130119
2	21	23	119.213547	15	14	18	107.534172
3	2	21	126.743538	15	14	19	129.213455
3	4	5	108.347214	15	16	17	104.105896
4	3	7	122.289848	15	16	20	133.60289
4	5	8	119.518494	15	24	25	116.89135
5	1	6	123.252548	15	24	26	119.21328
5	8	9	119.142555	16	15	24	126.745705
5	8	13	116.028496	16	17	18	108.345306
8	9	10	117.581642	17	16	20	122.289253
8	13	12	117.60186	18	14	19	123.251289
9	8	13	124.8069	22	21	23	123.894989
9	10	11	117.580673	25	24	26	123.895119

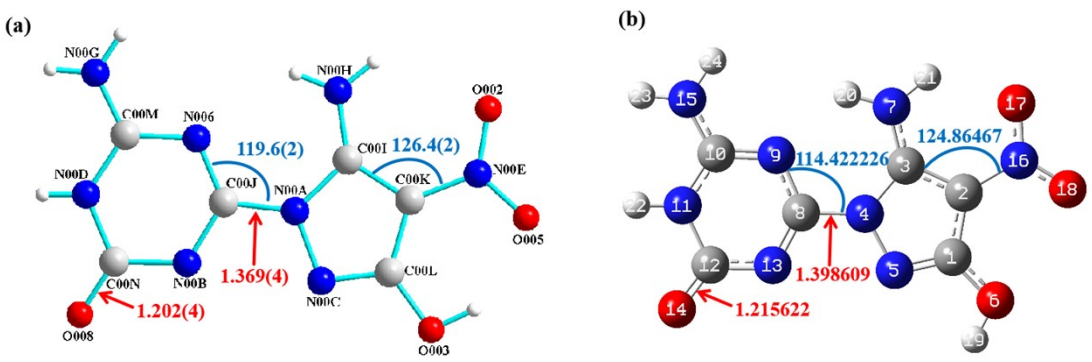


Fig S3. Molecular structure of **NPX-13**. (a) crystal structure; (b)geometrically optimized structure.

Table S21 Bond lengths of crystal **NPX-13**

Bond	Lengths	Bond	Lengths	Bond	Lengths
O002-N00E	1.234(3)	N00A-C00I	1.381(4)	N00D-C00N	1.374(4)
O003-C00L	1.333(4)	N00A-C00J	1.369(4)	N00E-C00K	1.384(4)
O005-N00E	1.242(4)	N00B-C00J	1.339(4)	N00G-C00M	1.298(4)
N006-C00J	1.306(4)	N00B-C00N	1.388(5)	N00H-C00I	1.315(4)
N006-C00M	1.359(4)	N00C-C00L	1.302(4)	C00I-C00K	1.402(4)
O008-C00N	1.202(4)	N00D-C00M	1.347(4)	C00K-C00L	1.412(4)
N00A-N00C	1.405(4)				

Table S22 Bond lengths of **NPX-13** based on structure optimization

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
1	2	1.431999	8	13	1.307858
1	5	1.307222	9	10	1.321879
1	6	1.335744	10	11	1.352561
2	3	1.405673	10	15	1.353682
2	16	1.40505	11	12	1.439131
3	4	1.383981	12	13	1.367555
3	7	1.33571	12	14	1.215622
4	5	1.400133	16	17	1.256508
4	8	1.398609	16	18	1.232355
8	9	1.369511			

Table S23 Bond angles of crystal **NPX-13**

Bond	Angles	Bond	Angles
C00J-N006-C00M	115.6(2)	N006-C00J-N00B	125.2(3)
N00C-N00A-C00I	113.4(2)	N00A-C00J-N00B	115.2(2)
N00C-N00A-C00J	117.5(2)	N00E-C00K-C00I	126.4(2)
C00I-N00A-C00J	129.0(2)	N00E-C00K-C00L	126.6(2)
C00J-N00B-C00N	121.3(3)	C00I-C00K-C00L	106.9(2)
N00A-N00C-C00L	103.6(2)	O003-C00L-N00C	119.2(3)
C00M-N00D-C00N	123.8(3)	O003-C00L-C00K	128.0(2)
O002-N00E-O005	122.8(3)	N00C-C00L-C00K	112.8(2)
O002-N00E-C00K	120.0(2)	N006-C00M-N00D	121.1(2)
O005-N00E-C00K	117.3(2)	N006-C00M-N00G	118.6(2)
N00A-C00I-N00H	125.8(3)	N00D-C00M-N00G	120.3(3)
N00A-C00I-C00K	103.2(2)	O008-C00N-N00B	123.4(3)
N00H-C00I-C00K	131.0(3)	O008-C00N-N00D	123.8(3)
N006-C00J-N00A	119.6(2)	N00B-C00N-N00D	112.8(3)

Table S24 Bond angles of **NPX-13** based on structure optimization

Atom 1	Atom 2	Atom 3	Angles	Atom 1	Atom 2	Atom 3	Angles
1	2	3	105.208595	4	8	13	117.145287
1	2	16	129.926727	5	1	6	121.972755
1	5	4	105.228424	5	4	8	119.03746
2	1	5	112.394585	8	9	10	114.802208
2	1	6	125.632652	8	13	12	118.05777
2	3	4	105.507805	9	8	13	128.432175
2	3	7	128.447525	9	10	11	121.36615
2	16	17	117.143524	9	10	15	119.523651
2	16	18	119.223656	10	11	12	122.040993
3	2	16	124.86467	11	10	15	119.101837
3	4	5	111.660591	11	12	13	115.299644
3	4	8	129.301697	11	12	14	117.861855
4	3	7	126.044586	13	12	14	126.83847
4	8	9	114.422226	17	16	18	123.632828

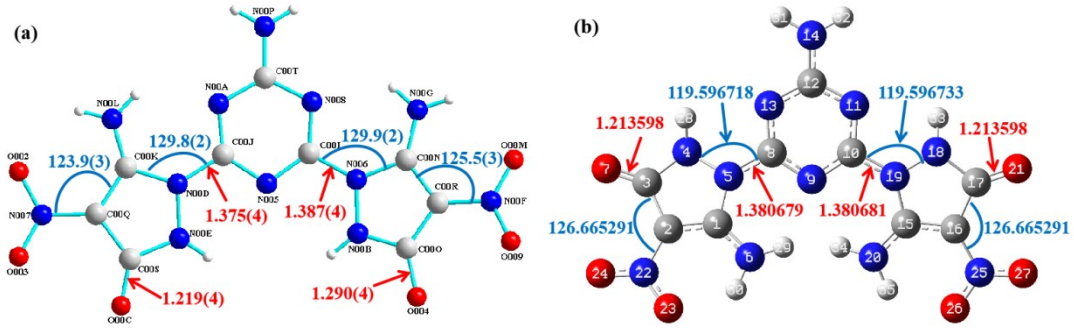


Fig S4. Molecular structure of **NPX-14**. (a) crystal structure; (b)geometrically optimized structure.

Table S25 Bond lengths of crystal **NPX-14**

Bond	Lengths	Bond	Lengths	Bond	Lengths
O002-N007	1.256(4)	N008-C00T	1.356(4)	N00F-O00M	1.212(4)
O003-N007	1.228(3)	O009-N00F	1.230(4)	N00F-C00R	1.403(4)
O004-C00O	1.290(4)	N00A-C00J	1.324(4)	N00G-C00N	1.315(4)
N005-C00I	1.324(3)	N00A-C00T	1.347(4)	C00K-N00L	1.295(4)
N005-C00J	1.341(4)	N00B-C00O	1.331(4)	C00K-C00Q	1.409(4)
N006-N00B	1.388(3)	O00C-C00S	1.219(4)	C00N-C00R	1.394(4)
N006-C00I	1.387(4)	N00D-N00E	1.392(4)	C00O-C00R	1.399(4)
N006-C00N	1.377(4)	N00D-C00J	1.375(4)	N00P-C00T	1.318(4)
N007-C00Q	1.387(4)	N00D-C00K	1.381(4)	C00Q-C00S	1.439(5)
N008-C00I	1.324(3)	N00E-C00S	1.369(4)		

Table S26 Bond lengths of **NPX-14** based on structure optimization

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
1	2	1.396833	12	13	1.349816

1	5	1.384635	12	14	1.342275
1	6	1.336333	15	16	1.396833
2	3	1.461526	15	19	1.384635
2	22	1.411847	15	20	1.336334
3	4	1.422861	16	17	1.461525
3	7	1.213598	16	25	1.411847
4	5	1.409872	17	18	1.422859
5	8	1.380679	17	21	1.213598
8	9	1.345696	18	19	1.409871
8	13	1.330576	22	23	1.2578
9	10	1.345695	22	24	1.226739
10	11	1.330576	25	26	1.2578
10	19	1.380681	25	27	1.226739
11	12	1.349816			

Table S27 Bond angles of crystal **NPX-14**

Bond	Angles	Bond	Angles
C00I-N005-C00J	111.5(2)	N00A-C00J-N00D	117.7(2)
N00B-N006-C00I	120.7(2)	N00D-C00K-N00L	123.7(3)
N00B-N006-C00N	109.0(2)	N00D-C00K-C00Q	105.2(2)
C00I-N006-C00N	129.9(2)	N00L-C00K-C00Q	131.1(3)
O002-N007-O003	122.6(3)	N006-C00N-N00G	123.3(3)
O002-N007-C00Q	117.3(2)	N006-C00N-C00R	105.7(2)
O003-N007-C00Q	120.1(3)	N00G-C00N-C00R	131.0(3)
C00I-N008-C00T	113.6(2)	O004-C00O-N00B	119.3(3)
C00J-N00A-C00T	114.5(2)	O004-C00O-C00R	132.9(3)
N006-N00B-C00O	108.9(2)	N00B-C00O-C00R	107.9(3)
N00E-N00D-C00J	120.4(2)	N007-C00Q-C00K	123.9(3)
N00E-N00D-C00K	109.7(2)	N007-C00Q-C00S	125.9(3)
C00J-N00D-C00K	129.8(2)	C00K-C00Q-C00S	110.2(3)
N00D-N00E-C00S	110.4(2)	N00F-C00R-C00N	125.5(3)
O009-N00F-O00M	123.9(3)	N00F-C00R-C00O	125.7(3)
O009-N00F-C00R	117.2(3)	C00N-C00R-C00O	108.5(3)
O00M-N00F-C00R	118.7(3)	O00C-C00S-N00E	123.0(3)
N005-C00I-N006	115.5(2)	O00C-C00S-C00Q	132.4(3)
N005-C00I-N008	128.9(2)	N00E-C00S-C00Q	104.5(3)
N006-C00I-N008	115.7(2)	N008-C00T-N00A	124.0(3)
N005-C00J-N00A	127.6(3)	N008-C00T-N00P	117.2(3)
N005-C00J-N00D	114.7(2)	N00A-C00T-N00P	118.8(3)

Table S28 Bond angles of **NPX-14** based on structure optimization

Atom 1	Atom 2	Atom 3	Angles	Atom 1	Atom 2	Atom 3	Angles
1	2	3	109.504845	10	11	12	114.270851

1	2	22	123.674942	10	19	15	131.157227
1	5	4	109.107857	10	19	18	119.596733
1	5	8	131.157257	11	10	19	115.473824
2	1	5	107.659668	11	12	13	124.95137
2	1	6	128.850418	11	12	14	117.524338
2	3	4	103.894638	13	12	14	117.524292
2	3	7	133.344757	15	16	17	109.504524
2	22	23	117.011604	15	16	25	123.67524
2	22	24	119.199226	15	19	18	109.10778
3	2	22	126.665291	16	15	19	107.659492
3	4	5	109.004166	16	15	20	128.85051
4	3	7	122.760216	16	17	18	103.894394
4	5	8	119.596718	16	17	21	133.344849
5	1	6	123.488327	16	25	26	117.011688
5	8	9	117.727287	16	25	27	119.199165
5	8	13	115.473846	17	16	25	126.665291
8	9	10	112.915291	17	18	19	109.00367
8	13	12	114.270874	18	17	21	122.7603
9	8	13	126.78775	19	15	20	123.488403
9	10	11	126.787804	23	22	24	123.788933
9	10	19	117.727257	26	25	27	123.78891

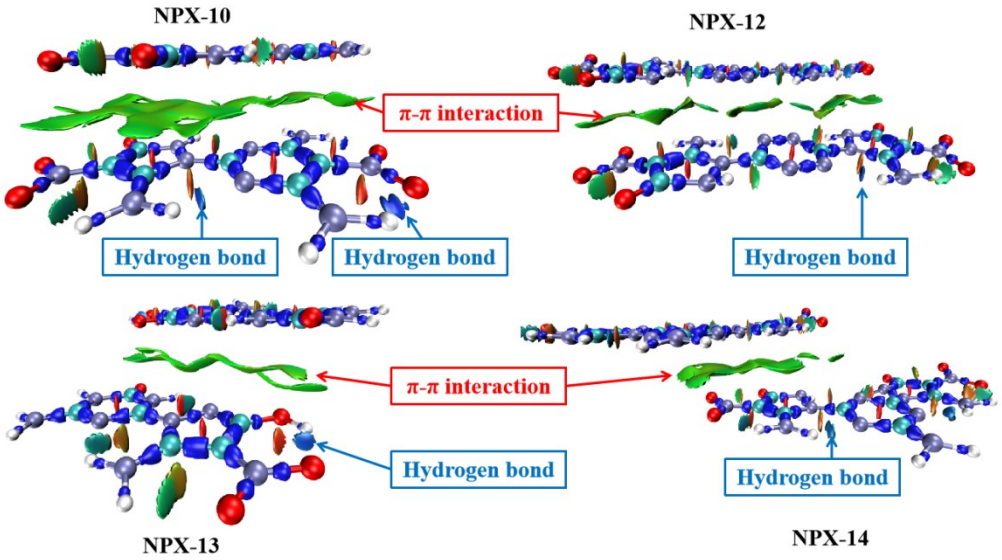


Fig S5. NCI analysis for **NPX-10**, **NPX-12**~**NPX-14**.

3. ^{1}H NMR and ^{13}C NMR spectra for NPX-10~ NPX-14

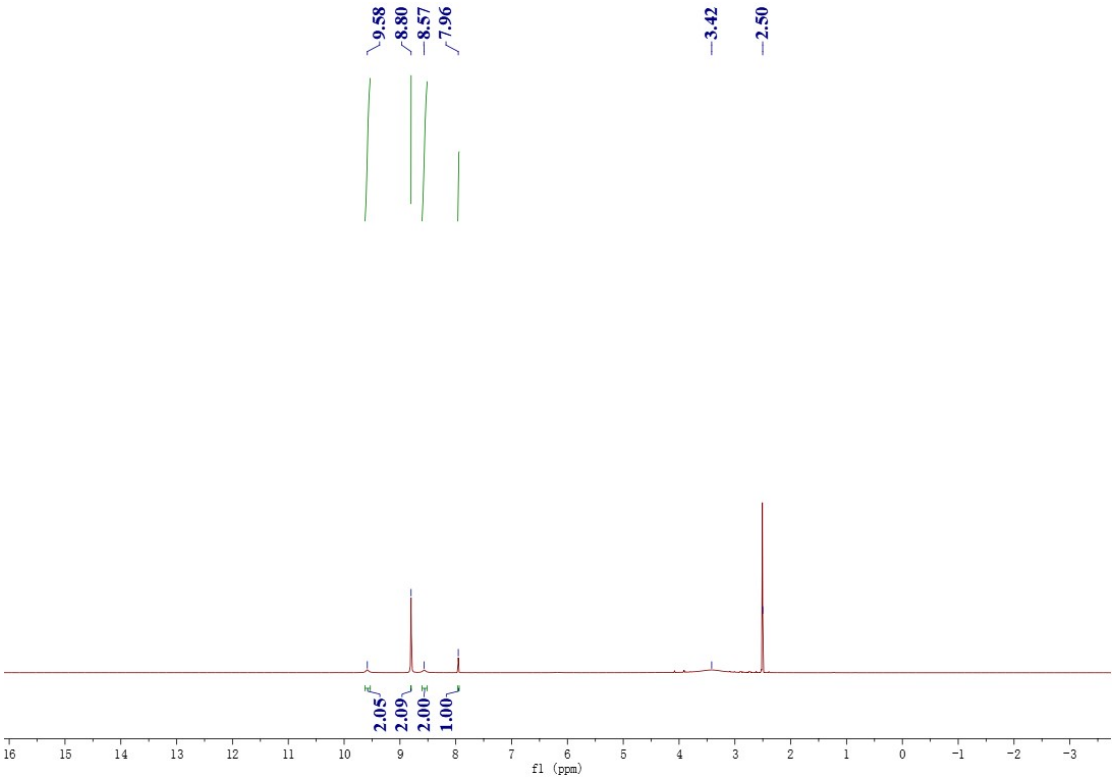


Fig S6. ^{1}H NMR spectrum of **NPX-10** in d_6-DMSO.

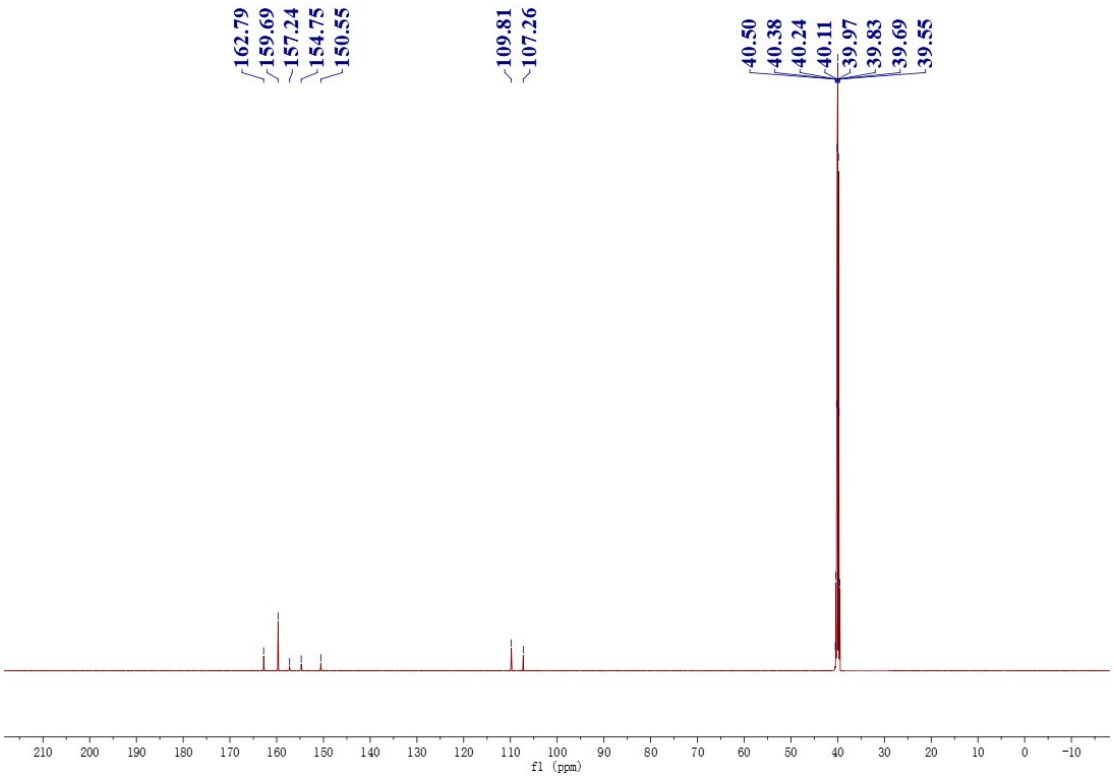


Fig S7. ^{13}C NMR spectrum of **NPX-10** in d_6-DMSO

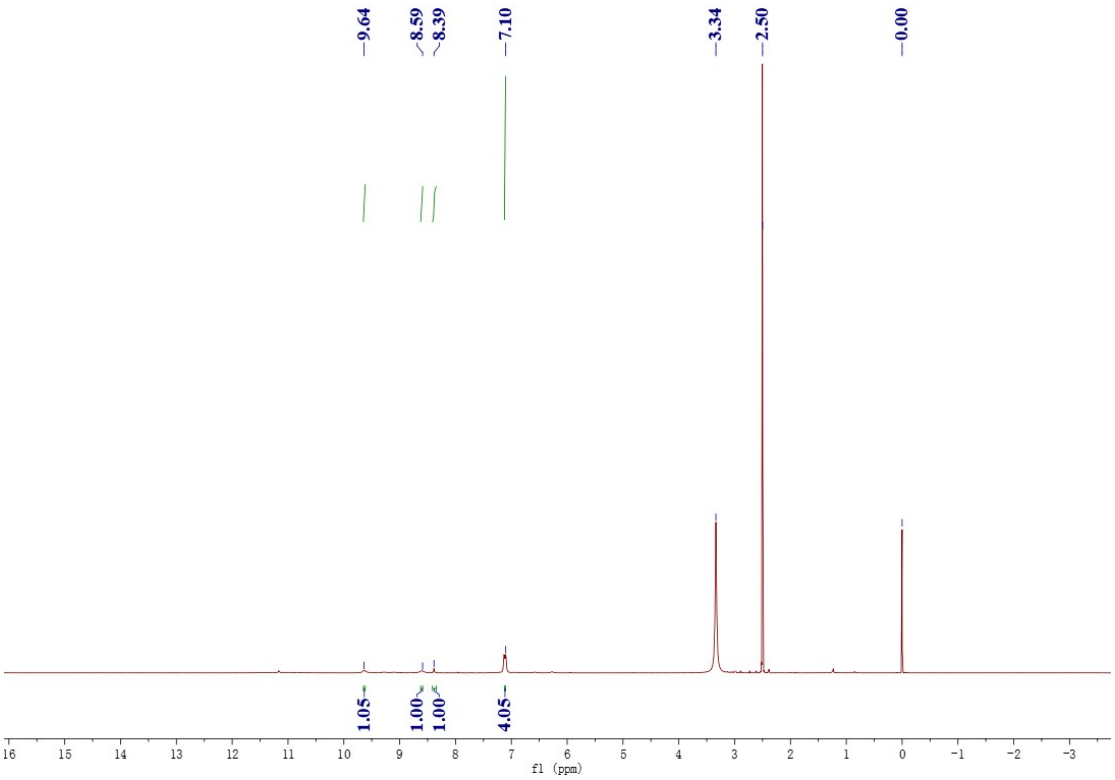


Fig S8. ^{1}H NMR spectrum of **NPX-11** in d_6-DMSO.

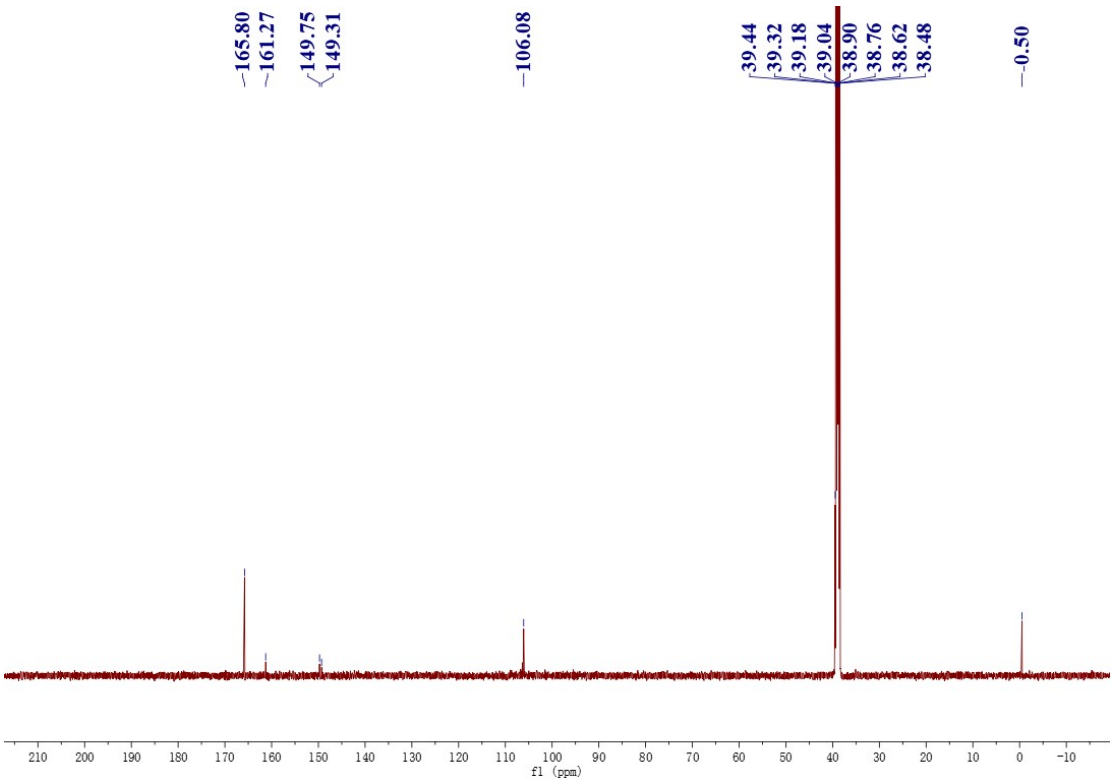


Fig S9. ^{13}C NMR spectrum of **NPX-11** in d_6-DMSO

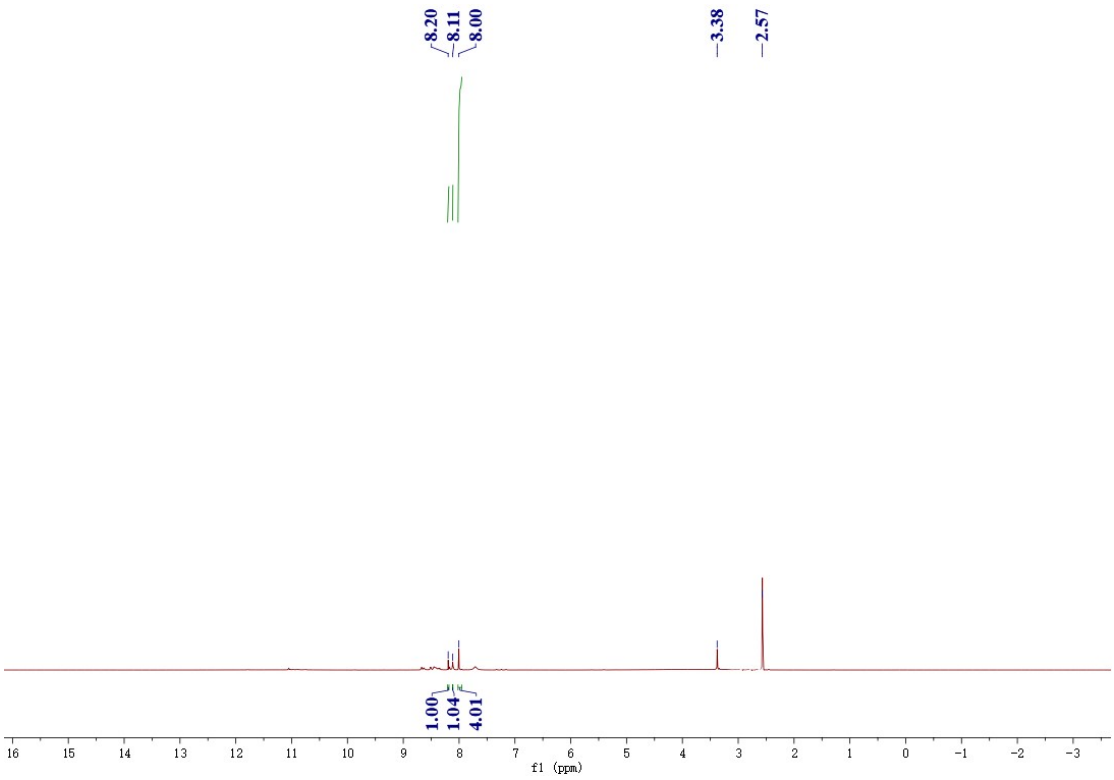


Fig S10. ^{1}H NMR spectrum of **NPX-12** in d_6-DMSO.

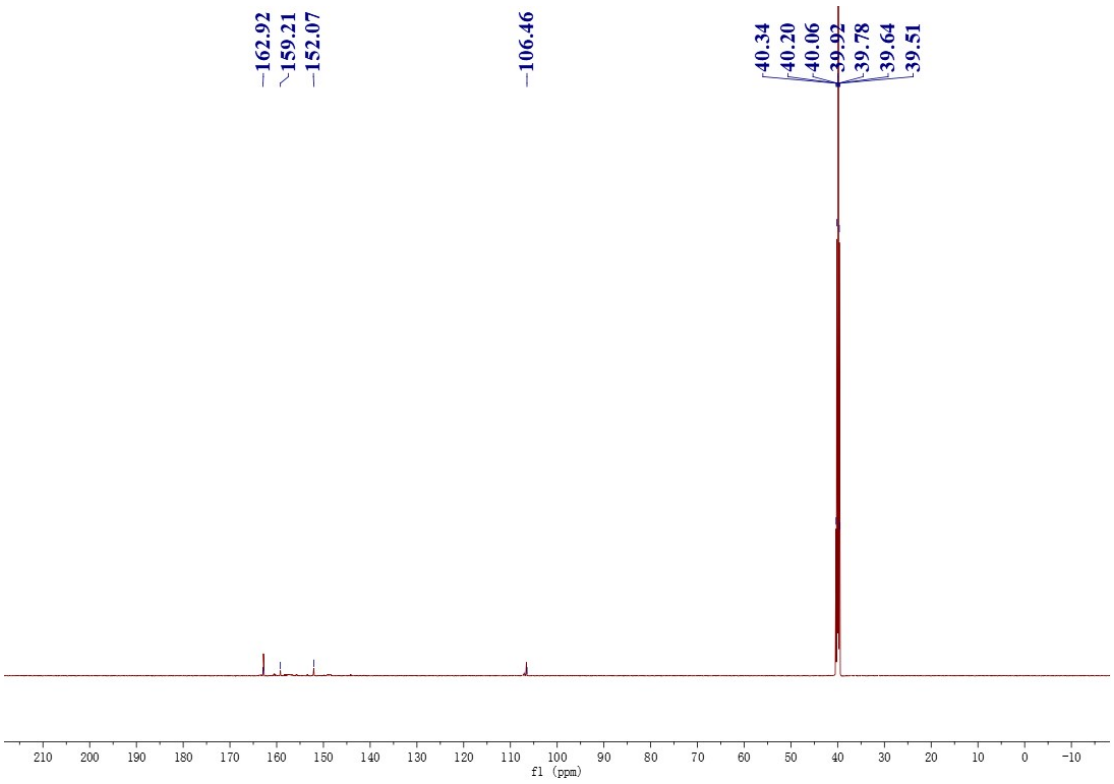


Fig S11. ^{13}C NMR spectrum of **NPX-12** in d_6-DMSO

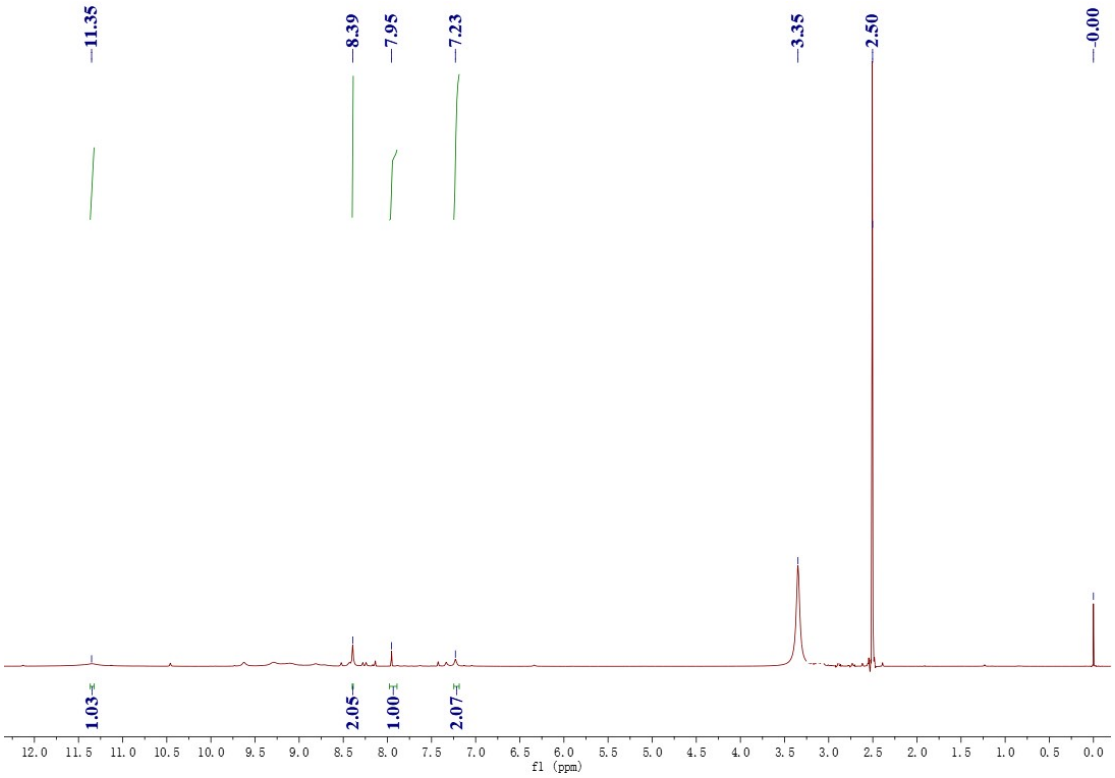


Fig S12. ^{1}H NMR spectrum of **NPX-13** in d_6-DMSO.

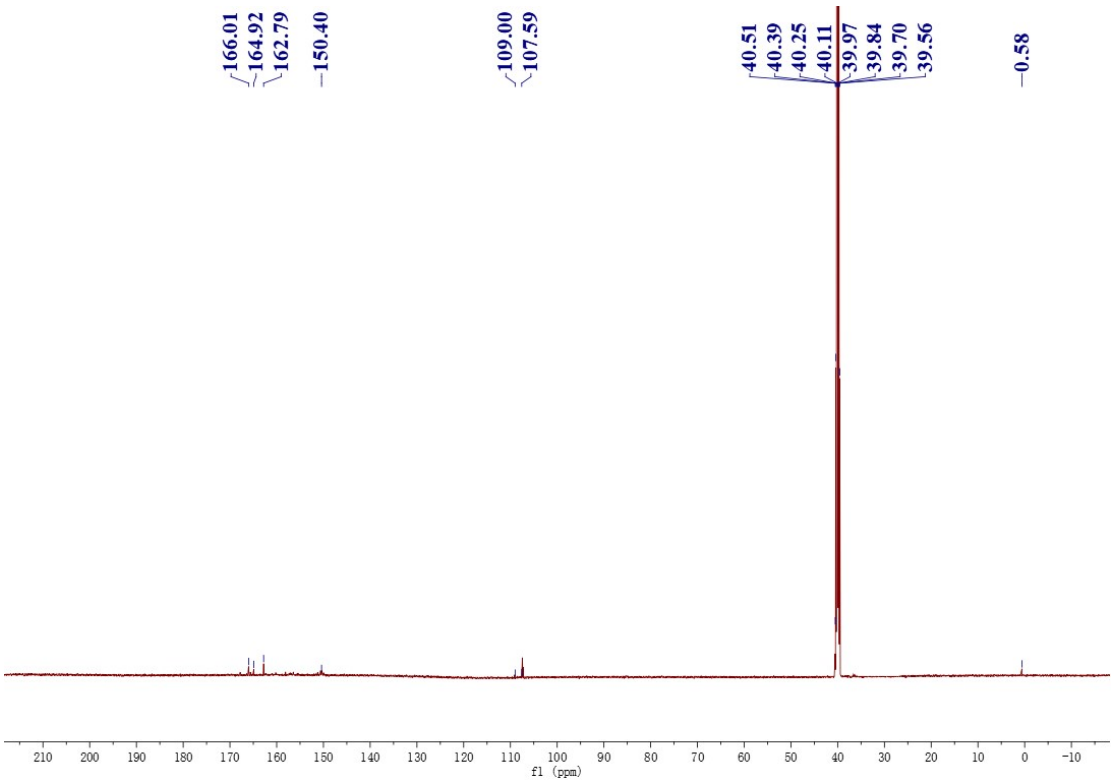


Fig S13. ^{13}C NMR spectrum of **NPX-13** in d_6-DMSO

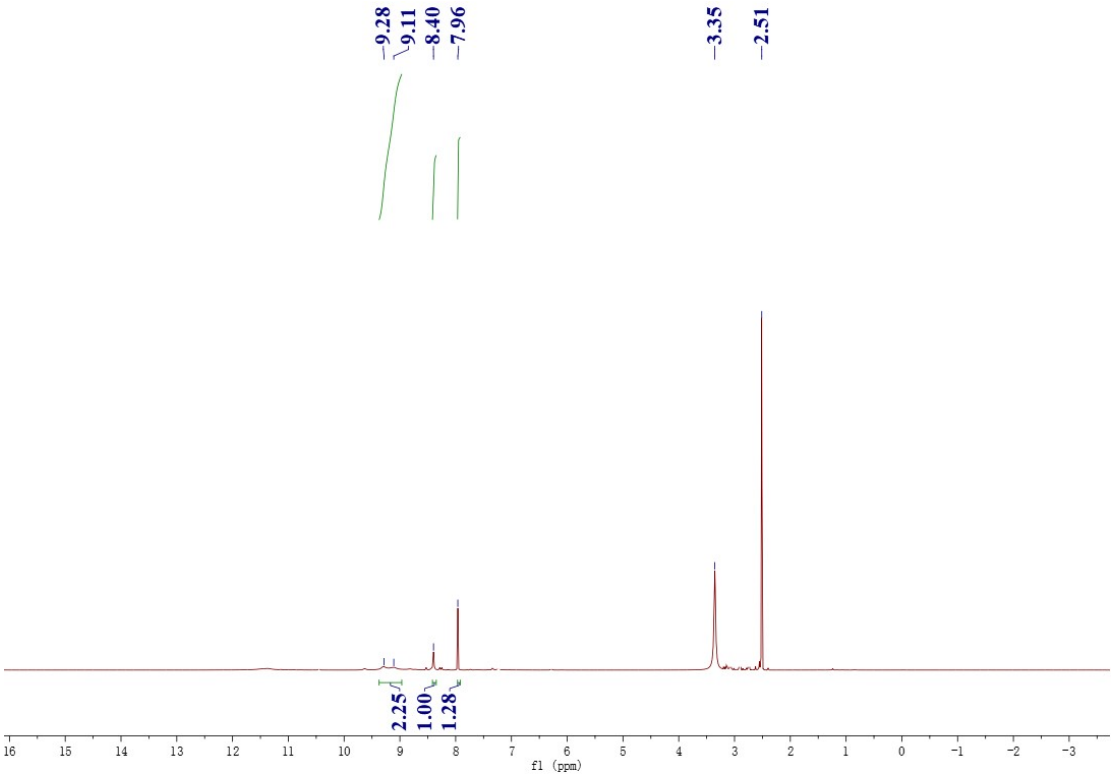


Fig S14. ^{1}H NMR spectrum of **NPX-14** in d_6-DMSO.

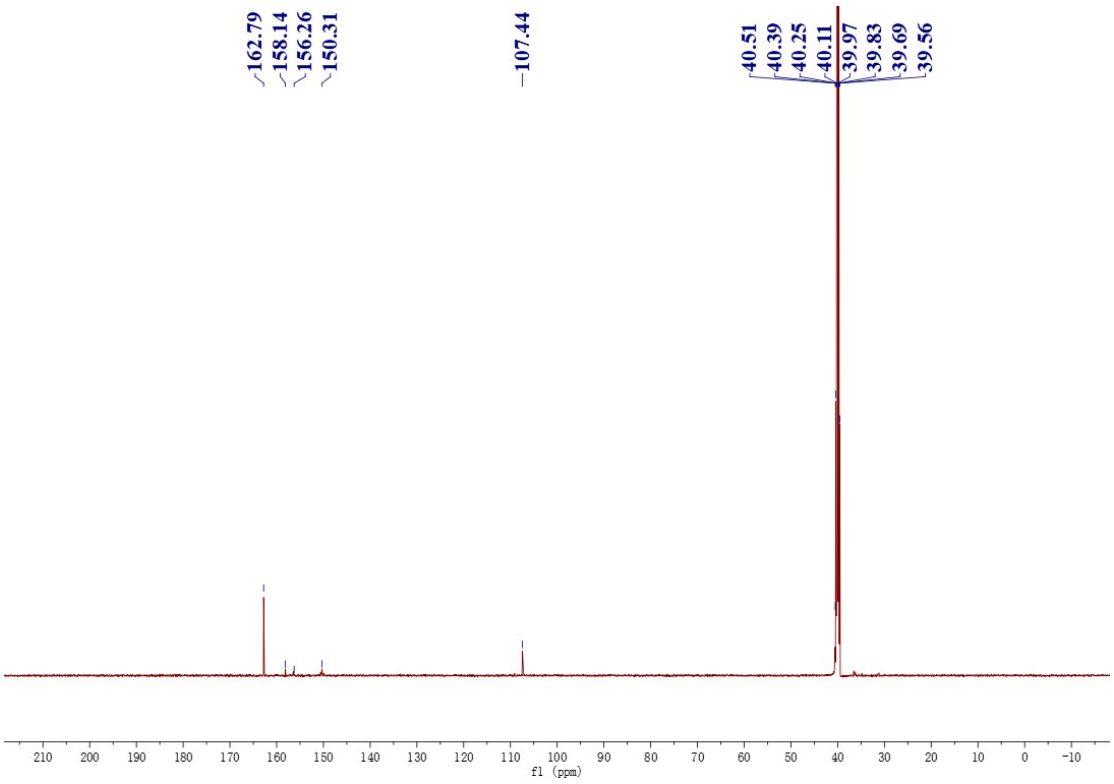


Fig S15. ^{13}C NMR spectrum of **NPX-14** in d_6-DMSO

4. IR spectra for compounds

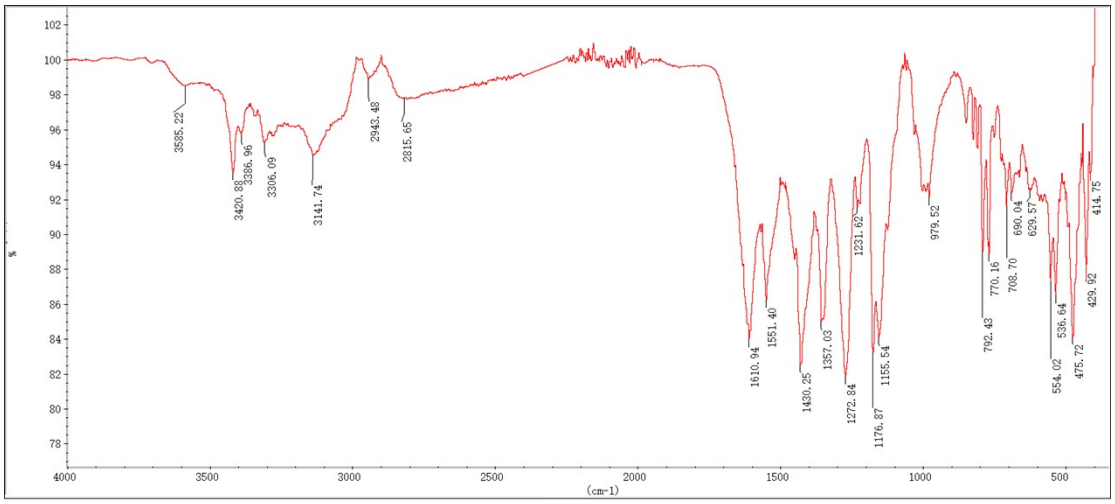


Fig S16. IR spectrum of **NPX-10**

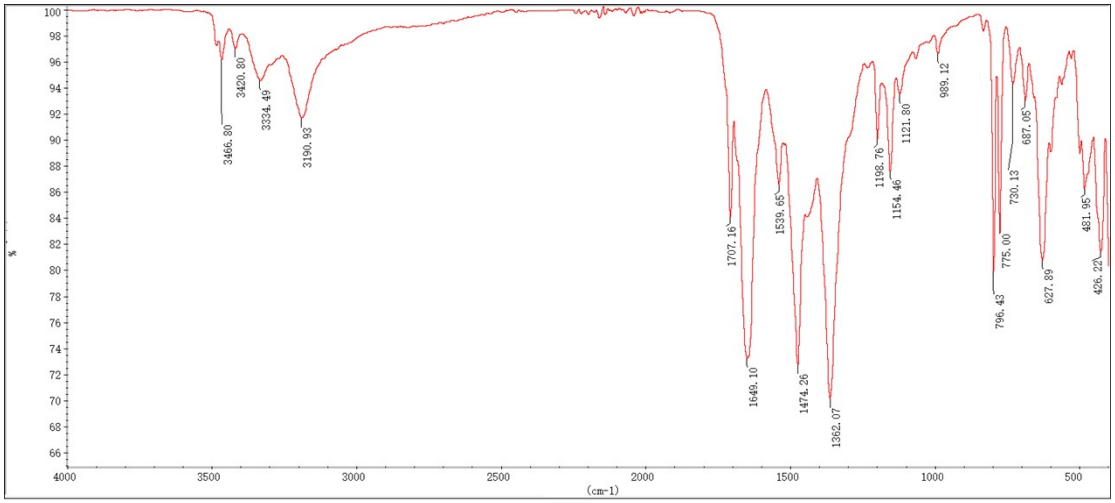


Fig S17. IR spectrum of **NPX-11**

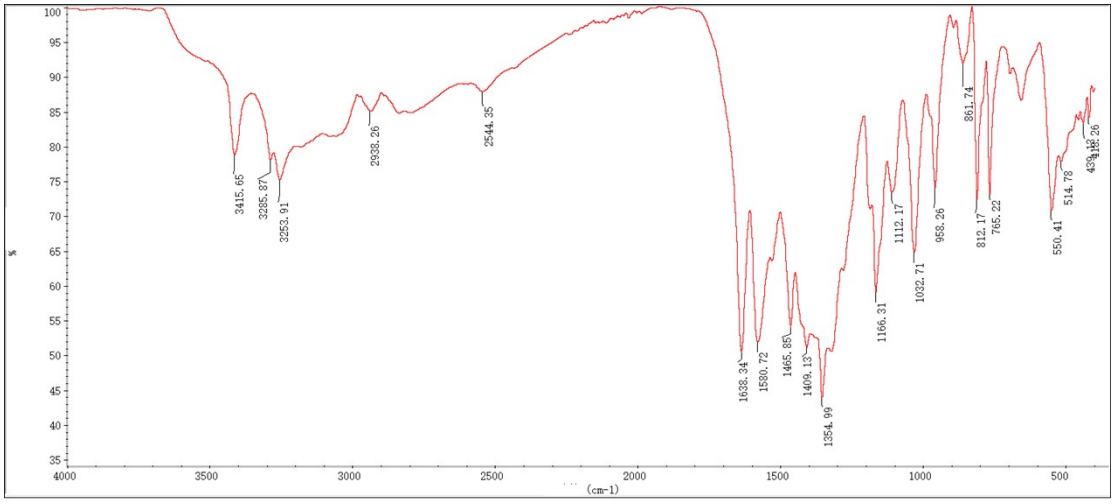


Fig S18. IR spectrum of **NPX-12**

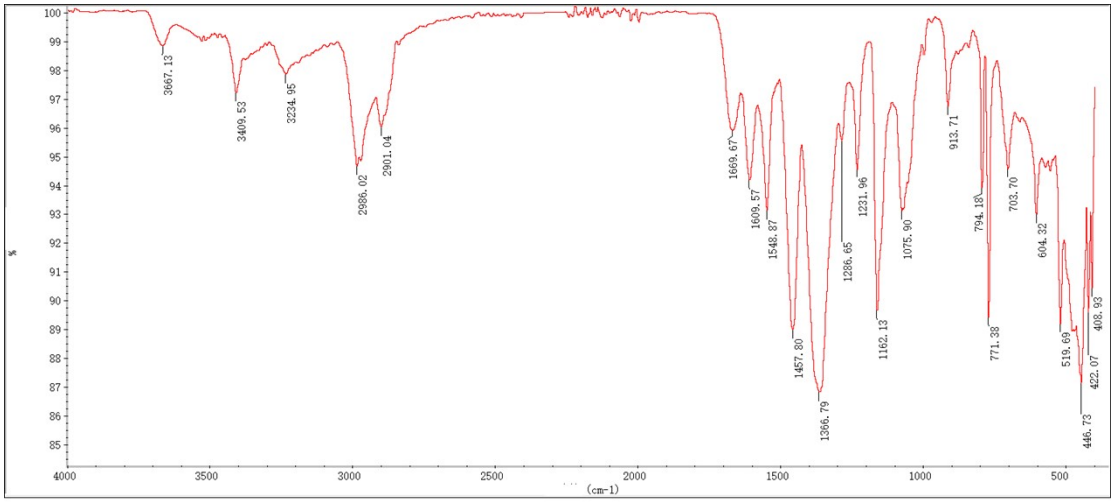


Fig S19. IR spectrum of **NPX-13**

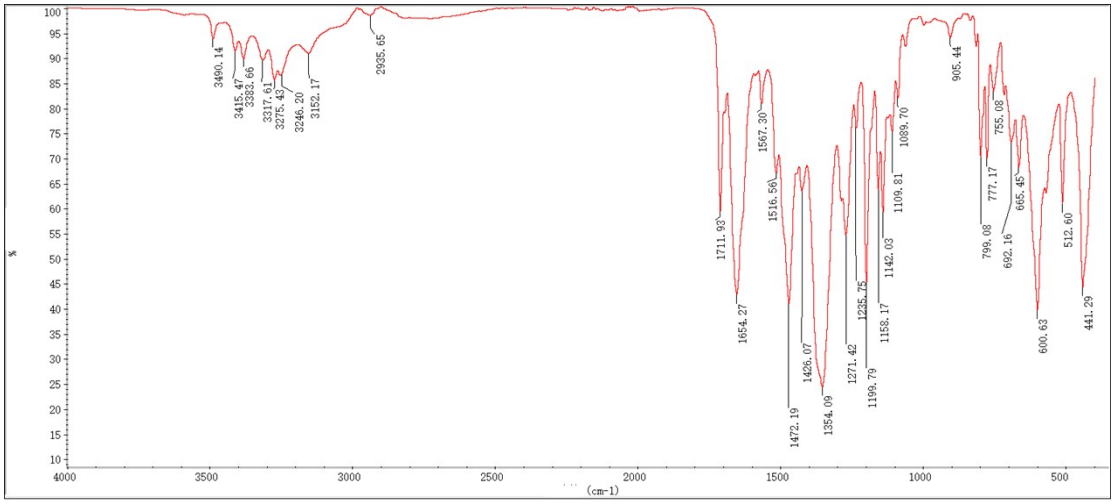
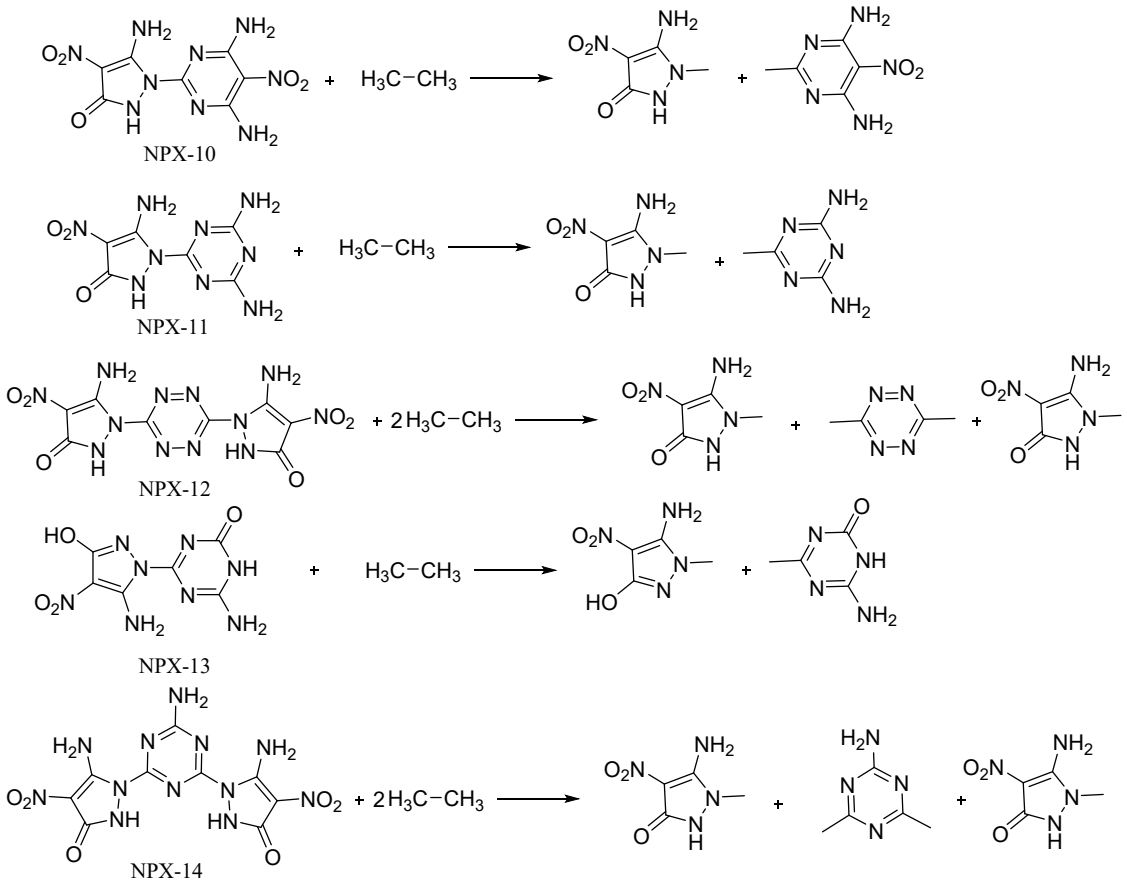


Fig S20. IR spectrum of **NPX-14**

5. Calculation procedures for heat of formation

Computations were carried out by using the Gaussian09 suite of programs.[1] The elementary geometric optimization and the frequency analysis were performed at the level of Becke three Lee-Yan-Parr (B3LYP) Functionals[3] with 6-31+G** basis set.[4]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.



Scheme S1. Isodemic reaction for computing the HOF

Reference

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

[2] M. Sućeska, EXPLO5 Program, Version 6.05; Brodarski Institut: Zagreb, Croatia, 2020.

[3] A. D. Becke. Density-functional thermochemistry. III. The role of exact exchange. J Phys Chem, 1993, 98, 5648-5652; b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. J Phys Chem, 1994, 98, 11623-11627.

[4] P. C. Hariharan, J. A. Pople. The influence of polarization functions on molecular orbital hydrogenation energies. Theorefica Chimica Acta, 1973, 28, 213-222.