Supporting Information (SI)

A dual strategy of peripheral modification and skeleton fusion for pyrazolo[3,4-b]pyridine coplanar fused insensitive high-energy materials

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1 Experimental section

Synthesis

1.1 Synthesis of *4,6-dichloro-3,5-dinitro-1H-pyrazolo[3,4-b]pyridine*(*2*)

Under ice bath conditions, first add 8 ml of 20% fuming sulfuric acid to the flask, then slowly titrate in 2.5 ml of fuming nitric acid until the acid solu tion is thoroughly mixed. Subsequently, add 4,6-dichloro-1H-pyrazolo[3,4-b]pyrid ine (0.5, 2.66 mmol) in batches. After stirring at room temperature for a perio d, heat to 80 °C and reacted for 2 h. The reaction was quenched with ice wat er, yielding a precipitate. Filtration and drying afforded the white solid compou nd **2** (0.53 g, 72%).^{1}H NMR (d_6-DMSO): δ = 2.50.^{13}C NMR (d_6-DMSO): δ = 149.12,147.95,141.92,141.00,131.04,105.11ppm.IR: ῡ= 3545.52,3231.43,2727.60,1 599.79,1538.27,1275.93,1090.02,835.60,665.77 cm^{-1}. Elemental analysis (EA) of $C_6HCl_2N_5O_4$ (278.01): calcd C, 25.92; H,0.36; N, 25.19 %. Found: C 25.28, H 1.36, N 23.73%.

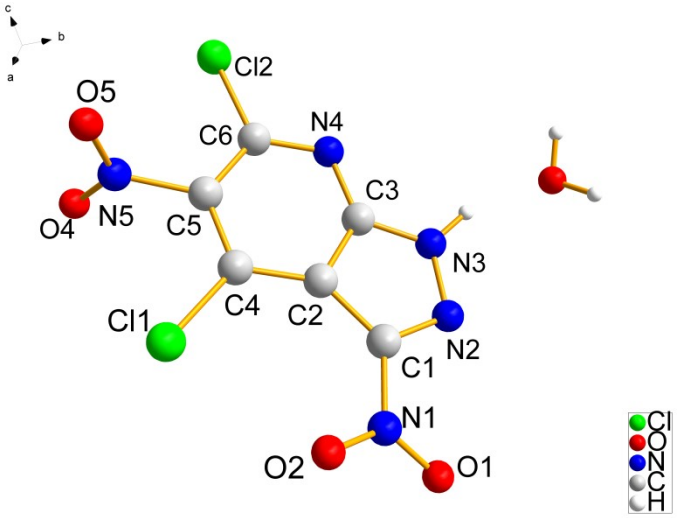


Fig. S1 the X-ray crystal structures of **2·H$_2$O**

1.2 Synthesis of *6-chloro-3,5-dinitro-1H-pyrazolo[3,4-b]pyridin-4-amine*(*3*)

Add 10 ml ethanol and 4,6-dichloro-3,5-dinitro-1H-pyrazolo[3,4-b]pyridine (0.2 g, 0.72 mmol) sequentially to a pressure-resistant flask until completely dis solved, then add 1 ml ammonia solution. Heat the mixture to 80 °C and conti nue the reaction for 2 h. Subsequently, the resulting suspension was cooled to room temperature and quenched with 50 g of ice water. The system was then acidified to pH 1-2 using 15% dilute hydrochloric acid. The precipitate was co

llected to afford the pale yellow solid compound **3** (0.16 g, 87%).^{1}H NMR (d_6 -DMSO): δ = 15.13 (s, 1H), 8.12 (s, 2H). ^{13}C NMR (d_6-DMSO): δ = 150.47,1 50.25,144.75,144.06,127.29,97.25 ppm. IR: $\tilde{\nu}$= 3434.92,3342.41,2861.24,1634.54,1 583.45,1517.39,1287.75,1181.45,969.38,798.61,780.24,466.14 cm^{-1}. Elemental anal ysis (EA) of $C_6H_3ClN_6O_4$ (258.58): calcd C, 27.87; H, 1.17; N, 32.50%. Foun d: C 27.26, H 1.41, N 31.77 %.

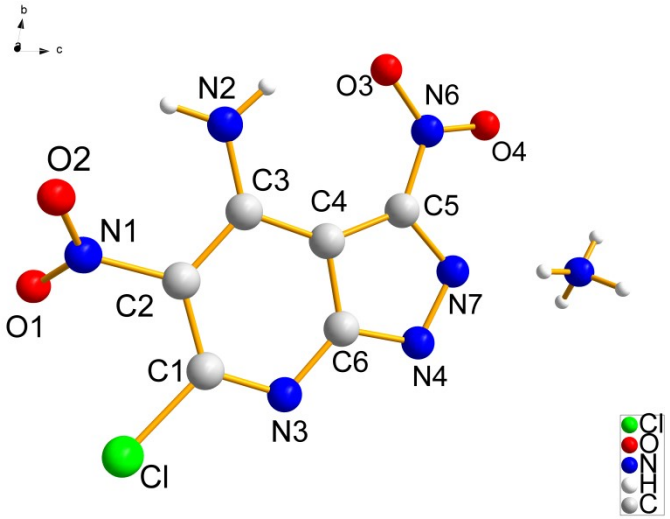


Fig. S2 the X-ray crystal structures of **3·NH$_4^+$**

General methods

^{1}H and ^{13}C NMR spectra were recorded on 600 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometers operating at 600 and 150 MHz, respectively, by using DMSO-d_6 as the solvent and locking solvent unless otherwise stated. Chemical shifts in ^{1}H and ^{13}C spectra are reported relative to DMSO. DSC was performed at a heating rate of 5 °C min^{-1} in closed Al containers with a nitrogen flow of 20 mL min^{-1} on an STD-Q600 instrument. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR equipped with an ATR unit at 25 °C. Impact sensitivities of samples are measured by using the standard BAM methods. The experimental density was determined by helium pycnometry and a Micromeritics AccuPyc II 1340 device at the ambient temperature.

X-ray crystallography

The data were collected with a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. A Kryo-Flex low-temperature device was used to keep the crystals at a constant 298 K during the data collection. The data collection

and the initial unit cell refinement were performed by using APEX2 (v2010.3-0). Data reduction was performed by using SAINT (v7.68A) and XPREP (v2008/2). Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS (v2008/1). The structure was solved and refined with the aid of the programs in the SHELXTL-plus (v2008/4) system of programs. The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included in a riding model. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The nonhydrogen atoms were refined anisotropically. The hydrogen atoms were located and refined.

2 Crystallographic data for 2, 3, CF-1, CF-2 and CF-3

Table S1. Crystal data and details of the structure determination of 2,3 and CF-1

	2·H_2O	3·NH_4^+	CF-1·DMF
CCDC number	2488458	2488457	2486535
Empirical formula	$C_6H_3Cl_2N_5O_5$	$C_6H_6ClN_7O_4$	$C_9H_{12}N_8O_5$
Formula weight	296.03	275.63	312.27
Temperature/K	150	170	173
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	P-1	P-1
a/Å	7.3927(12)	3.7744(18)	5.4535(7)
b/Å	23.237(4)	8.801(4)	10.0932(16)
c/Å	6.1818(10)	15.470(8)	12.545(2)
α/°	90	78.931(15)	74.026(5)
β/°	98.353(6)	87.267(16)	79.421(5)
γ/°	90	83.599(14)	80.912(5)
Volume/Å^3	1050.7(3)	501.0(4)	648.35(17)
Z	4	2	2
ρ_{calc}g/cm^3	1.871	1.827	1.600
μ/mm^{-1}	0.642	0.406	0.133
F(000)	592	280	324
Crystal size/mm^3	0.15 × 0.06 ×	0.12 × 0.06 ×	0.11 × 0.04 ×

	0.05	0.04	0.03
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.57 to 52.818	4.742 to 50.244	4.224 to 52.778
Index ranges	$-9 \le h \le 9$, $-29 \le k \le 29$, $-7 \le l \le 7$	$-4 \le h \le 4$, $-10 \le k \le 10$, $0 \le l \le 18$	-
Reflections collected	8275	1776	2605
Independent reflections	2139 [R_{int} = 0.0926, R_{sigma} = 0.0859]	1776 [R_{int} = ?, R_{sigma} = 0.1579]	2605 [R_{int} = 0, R_{sigma} = 0.2230]
Data/restraints/parameters	2139/0/175	1776/4/175	2605/52/240
Goodness-of-fit on F^2	1.081	1.07	1.094
Final R indexes [I>=2σ (I)]	R_1 = 0.0583, wR_2 = 0.1127	R_1 = 0.1034, wR_2 = 0.2778	R_1 = 0.0751, wR_2 = 0.1723
Final R indexes [all data]	R_1 = 0.1042, wR_2 = 0.1321	R_1 = 0.1793, wR_2 = 0.3381	R_1 = 0.1791, wR_2 = 0.2018
Largest diff. peak/hole / e $Å^{-3}$	0.37/-0.40	0.45/-0.59	0.34/-0.28

Table S2. Crystal data and details of the structure determination of CF-2 and CF-3

	CF-2	4CF-3·3H_2O
CCDC number	2486536	2486537
Empirical formula	$C_6H_3N_9O_4$	$C_{24}H_{26}N_{28}O_{23}$
Formula weight	265.17	1074.73
Temperature/K	170	170
Crystal system	orthorhombic	monoclinic
Space group	Cmce	C2
a/Å	6.3544(6)	19.218(2)
b/Å	25.956(3)	8.1903(8)
c/Å	15.2262(14)	26.295(4)
α/°	90	90
β/°	90	108.828(8)

γ/°	90	90
Volume/Å^3	2511.4(4)	3917.3(9)
Z	8	4
ρ_{calc}g/cm^3	1.403	1.822
μ/mm^{-1}	1.056	1.431
F(000)	1072	2200
Crystal size/mm^3	0.11 × 0.03 × 0.02	0.12 × 0.03 × 0.02
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.952 to 127.342	3.55 to 127.51
Index ranges	-7 ≤ h ≤ 7, -29 ≤ k ≤ 29, -16 ≤ l ≤ 17	-19 ≤ h ≤ 22, -8 ≤ k ≤ 9, -30 ≤ l ≤ 30
Reflections collected	6702	13253
Independent reflections	1121 [R_{int} = 0.0818, R_{sigma} = 0.0491]	5065 [R_{int} = 0.1092, R_{sigma} = 0.1266]
Data/restraints/parameters	1121/0/115	5065/1/724
Goodness-of-fit on F^2	1.093	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0989, wR_2 = 0.2670	R_1 = 0.0893, wR_2 = 0.2003
Final R indexes [all data]	R_1 = 0.1133, wR_2 = 0.2799	R_1 = 0.1256, wR_2 = 0.2219
Largest diff. peak/hole / e Å^{-3}	0.42/-0.47	0.38/-0.38

Table S3. Bond Lengths for **2·H_2O**

Atom-Atom	Length/Å	Atom-Atom	Length/Å
C12-C6	1.715(4)	N1-C1	1.439(5)
C11-C4	1.698(4)	N3-N2	1.332(5)
O1-N1	1.235(4)	N3-C3	1.355(5)
O4-N5	1.213(4)	N2-C1	1.314(5)
O2-N1	1.229(4)	C5-C6	1.396(6)
N5-O5	1.215(4)	C5-C4	1.370(5)
N5-C5	1.482(4)	C3-C2	1.402(6)

N4-C3	1.340(5)	C2-C1	1.421(5)
N4-C6	1.323(5)	C2-C4	1.413(5)

Table S4. Bond Angles for **2·H_2O**

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
O4-N5-O5	125.8(3)	N3-C3-C2	107.4(4)
O4-N5-C5	117.7(3)	C3-C2-C1	102.4(3)
O5-N5-C5	116.5(3)	C3-C2-C4	116.2(4)
C6-N4-C3	114.2(3)	C4-C2-C1	141.3(4)
O1-N1-C1	117.9(3)	N4-C6-C12	117.3(3)
O2-N1-O1	124.6(4)	N4-C6-C5	122.9(4)
O2-N1-C1	117.5(3)	C5-C6-C12	119.9(3)
N2-N3-C3	111.9(3)	N2-C1-N1	117.9(3)
C1-N2-N3	106.0(3)	N2-C1-C2	112.4(4)
C6-C5-N5	118.3(3)	C2-C1-N1	129.8(3)
C4-C5-N5	118.8(4)	C5-C4-C11	120.0(3)
C4-C5-C6	122.9(3)	C5-C4-C2	115.8(4)
N4-C3-N3	124.7(4)	C2-C4-C11	124.2(3)
N4-C3-C2	128.0(3)		

Table S5. Bond Lengths for **3·$NH4^+$**

Atom-Atom	Length/Å	Atom-Atom	Length/Å
C11-C1	1.713(11)	N3-C6	1.367(12)
O4-N6	1.233(10)	N3-C1	1.298(13)
O3-N6	1.235(10)	N1-C2	1.471(13)
N6-C5	1.413(12)	N2-C3	1.347(12)
O2-N1	1.224(11)	C6-C4	1.403(12)
N7-N4	1.329(11)	C4-C5	1.405(13)
N7-C5	1.351(12)	C4-C3	1.414(13)
O1-N1	1.226(12)	C2-C1	1.406(14)
N4-C6	1.346(12)	C2-C3	1.410(14)

Table S6. Bond Angles for **3·$NH4^+$**

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
O4-N6-O3	122.8(8)	C5-C4-C3	140.9(9)
O4-N6-C5	119.0(8)	N7-C5-N6	116.7(8)
O3-N6-C5	118.3(8)	N7-C5-C4	111.7(8)
N4-N7-C5	107.5(8)	C4-C5-N6	131.5(9)
N7-N4-C6	108.5(7)	C1-C2-N1	120.1(9)
C1-N3-C6	115.2(8)	C1-C2-C3	122.8(9)
O2-N1-O1	124.5(9)	C3-C2-N1	117.0(8)
O2-N1-C2	117.4(9)	N3-C1-C11	117.3(8)
O1-N1-C2	118.1(9)	N3-C1-C2	123.3(9)
N4-C6-N3	122.3(8)	C2-C1-C11	119.4(8)
N4-C6-C4	111.4(8)	N2-C3-C4	121.4(9)
N3-C6-C4	126.2(8)	N2-C3-C2	124.7(9)
C6-C4-C5	100.7(8)	C2-C3-C4	113.8(8)
C6-C4-C3	118.4(9)		

Table S7. Bond Lengths for **CF-1·DMF**

Atom-Atom	Length/Å	Atom-Atom	Length/Å
O3-N4	1.236(4)	N8-C9	1.472(10)
O2-N2	1.246(4)	N8-C7	1.462(9)
O4-N4	1.222(4)	N8-C10	1.472(10)
N7-C5	1.330(5)	N4-C6	1.443(5)
N7-C1	1.335(5)	N2-C2	1.428(5)
O1-N2	1.236(4)	N5-C6	1.320(5)
N3-C3	1.325(4)	C5-C4	1.415(4)
N1-C1	1.326(5)	C3-C4	1.422(5)
N6-N5	1.347(4)	C3-C2	1.432(5)
N6-C5	1.356(5)	C6-C4	1.415(5)
N8-C11	1.277(8)	C1-C2	1.461(5)
N8-C12	1.329(9)	C11-O6	1.21(2)
N8-C8	1.401(9)	C12-O5	1.25(2)

Table S8. Bond Angles for **CF-2·DMF**

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°

C5-N7-C1	115.5(3)	N3-C3-C4	120.2(3)
N5-N6-C5	113.0(3)	N3-C3-C2	124.7(3)
C11-N8-C9	123.2(6)	C4-C3-C2	115.0(3)
C11-N8-C7	120.7(6)	N5-C6-N4	115.5(4)
C12-N8-C8	123.9(6)	N5-C6-C4	113.7(3)
C12-N8-C10	119.4(6)	C4-C6-N4	130.8(3)
C8-N8-C10	116.7(6)	C5-C4-C3	117.0(3)
C7-N8-C9	114.2(6)	C5-C4-C6	102.3(3)
O3-N4-C6	117.6(3)	C6-C4-C3	140.7(3)
O4-N4-O3	123.0(3)	N7-C1-C2	121.5(3)
O4-N4-C6	119.4(3)	N1-C1-N7	114.8(3)
O2-N2-C2	119.7(3)	N1-C1-C2	123.8(4)
O1-N2-O2	119.6(3)	N2-C2-C3	119.2(3)
O1-N2-C2	120.7(3)	N2-C2-C1	119.0(3)
C6-N5-N6	104.3(3)	C3-C2-C1	121.8(3)
N7-C5-N6	124.0(3)	O6-C11-N8	126.1(12)
N7-C5-C4	129.3(4)	O5-C12-N8	125.4(12)
N6-C5-C4	106.7(3)		

Table S9. Bond Lengths for **CF-2**

Atom-Atom	Length/Å	Atom-Atom	Length/Å
O3-N3	1.252(8)	N8-C2	1.353(11)
N9-N5	1.375(9)	N3-C6	1.397(10)
N9-C3	1.389(10)	N4-C5	1.339(10)
N9-C5	1.333(10)	O2-N1	1.200(9)
O4-N3	1.242(8)	N1-C2	1.419(11)
N5-N6	1.326(9)	C1-C4	1.452(11)
O1-N1	1.222(9)	C1-C3	1.359(11)
N7-N8	1.362(10)	C1-C2	1.441(12)
N7-C3	1.346(11)	C4-C6	1.442(11)
N2-C4	1.310(11)	C5-C6	1.432(12)

N6-N4	1.372(9)		

Table S10. Bond Angles for **CF-2**

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
N5-N9-C3	126.0(7)	C2-C1-C4	136.6(7)
C5-N9-N5	110.1(6)	N2-C4-C1	122.1(7)
C5-N9-C3	123.9(7)	N2-C4-C6	124.1(8)
N6-N5-N9	103.7(6)	C6-C4-C1	113.8(7)
C3-N7-N8	102.7(6)	N7-C3-N9	124.1(7)
N5-N6-N4	112.4(6)	N7-C3-C1	117.8(7)
C2-N8-N7	110.6(6)	C1-C3-N9	118.1(7)
O3-N3-C6	118.5(6)	N8-C2-N1	118.0(8)
O4-N3-O3	121.6(7)	N8-C2-C1	109.5(7)
O4-N3-C6	119.9(7)	N1-C2-C1	132.4(8)
C5-N4-N6	104.8(6)	N9-C5-N4	109.0(7)
O1-N1-C2	119.1(8)	N9-C5-C6	118.8(7)
O2-N1-O1	121.4(7)	N4-C5-C6	132.2(7)
O2-N1-C2	119.4(7)	N3-C6-C4	121.1(7)

C3-C1-C4	124.0(7)	N3-C6-C5	117.5(7)
C3-C1-C2	99.3(7)	C5-C6-C4	121.4(7)

Table S11. Bond Lengths for **4CF-3·3H$_2$O**

Atom-Atom	Length/Å	Atom-Atom	Length/Å
O49-N40	1.393(11)	N28-O29	1.239(15)
N40-C41	1.365(13)	N28-C26	1.433(15)
N40-C39	1.348(14)	O69-N68	1.253(16)
N21-O36	1.377(11)	N16-C3	1.386(15)
N21-C20	1.360(14)	N16-O17	1.280(15)
N21-C22	1.356(15)	C20-N19	1.351(15)
O18-N16	1.240(14)	C20-C25	1.361(15)
O53-N51	1.238(13)	N8-C9	1.343(16)
O72-N55	1.390(12)	C45-C44	1.419(15)
O14-N5	1.386(12)	C45-C37	1.428(15)
N42-C41	1.340(14)	C3-C2	1.449(15)
N42-N43	1.375(13)	C3-C4	1.456(16)
N1-C2	1.331(14)	N61-O63	1.237(16)
N54-C37	1.296(15)	N61-C58	1.457(17)
O52-N51	1.243(12)	C56-C57	1.418(15)
N5-C6	1.371(13)	C10-C2	1.394(15)
N5-C4	1.318(15)	C10-C6	1.405(15)
N71-C64	1.317(15)	C10-C9	1.437(15)
O34-N32	1.226(13)	N50-C39	1.343(14)
N55-C56	1.341(14)	N19-N27	1.357(13)
N55-C66	1.335(16)	N51-C38	1.408(14)
N7-N8	1.362(14)	C57-C58	1.438(16)
N7-C6	1.306(15)	C57-C64	1.422(16)
N31-C24	1.349(14)	N27-C26	1.327(16)
N60-C56	1.317(15)	N43-C44	1.337(16)
N60-N59	1.367(15)	N15-C4	1.369(15)

O48-N46	1.240(15)	C65-N68	1.419(16)
O30-N28	1.235(14)	C65-C66	1.443(17)
C41-C45	1.379(15)	C65-C64	1.437(16)
O47-N46	1.242(14)	C24-C25	1.432(16)
N11-O12	1.216(16)	N59-C58	1.314(16)
N11-C9	1.419(16)	C38-C37	1.453(14)
N11-O13	1.261(15)	C38-C39	1.414(15)
O62-N61	1.187(16)	N46-C44	1.429(15)
O33-N32	1.236(14)	N68-O70	1.245(15)
N32-C23	1.436(15)	C25-C26	1.430(16)
C23-C24	1.417(15)	N35-C22	1.318(14)
C23-C22	1.432(15)	N67-C66	1.321(16)

Table S12. Bond Angles for **4CF-3·3H_2O**

Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
C41-N40-O49	119.6(8)	C20-N19-N27	107.6(9)
C39-N40-O49	119.5(8)	O53-N51-O52	119.7(9)
C39-N40-C41	120.8(9)	O53-N51-C38	119.9(9)
C20-N21-O36	120.3(9)	O52-N51-C38	120.4(10)
C22-N21-O36	117.7(8)	C56-C57-C58	99.9(9)
C22-N21-C20	121.1(9)	C56-C57-C64	119.0(9)
C41-N42-N43	107.3(9)	C64-C57-C58	141.0(11)
C6-N5-O14	118.4(9)	C26-N27-N19	106.8(9)
C4-N5-O14	119.1(9)	C44-N43-N42	106.1(8)
C4-N5-C6	121.6(10)	N68-C65-C66	117.7(10)
C56-N55-O72	118.8(9)	N68-C65-C64	118.8(11)
C66-N55-O72	117.9(9)	C64-C65-C66	123.5(10)
C66-N55-C56	122.8(10)	N31-C24-C23	124.0(10)
C6-N7-N8	109.0(10)	N31-C24-C25	120.0(10)
C56-N60-N59	109.4(10)	C23-C24-C25	115.9(10)
N40-C41-C45	122.2(9)	C58-N59-N60	106.9(9)
N42-C41-N40	124.3(9)	N5-C4-C3	119.5(9)
N42-C41-C45	113.5(9)	N5-C4-N15	116.2(11)

O12-N11-C9	121.3(11)	N15-C4-C3	124.3(11)
O12-N11-O13	123.6(12)	N51-C38-C37	119.4(10)
O13-N11-C9	115.1(13)	N51-C38-C39	118.5(9)
O34-N32-O33	121.4(11)	C39-C38-C37	122.1(9)
034-N32-C23	119.4(10)	048-N46-O47	123.5(10)
033-N32-C23	119.3(9)	048-N46-C44	117.6(10)
C24-C23-N32	119.9(10)	047-N46-C44	118.9(12)
C24-C23-C22	122.1(10)	069-N68-C65	118.5(11)
C22-C23-N32	117.9(9)	070-N68-O69	120.9(11)
O30-N28-O29	123.1(11)	070-N68-C65	120.5(12)
O30-N28-C26	117.2(12)	C45-C44-N46	131.0(11)
O29-N28-C26	119.4(11)	N43-C44-C45	113.0(10)
O18-N16-C3	120.1(10)	N43-C44-N46	115.9(10)
O18-N16-O17	119.2(11)	C20-C25-C24	119.9(10)
O17-N16-C3	120.8(11)	C20-C25-C26	100.6(10)
N21-C20-C25	123.0(11)	C26-C25-C24	139.4(10)
N19-C20-N21	124.2(10)	N11-C9-C10	129.0(11)
N19-C20-C25	112.8(10)	N8-C9-N11	118.8(11)
C9-N8-N7	106.3(10)	N8-C9-C10	112.1(10)
C41-C45-C44	100.1(9)	C57-C58-N61	128.9(11)
C41-C45-C37	121.1(9)	N59-C58-N61	118.8(11)
C44-C45-C37	138.8(11)	N59-C58-C57	112.4(11)
N16-C3-C2	120.8(10)	N21-C22-C23	117.8(9)
N16-C3-C4	119.2(9)	N35-C22-N21	116.2(10)
C2-C3-C4	120.0(10)	N35-C22-C23	126.0(10)
O62-N61-O63	126.2(13)	N54-C37-C45	122.5(10)
O62-N61-C58	119.6(11)	N54-C37-C38	123.3(10)
O63-N61-C58	114.2(13)	C45-C37-C38	114.1(10)
N55-C56-C57	122.8(10)	N55-C66-C65	116.8(10)
N60-C56-N55	125.8(10)	N67-C66-N55	117.0(12)
N60-C56-C57	111.3(10)	N67-C66-C65	126.2(12)
C2-C10-C6	120.2(9)	N27-C26-N28	117.9(11)

C2-C10-C9	140.6(10)	N27-C26-C25	112.2(10)
C6-C10-C9	99.2(9)	C25-C26-N28	129.8(12)
N1-C2-C3	121.8(11)	N71-C64-C57	119.7(10)
N1-C2-C10	121.4(10)	N71-C64-C65	125.3(10)
C10-C2-C3	116.8(10)	C57-C64-C65	114.9(10)
N5-C6-C10	122.0(10)	N40-C39-C38	119.2(9)
N7-C6-N5	124.6(10)	N50-C39-N40	113.8(10)
N7-C6-C10	113.4(9)	N50-C39-C38	126.9(10)

3 Theoretical study

Theoretical calculations were performed by using the Gaussian 09 (Revision D.01) suite of programs.[1] The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP) functional with the 6-311G** basis set.[2] All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. Atomization energies were calculated by the CBS-4M.[3] All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.[4]

The predictions of heat of formation (*HOF*) adopt the hybrid DFT-B3LYP methods with 6-311G** basis set 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 the title 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 $\sum \Delta_f H_P$ and $\sum \Delta_f H_R$ 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 ΔE_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 $\Delta(nRT)$ for the reactions of ideal gas. For the

isodesmic reaction, Δn = 0, so Δ(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 is available from the experiments. The heat of sublimation can be estimated following the Trouton's rule: ΔH_{sub}=188/J mol^{-1}K^{-1}*T*. *T* represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition.[5] The isosteric reaction schemes for target products **CF-1, CF-2**, and **CF-3** are shown in Fig S3:

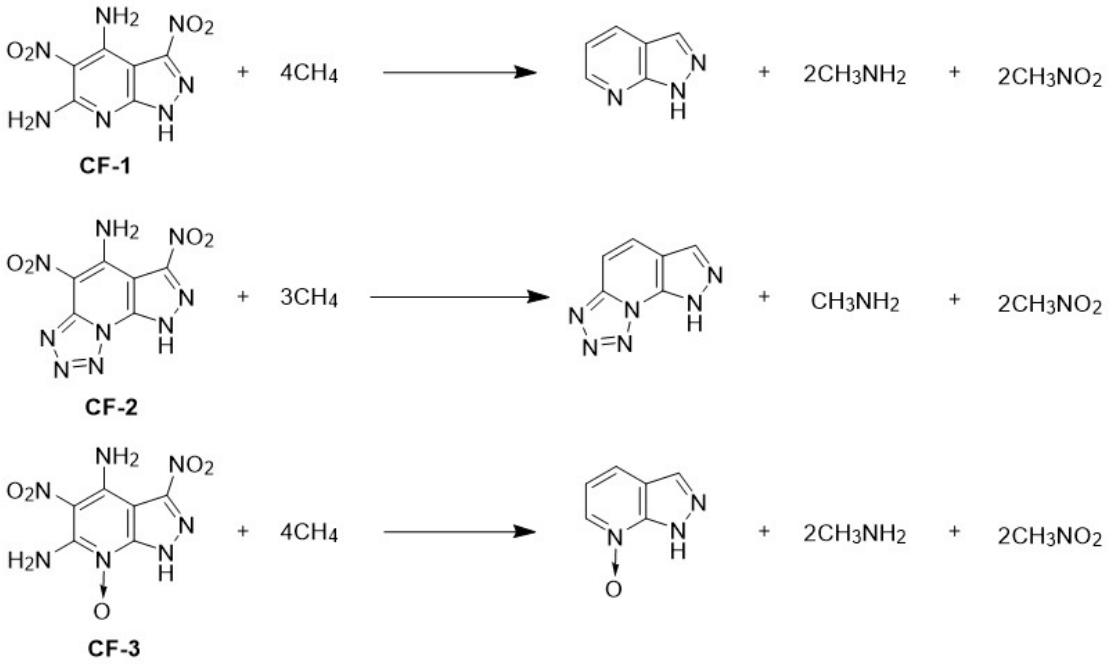
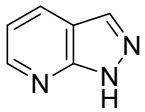
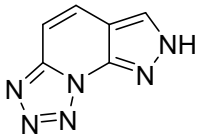


Fig. S3 Isodesmic reactions for **CF-1**, **CF-2** and **CF-3**

Table S13. Calculated zero-point energy (ZPE), values of the correction (H_T), total energy (E_0) and gas-state heats of formation (ΔH_f).

Compound	ZPE (a.u.)	H_T (a.u.)	E_0 (a.u.)	Corrected E_0 (a.u.)	ΔH_f (kJ mol^{-1})
CH_4	0.044572	10.008406	-40.489173	-40.445492	-74.6
CH_3NH_2	0.063810	11.436678	-95.824629	-95.762095	-23.5
CH_3NO_2	0.049661	11.599459	-245.032025	-244.983357	-81.0
	0.106437	17.900659	-395.875263	-395.770954	334.7
	0.111292	22.006941	-559.495456	-559.386389	632.0

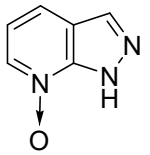
	0.110380	20.344999	-471.049166	-470.940993	348.2
CF-1	0.143217	37.500016	-915.699569	-915.559216	229.3
CF-2	0.132390	38.920412	-1023.945928	-1023.816186	584.2
CF-3	0.146339	38.195774	-990.862808	-990.719395	267.0

Table S14. The gas-phase heats of formation (ΔH_f), sublimation enthalpies (ΔH_{sub}) and solid-phase heat of formation ($\Delta H_{f,s}^{298}$) for target energetic materials.

Compound	ΔH_f (kJ mol^{-1})	ΔH_{sub} (kJ mol^{-1})	$\Delta H_{f,s}^{298}$ (kJ mol^{-1})
CF-1	229.3	109.4	119.9
CF-2	584.2	93.5	490.7
CF-3	267.0	94.6	172.4

4 References

[1] Frisch MJ, Trucks GW, Schlegel HB, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ. Gaussian 09, Revision D. 01, Gaussian. Inc. Wallingford CT, 2009.

[2] Hariharan PC, Pople JA, Influence of polarization functions on MO hydrogenation energies, Theor Chim Acta. 1973; 28, 3, 213-222.

[3] Ochterski JW, Petersson GA, Montgomery JA, Lattice dynamics and hyperfine interactions of $C_{60}Fe(CO)_4$, J Chem Phys. 1996; 104, 7, 2598-2619.

[4] Jenkins HDB, Tudeal D, Glasser L, Lattice potential energy estimation for complex ionic salts from density measurements, Inorg Chem. 2002; 41, 9, 2364-2367.

[5] (a) F. Trouton Philos. Mag., 1884, 18, 54 -57. (b) P. Atkins Physical Chemistry, Oxford University Press, 1978.

5 ^{1}H and ^{13}C NMR spectra of 2, 3, CF-1, CF-2 and CF-3

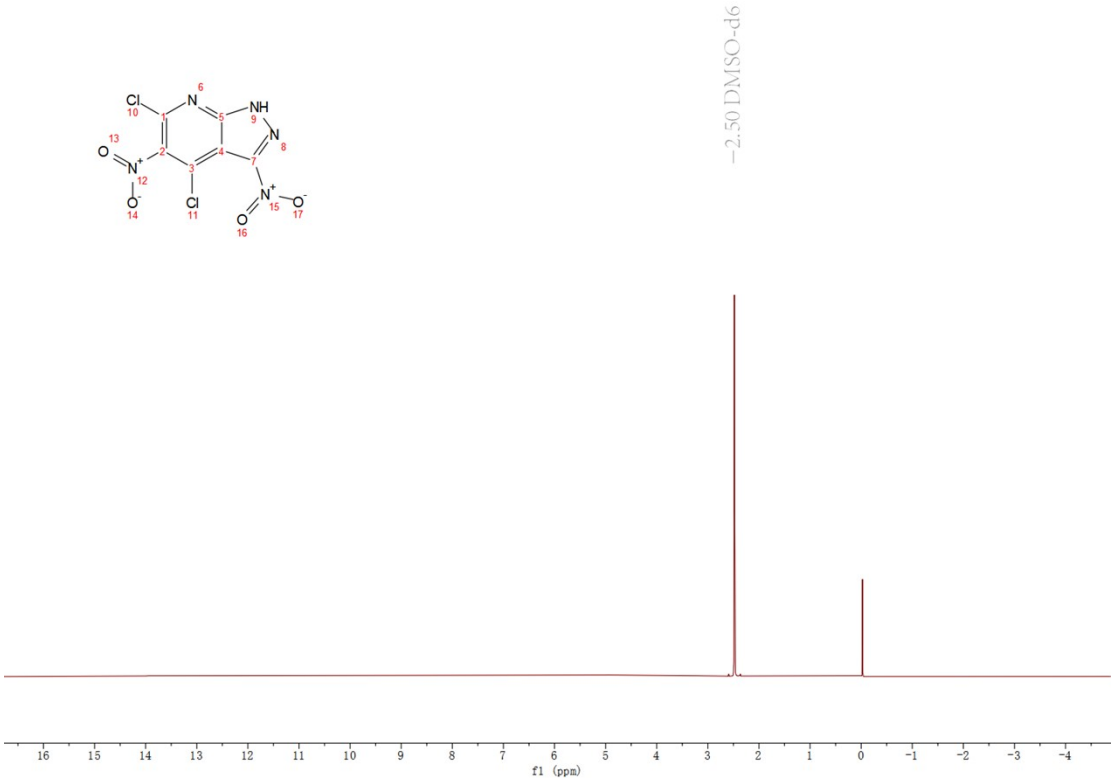


Fig. S4 ^{1}H NMR of **2** (DMSO-d_6)

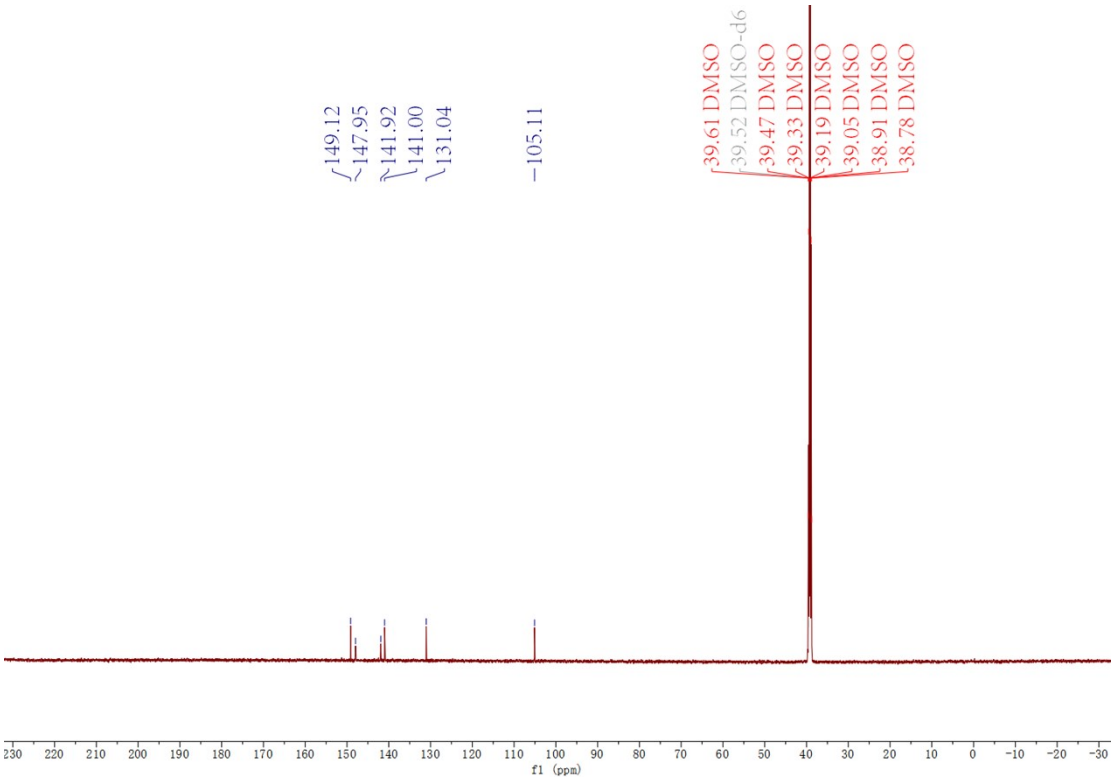


Fig. S5 ^{13}C NMR of **2** (DMSO-d_6)

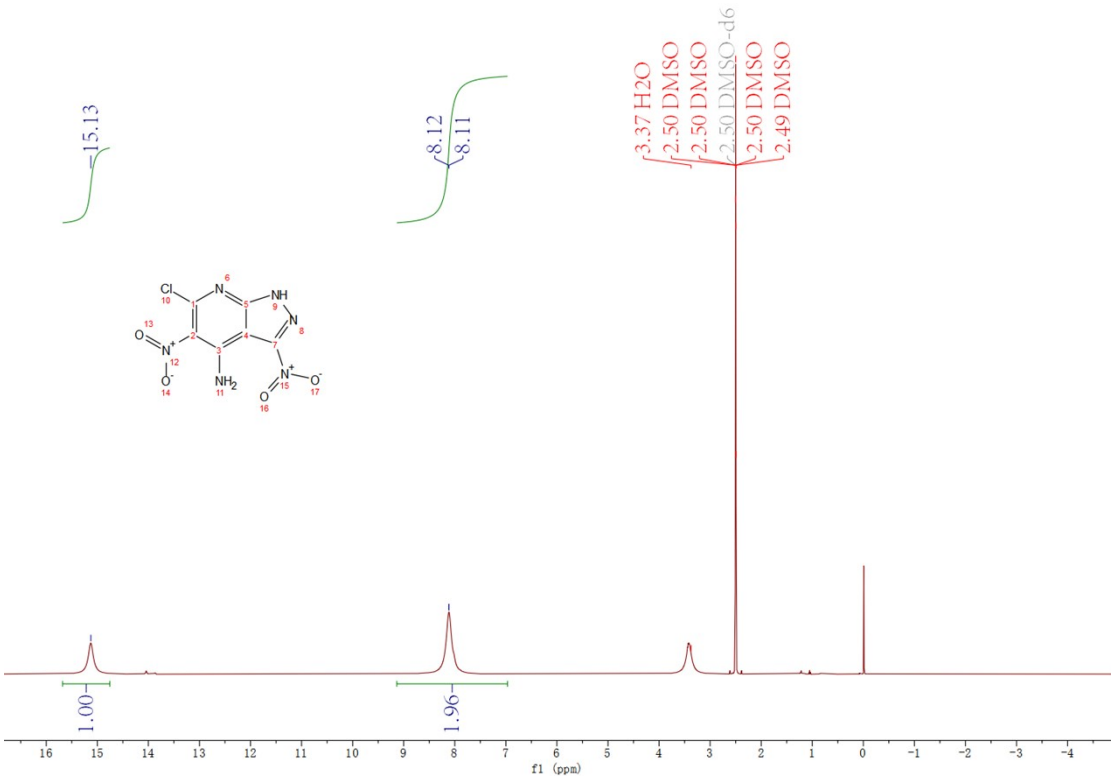


Fig. S6 ^{1}H NMR of **3** (DMSO-d_6)

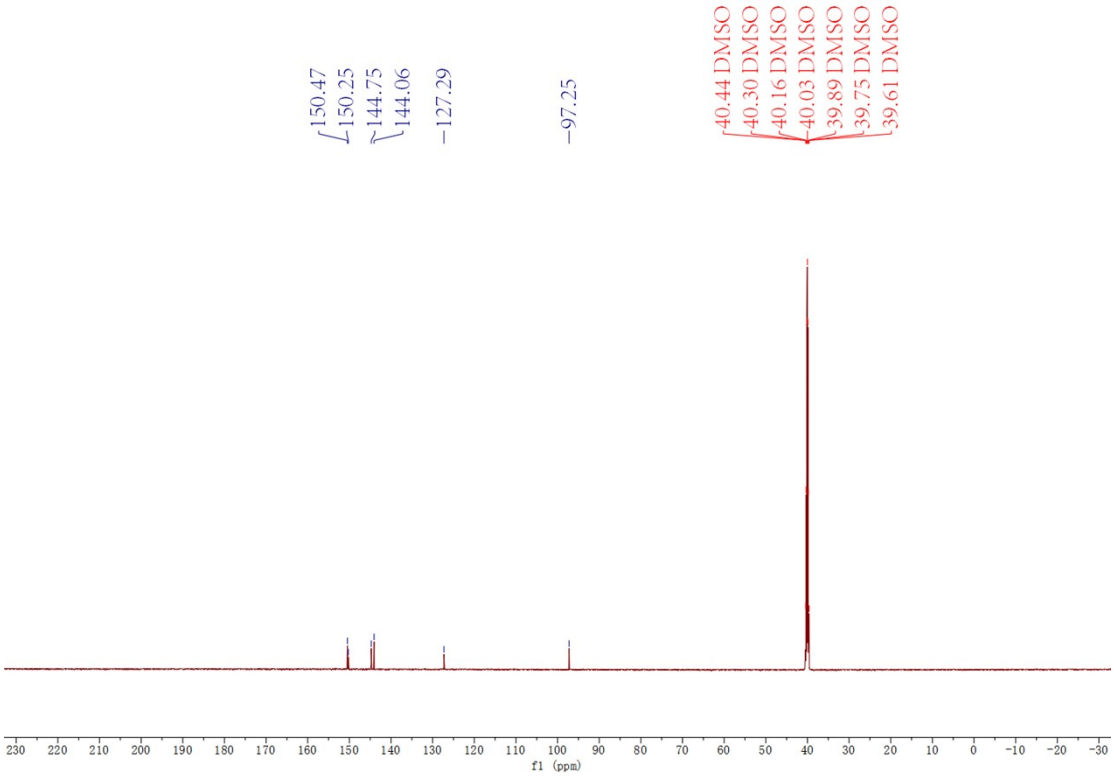


Fig. S7 ^{13}C NMR of **3** (DMSO-d_6)

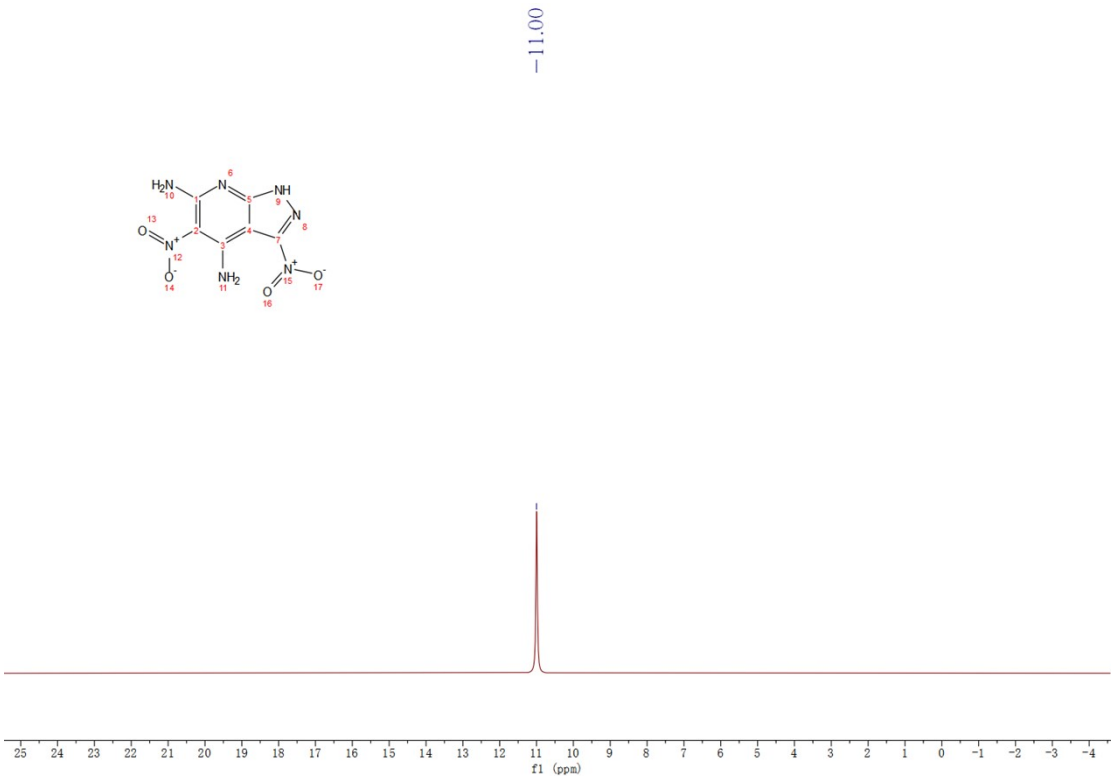


Fig. S8 ^{1}H NMR of **CF-1** (D_2SO_4)

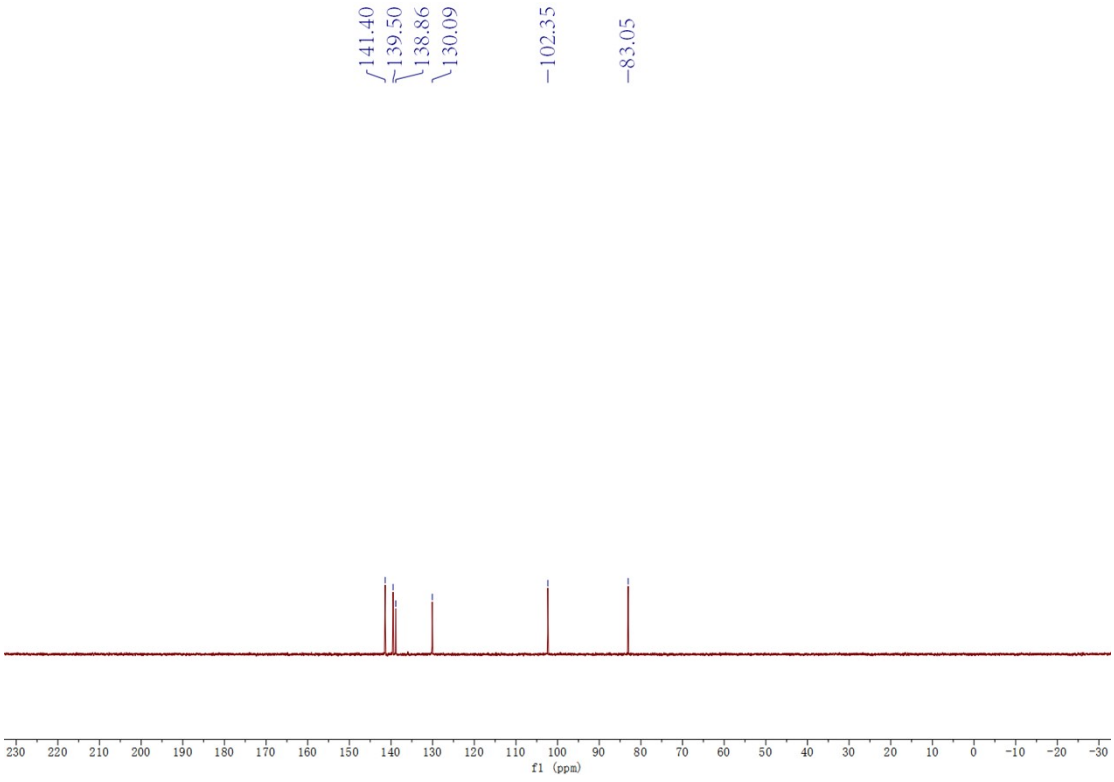


Fig. S9 ^{13}C NMR of **CF-1** (D_2SO_4)

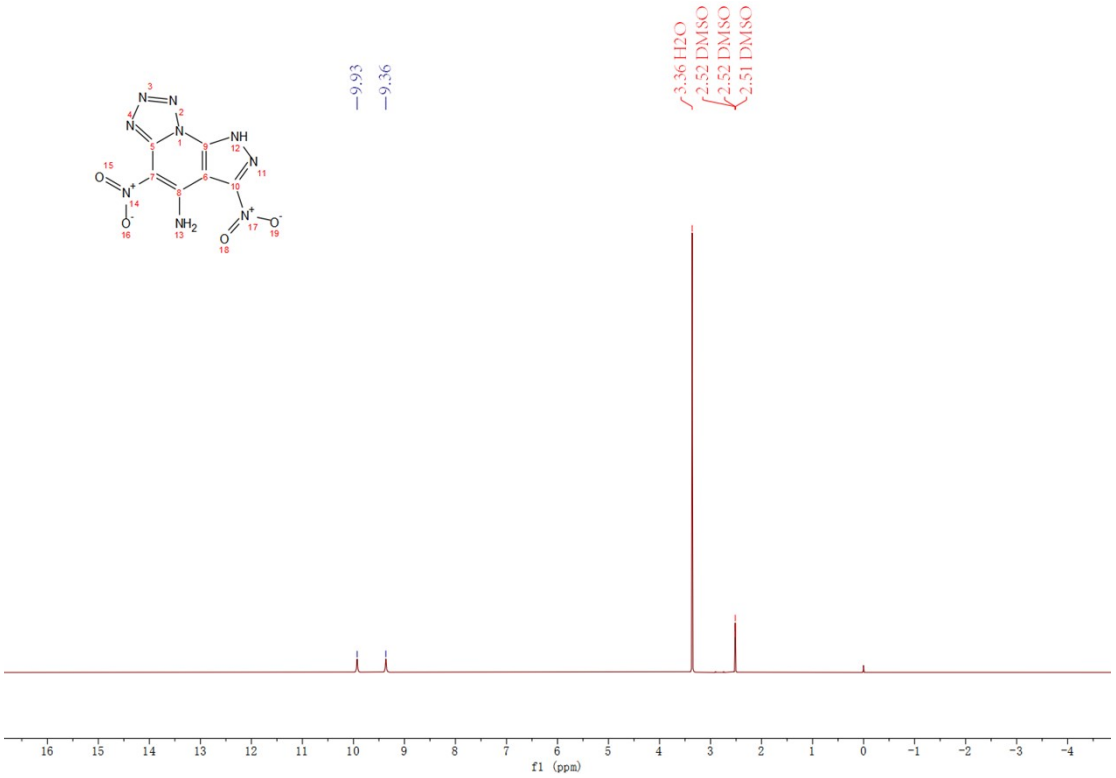


Fig. S10 ^{1}H NMR of **CF-2** (DMSO-d_6)

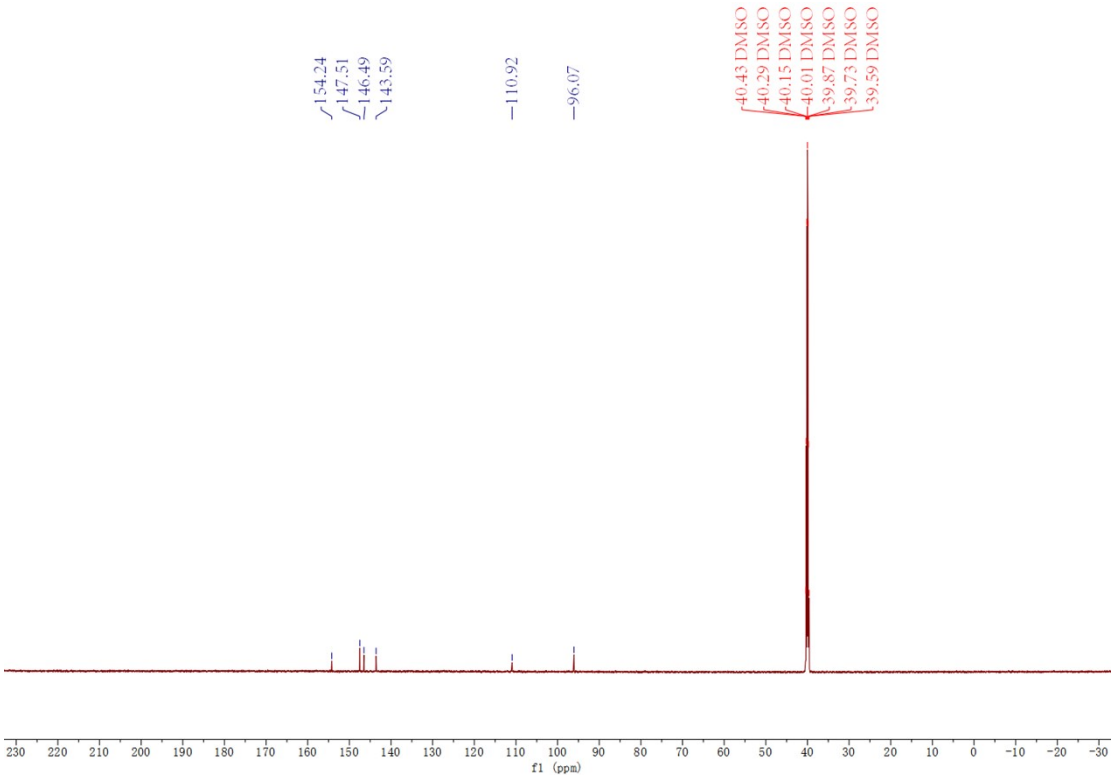


Fig. S11 ^{13}C NMR of **CF-2** (DMSO-d_6)

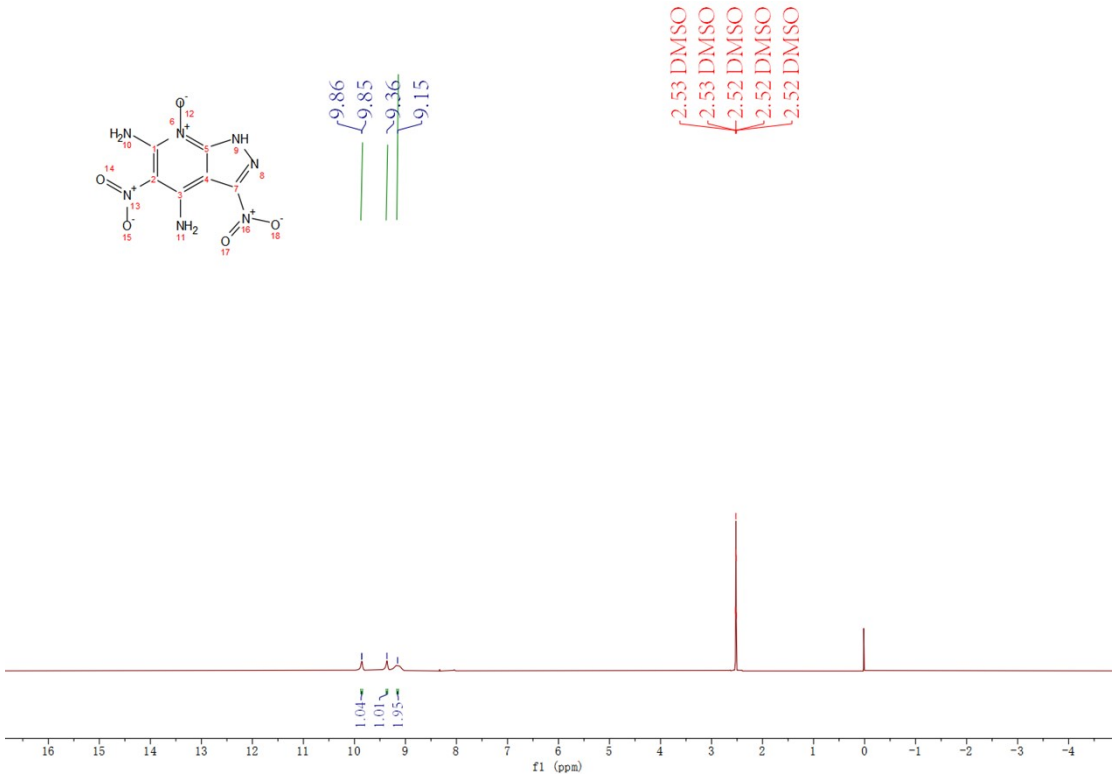


Fig. S12 ^{1}H NMR of **CF-3** (DMSO-d_6)

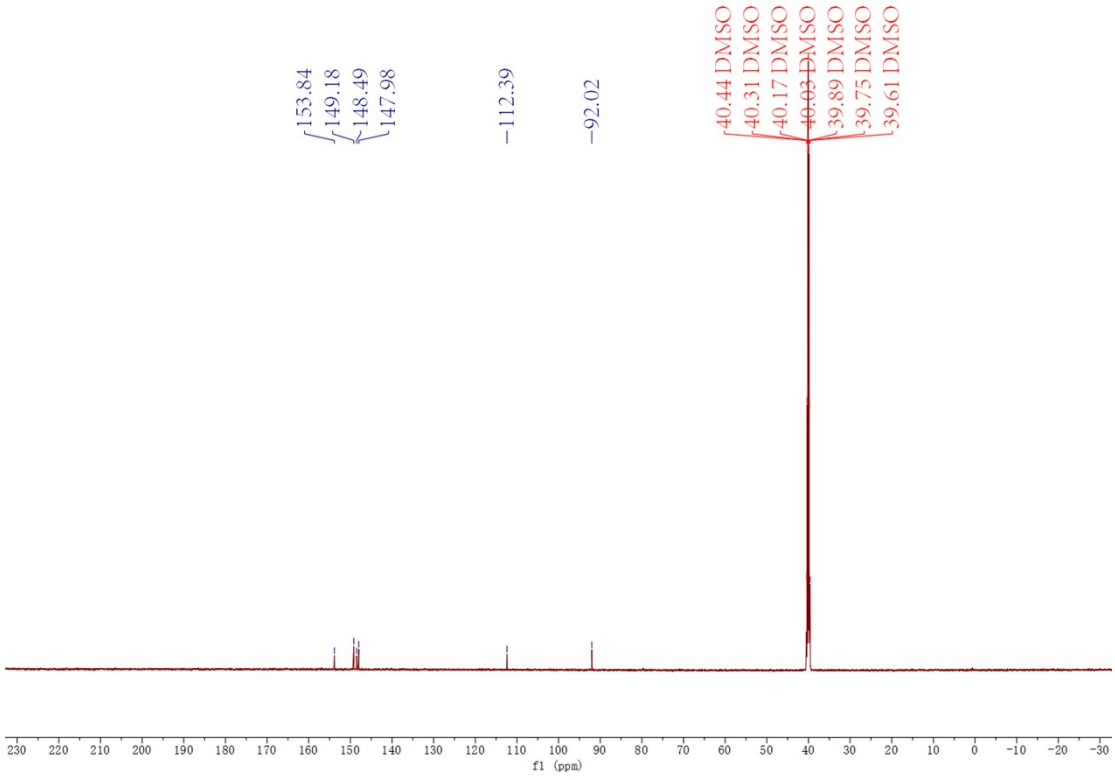


Fig. S13 ^{13}C NMR of **CF-3** (DMSO-d_6)

6 FT-IR spectra of 2, 3, CF-1, CF-2 and CF-3

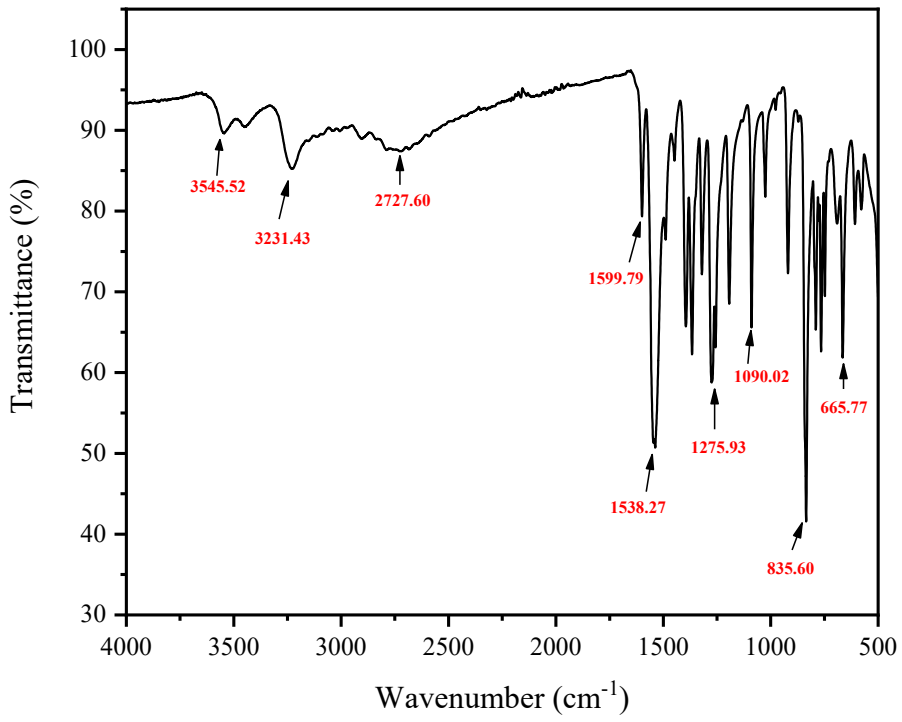


Fig. S14 FT-IR of **2**

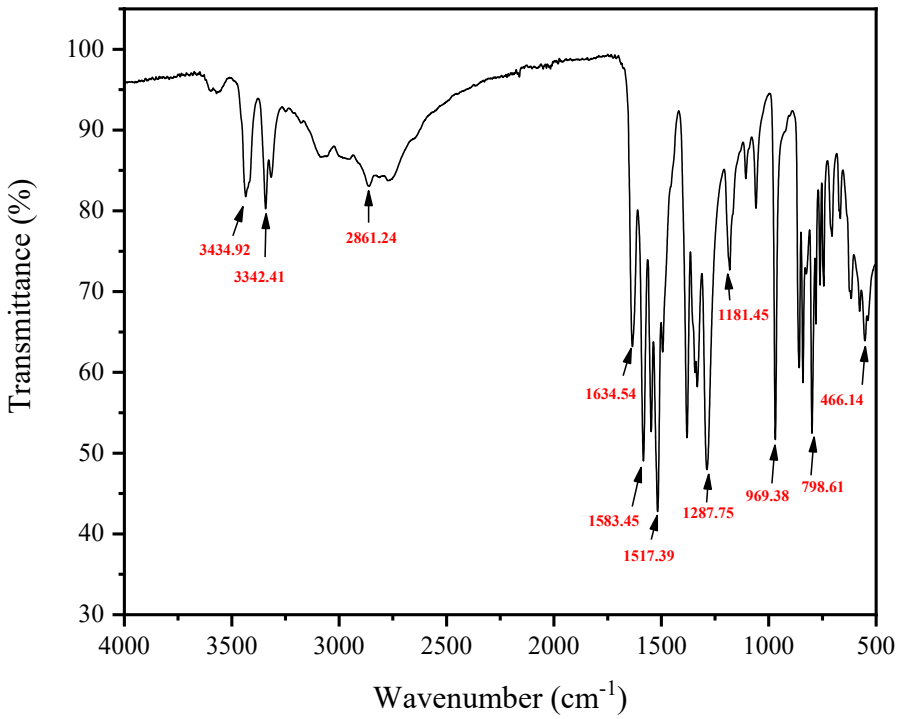


Fig. S15 FT-IR of **3**

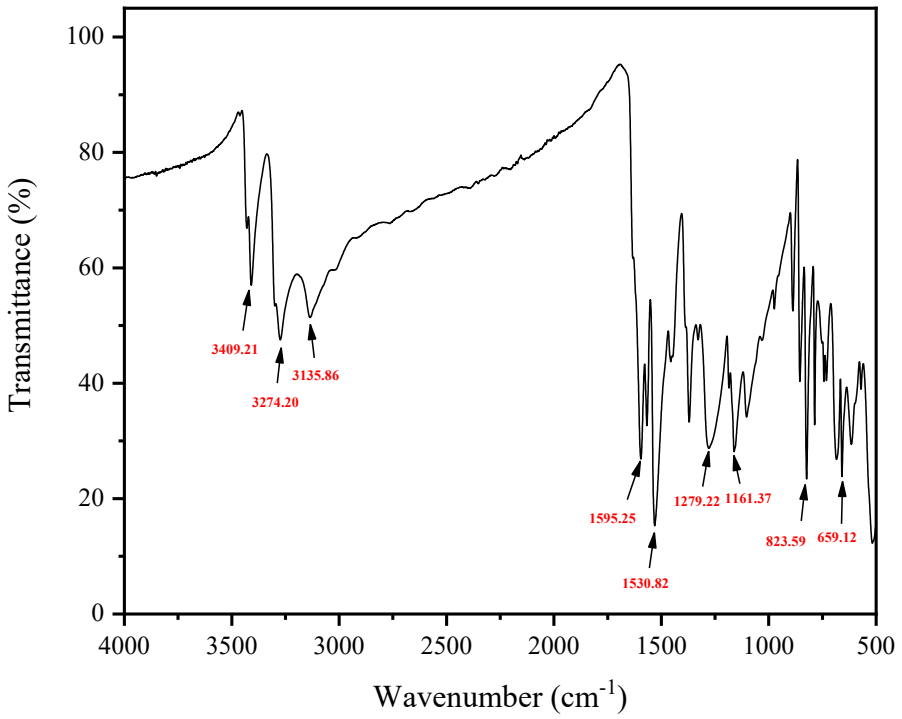


Fig. S16 FT-IR of **CF-1**

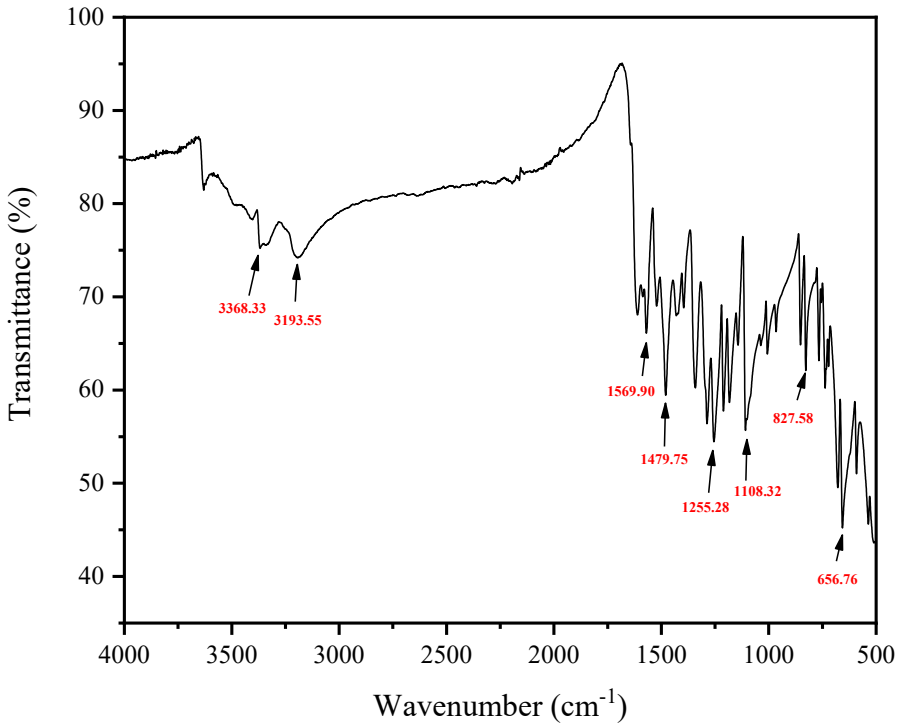


Fig. S17 FT-IR of **CF-2**

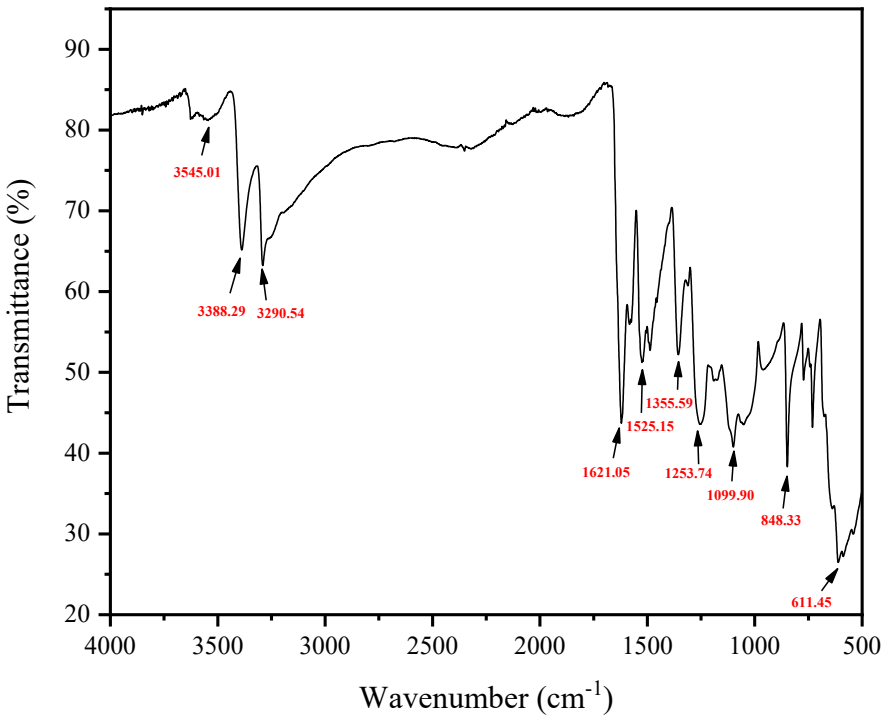


Fig. S18 FT-IR of **CF-3**

7 TG-DSC curves of CF-1, CF-2 and CF-3

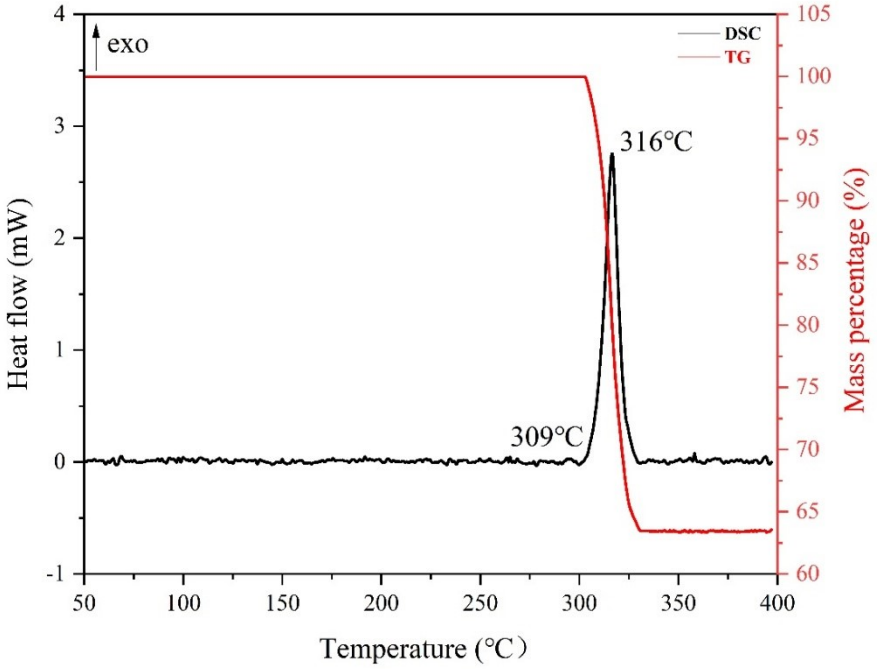


Fig. S19 TG-DSC curves of CF-1

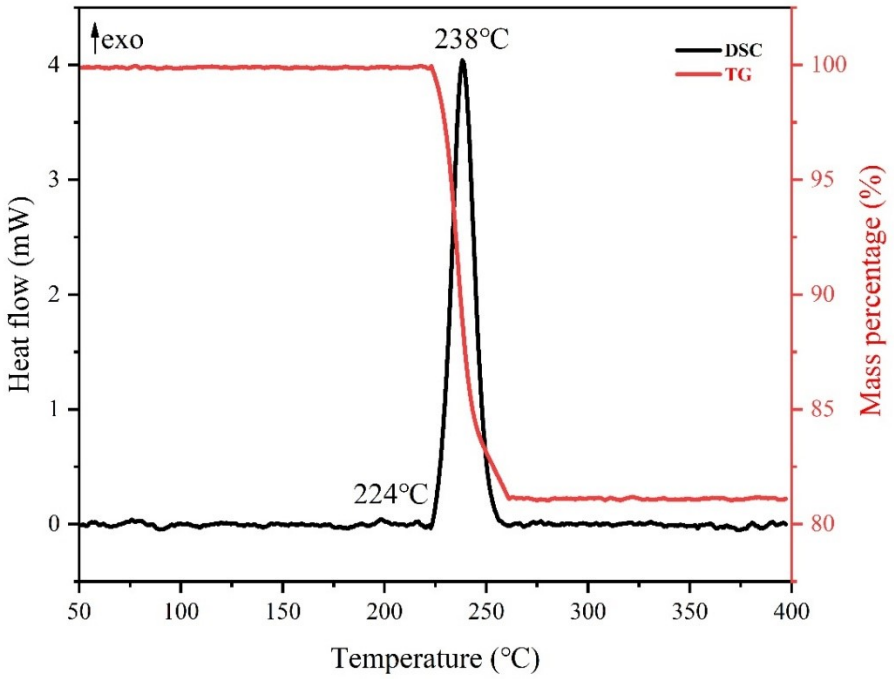


Fig. S20 TG-DSC curves of CF-2

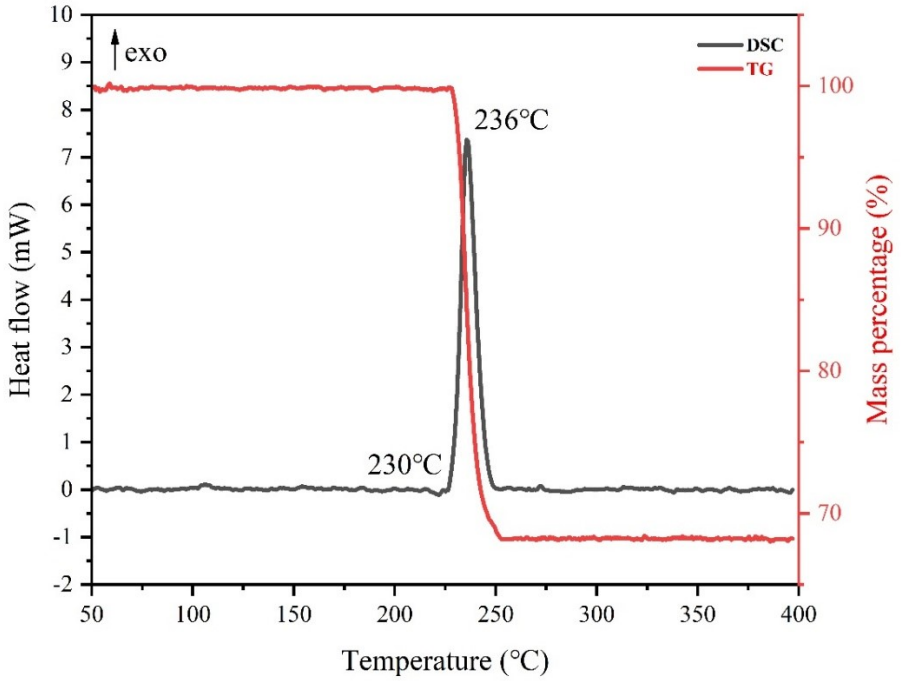


Fig. S21 TG-DSC curves of CF-3

8 PH values of CF-1, CF-2 and CF-3

Take 50 mg of compounds CF-1, CF-2 and CF-3 separately, dissolve and disperse them in 10 ml of distilled water, and measure the pH value using a desktop pH meter model FE28-Standard.

Table S15. PH values of **CF-1, CF-2 and CF-3**

Materials	distilled water	CF-1	CF-2	CF-3
PH values	6.56	6.72	9.15	6.37

9 Mass spectrometry data of CF-1, CF-2 and CF-3

The solvent used in HRMS is dimethyl sulfoxide

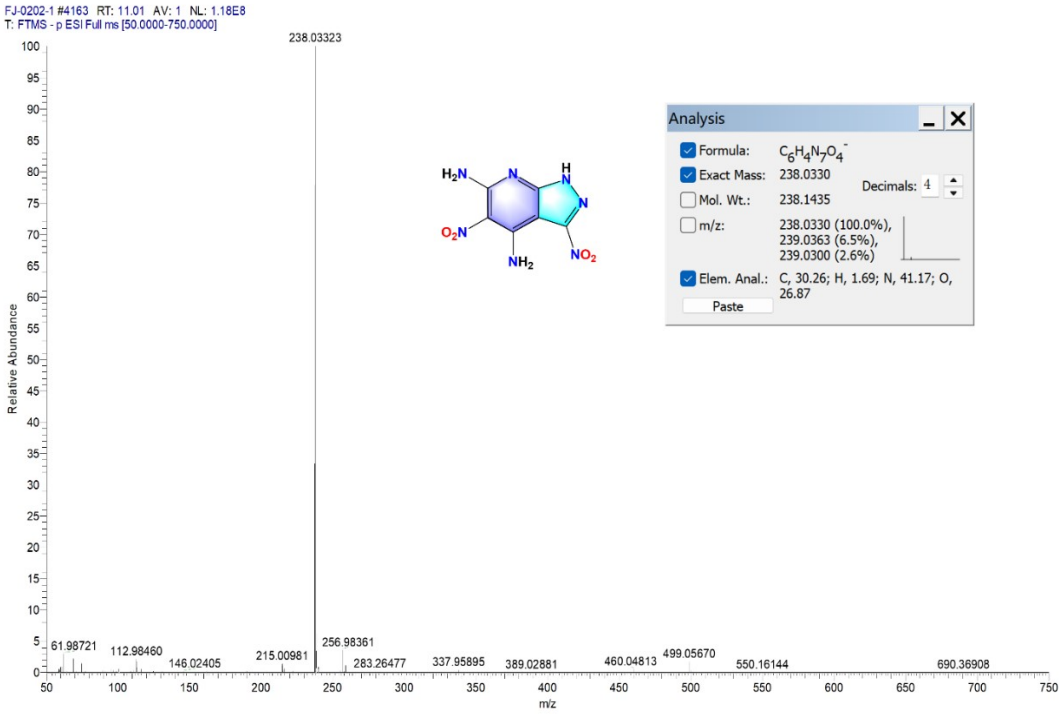


Fig. S22 Negative ion mass spectrum of **CF-1** (calcd for $C_6H_5N_7O_4^-$: 238.0330).

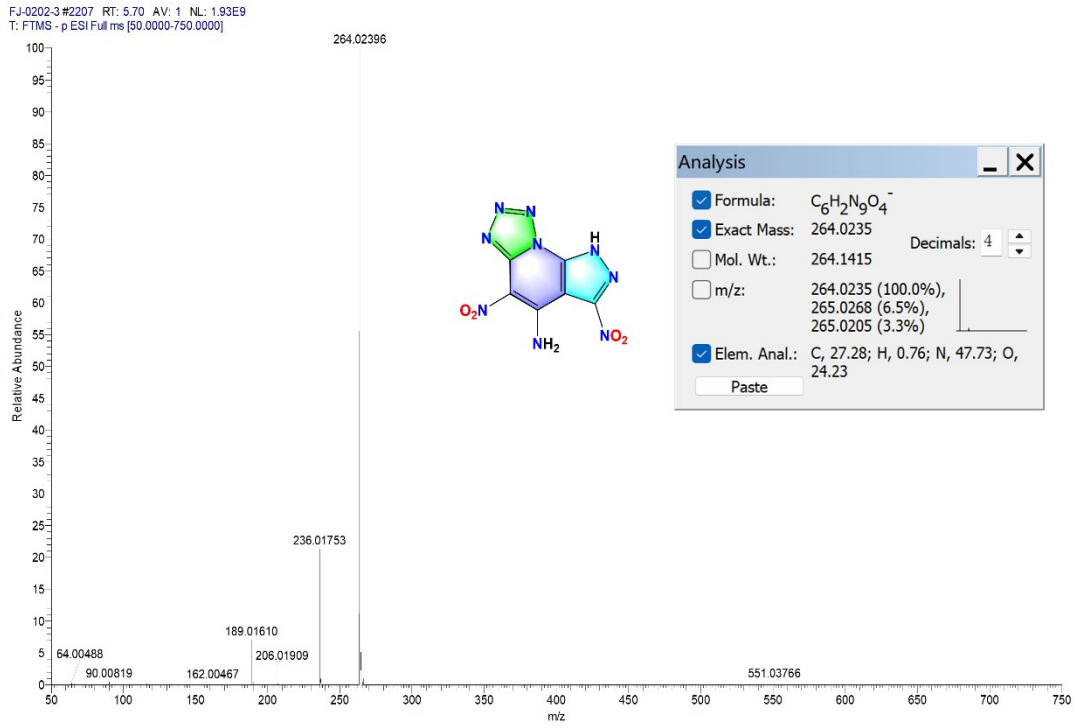


Fig. S23 Negative ion mass spectrum of **CF-2** (calcd for $C_6H_3N_9O_4^-$: 264.0235).

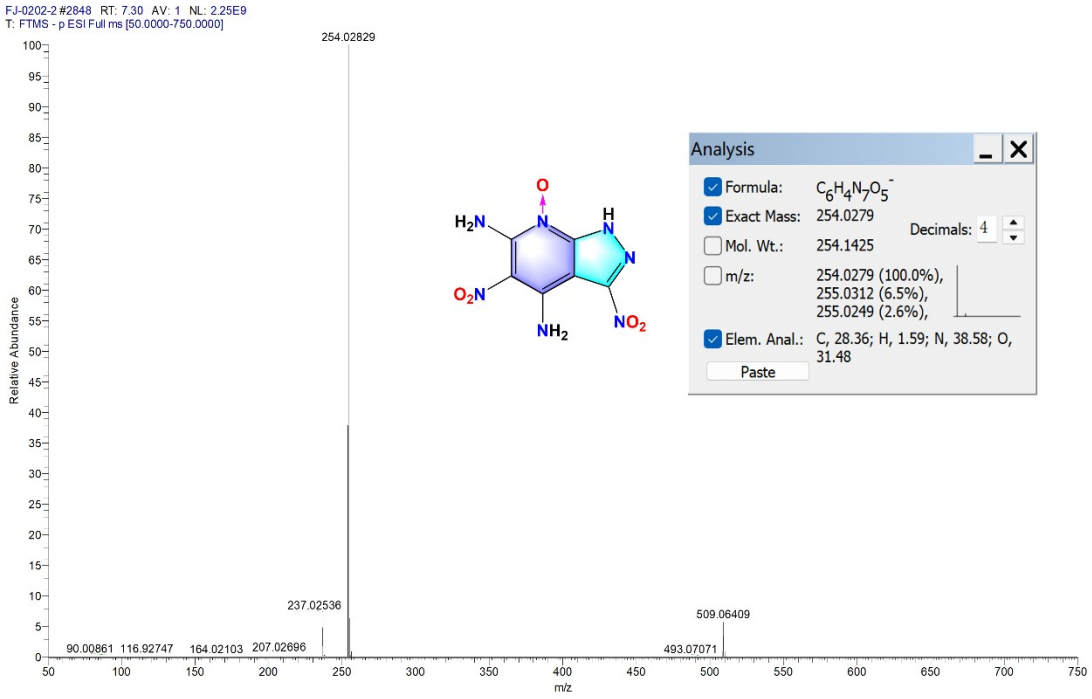


Fig. S24 Negative ion mass spectrum of **CF-3** (calcd for $C_6H_5N_7O_5^-$: 254.0279).

10 Electronic structures of CF-1, CF-2, and CF-3 in comparison with TATB, ICM-102, and IHEM-1

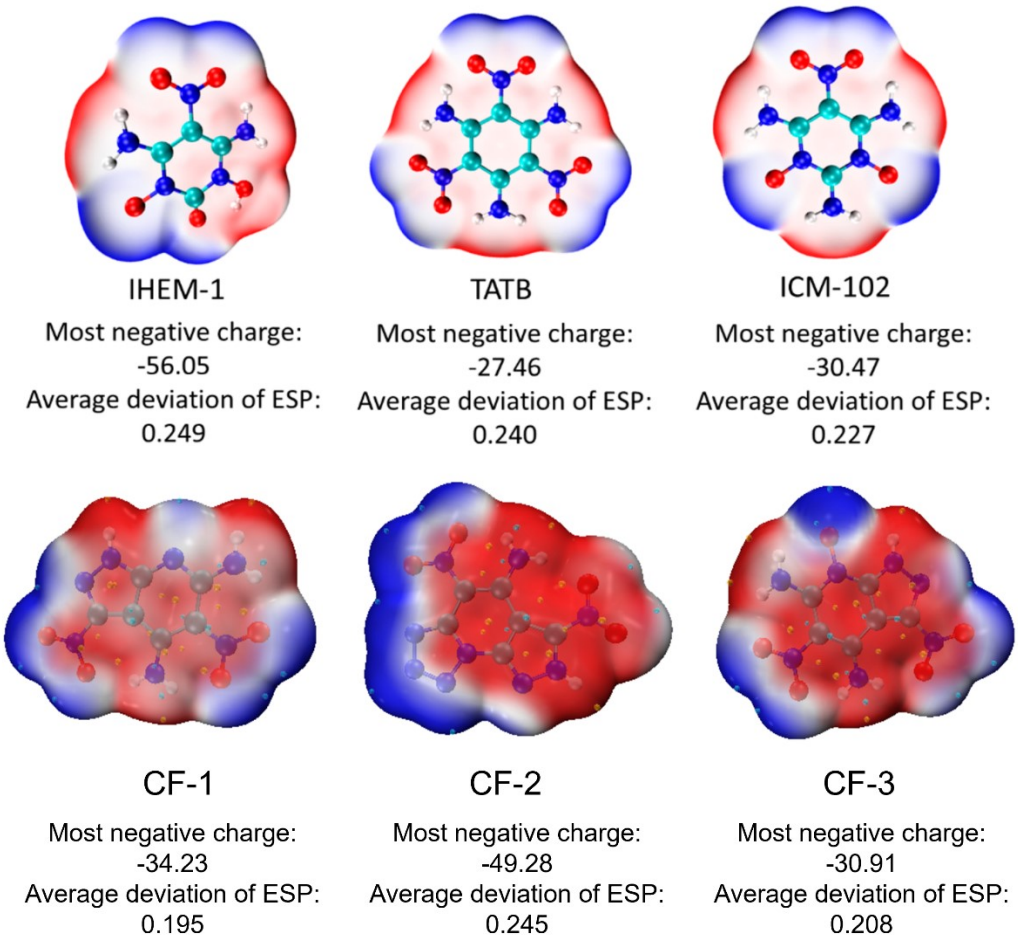


Fig. S25 Calculations of ESP for **CF-1**, **CF-2**, **CF-3**, TATB, ICM-102 and IHEM-1.