Electronic Supplementary Information

Achieving heat-resistant energetic compounds via silver-catalyzed one-pot cycloaddition of ethyl 2-isocyanoacetate and nitrogen-rich diazonium

Yaqun Dong,[a] Miao Li,[a] Guangbin Cheng,[a] Wei Huang,[a] Yuji Liu,*[a] Chuan Xiao,*[b] Yongxing Tang*[a]

[a]*School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China. E-mail: yujiliu@njust.edu.cn; yongxing@njust.edu.cn*

[b]*China Northern Industries Group Co., Ltd. (NORINCO GROUP), Beijing 100089, China*

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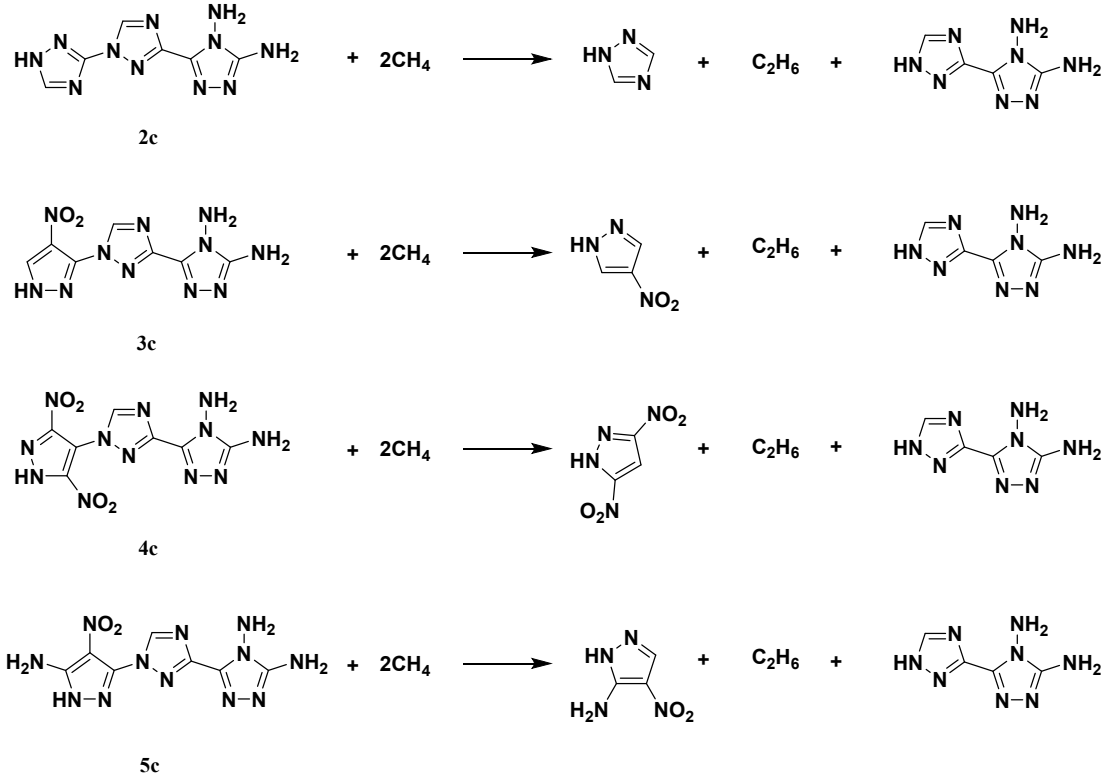
1. General methods

Chemical reagents were purchased from Aladdin and Bide Pharm in analytical grade and were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 300 MHz nuclear magnetic resonance spectrometer. DMSO-d_6 was used as a locking solvent. The working frequencies for ^{1}H and ^{13}C are 300 MHz and 76 MHz, respectively. Chemical shifts were reported relative to tetramethylsilane as internal standard. Decomposition temperatures were obtained on a TA Instruments DSC25 differential scanning calorimeter at a heating rate of 5 °C min^{-1}. Infrared spectra (IR) were recorded on a PerkinElmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Elemental analyses of C/H/N were performed on a Vario EL III Analyzer. Impact and friction sensitivities were measured with a BAM fallhammer and friction tester. X-ray intensity data were collected on a Bruker D8 VENTURE PHOTON II system equipped with an Incoatecius 3.0 Microfocus sealed tube. The structures were solved and refined using Bruker SHELXTL Software Package. The data were refined against F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed to their parent atoms using a riding model and refined isotropically.

2. Computational methods

The gas-phase heats of formation were calculated based on isodesmic reactions (Scheme S1). The enthalpies of reaction were obtained by combining the MP2/6-311++G** energy difference for the reactions, the scaled zero-point energies (ZPE), values of thermal correction (HT), and other thermal factors. The solid-state heats of formation were calculated with Trouton's rule according to equation 1 (T represents either melting point or decomposition temperature when no melting occurs prior to decomposition).[1]

$$\Delta H\_{sub}=188/\mathrm{J\ mol^{-1}\ K^{-1}}\times T \qquad (1)$$



Scheme S1. Isodesmic reactions for **2c**, **3c**, **4c** and **5c**.

3.Crystal structure data

Table S1. Crystal data and structure refinement for **2c**$^{-}\cdot NO_3^{+}\cdot H_2O$ and **3c**.

compound	**2c**$^{-}\cdot NO_3^{+}\cdot H_2O$	**3c**
Empirical formula	$C_6H_{10}N_{12}O_4$	$C_7H_7N_{11}O_2$
Formula weight	314.26	277.24
Temperature [K]	200(2)	193.00
Crystal system	monoclinic	monoclinic
Space group	$P2_1/m$	$P2_1/c$
***a* [Å]**	7.7084(8)	5.7986(5)
***b* [Å]**	6.2936(6)	13.7372(14)
***c* [Å]**	13.2830(11)	14.8998(10)
***α* [Å]**	90	90
***β* [Å]**	90.277(7)	100.940(5)
***γ* [Å]**	90	90
V [Å^3]	644.40(11)	1165.30(18)
Z	2	4
ρ_{calcd} **[Mg·m^{-3}]**	1.620	1.580
μ/mm^{-1}	1.191	1.080
F(000)	324	568.0
Crystal size	0.1×0.03×0.02	0.13×0.11×0.1
Theta range for data collection	6.65 to 136.11 (0.83 Å)	8.83 to 137.462
index range	−9 ≤h≤ 8, −7 ≤k≤ 7, −15 ≤l≤ 15	-6 ≤h≤ 6, -16 ≤k≤ 15, -16 ≤l≤ 17
reflections collected	4552	7464
independent reflections (Rint)	1425[R_{int} =0.1285,R_{sigma}=0.0733]	2129[R_{int}=0.0803,R_{sigma}=0.0613]
data/restraints/ paraneters	1251/13/143	2129/3/197
GOF on F^2	0.960	0.956
Final R indexes [I>=2σ (I)]	R_1 = 0.0823, wR_2 = 0.2139	R_1 =0.0475, wR_2 = 0.1141
Final R indexes [all data]	R_1 = 0.1273, wR_2 = 0.2555	R_1 = 0.0839, wR_2 = 0.1318
Largest diff. peak and hole [eÅ^{-3}]	0.28/-0.34	0.19/-0.23
CCDC number	2289565	2289566

Table S1. Crystal data and structure refinement for **4c** and **5c**$^{-}\cdot NO_3^{+}\cdot H_2O$.

compound	4c	**5c**$^{-}\cdot NO_3^{+}\cdot H_2O$
Empirical formula	$C_7H_6N_{12}O_4$	$C_7H_{11}N_{13}O_6$
Formula weight	322.24	373.29
Temperature [K]	273(2) K	193.00
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	P-1
***a* [Å]**	5.6440(8)	7.1369(4)
***b* [Å]**	11.4599(13)	8.9590(5)
***c* [Å]**	19.273(3)	12.3118(8)
***α* [Å]**	90	99.449(2)
***β* [Å]**	96.607(7)	101.389(2)
***γ* [Å]**	90	110.266(2)
V [Å^3]	1238.3(3)	700.40(7)
Z	4	2
ρ_{calcd} **[Mg·m^{-3}]**	1.729	1.770
μ/mm^{-1}	1.268	0.153
F(000)	656	384.0
Crystal size	0.220 × 0.200 × 0.180	0.13 × 0.11 × 0.1
Theta range for data collection	4.497 to 66.881 (0.83 Å)	5.01 to 55.162
index range	-5 ≤h≤ 6, -13 ≤k≤ 13, -22 ≤l≤ 22	-8 ≤h≤ 9, -11 ≤k≤ 11, -15 ≤l≤ 15
reflections collected	10577	15036
independent reflections (Rint)	2170 [R(int) = 0.1287]	3223 [R_{int}= 0.0674, R_{sigma}= 0.0473]
data/restraints/ paraneters	2170/0/208	3223/0/239
GOF on F^2	1.081	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0683, wR_2 = 0.1892	R_1 = 0.0481, wR_2 = 0.1149
Final R indexes [all data]	R_1 = 0.0855, wR_2 = 0.2052	R_1 = 0.0661, wR_2 = 0.1325
Largest diff. peak and hole [eÅ^{-3}]	0.426 and -0.346	0.36 and -0.46
CCDC number	2289564	2289562

Table S3. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **2c**$^-\cdot NO_3^+ \cdot H_2O$. Ueq is defined as 1/3 of the trace of the orthogonalised Uij tensor.

	x	y	z	U(eq)
N1	0.1975(9)	0.250000	0.4621(5)	0.0510(16)
C4	0.1382(10)	0.250000	0.3672(5)	0.0477(18)
N3	0.0513(9)	0.250000	0.5162(5)	0.0478(15)
N12	0.2028(9)	0.250000	0.6726(5)	0.0521(17)
N4	-0.0382(10)	0.250000	0.3596(5)	0.0526(16)
C3	-0.0865(11)	0.250000	0.4542(6)	0.0491(18)
H3	-0.203702	0.250000	0.475873	0.059
C6	0.2544(11)	0.250000	0.2834(5)	0.0500(19)
N10	0.5380(11)	0.250000	0.3830(5)	0.070(2)
H10A	0.521296	0.135840	0.424210	0.104
H10B	0.539705	0.375827	0.417126	0.104
C1	0.0575(11)	0.250000	0.6235(6)	0.0475(17)
N8	0.4359(10)	0.250000	0.2947(5)	0.0537(17)
N2	0.1467(9)	0.250000	0.7695(5)	0.0562(18)
H2A	0.214346	0.250000	0.823053	0.067
N11	-0.0870(9)	0.250000	0.6772(5)	0.0513(17)
C2	-0.0224(12)	0.250000	0.7710(6)	0.0522(19)
H2	-0.090451	0.250000	0.830471	0.063
O5	0.5590(9)	0.250000	0.5920(4)	0.0699(18)
H5A	0.466(7)	0.250000	0.626(6)	0.105
H5B	0.639(9)	0.250000	0.636(6)	0.105
C7	0.5021(11)	0.250000	0.2015(6)	0.052(2)
N9	0.5404(10)	0.250000	-0.0994(5)	0.0567(18)
N7	0.6744(10)	0.250000	0.1834(5)	0.0566(17)
H7A	0.718(7)	0.250000	0.121(2)	0.085
H7B	0.755(6)	0.27(6)	0.231(4)	0.085
N5	0.2153(10)	0.250000	0.1877(6)	0.0600(18)
O4	0.5612(9)	0.250000	-0.1912(4)	0.0738(19)
N6	0.3711(9)	0.250000	0.1391(5)	0.0555(18)
H6	0.381798	0.250000	0.073147	0.067
O2	0.3859(9)	0.250000	-0.0669(5)	0.0723(19)
O3	0.6634(10)	0.250000	-0.0392(5)	0.078(2)

Table S4. Bond lengths [Å] and angles [°] for **2c**$^{-}\cdot NO_3^{+}\cdot H_2O$.

N1–C4	1.339(10)	**C4–N1–N3**	102.8(6)
N1–N3	1.340(9)	**N1–C4–N4**	113.9(7)
C4–N4	1.364(11)	**N1–C4–C6**	121.3(7)
C4–C6	1.431(10)	**N4–C4–C6**	124.8(7)
N3–C3	1.341(10)	**N1–N3–C3**	109.6(6)
N3–C1	1.426(9)	**N1–N3–C1**	120.8(6)
N12–C1	1.293(11)	**C3–N3–C1**	129.6(7)
N12–N2	1.360(9)	**C1–N12–N2**	101.4(6)
N4–C3	1.311(11)	**C3–N4–C4**	102.5(7)
C6–N5	1.306(10)	**N4–C3–N3**	111.2(7)
C6–N8	1.406(11)	**N5–C6–N8**	109.2(7)
N10–N8	1.410(9)	**N5–C6–C4**	127.9(8)
C1–N11	1.325(11)	**N8–C6–C4**	122.9(7)
N8–C7	1.341(10)	**N12–C1–N11**	117.2(6)
N2–C2	1.304(11)	**N12–C1–N3**	121.9(7)
N11–C2	1.340(10)	**N11–C1–N3**	120.9(7)
C7–N6	1.304(11)	**C7–N8–C6**	106.6(7)
C7–N7	1.351(12)	**C7–N8–N10**	123.7(7)
N9–O4	1.230(9)	**C6–N8–N10**	129.8(7)
N9–O3	1.238(10)	**C2–N2–N12**	109.7(7)
N9–O2	1.269(10)	**C1–N11–C2**	101.0(7)
N5–N6	1.367(10)	**N2–C2–N11**	110.6(7)
		N6–C7–N8	106.8(7)
		N6–C7–N7	130.3(7)
		N8–C7–N7	122.9(8)
		O4–N9–O3	122.5(8)
		O4–N9–O2	117.7(8)
		O3–N9–O2	119.8(7)
		C6–N5–N6	105.1(7)
		C7–N6–N5	112.3(6)

Table S5. Anisotropic displacement parameters (Å^2 x 10^3) for **2c**$^{-}\cdot NO_3^{+}\cdot H_2O$. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2a^{*2}U^{11}$+ ... + 2 h k a* b* U^{12}].

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N1	0.049(4)	0.067(4)	0.037(3)	0.000	0.010(3)	0.000
C4	0.055(5)	0.056(5)	0.032(3)	0.000	0.005(3)	0.000
N3	0.049(4)	0.054(4)	0.040(3)	0.000	0.000(3)	0.000
N12	0.063(4)	0.062(4)	0.031(3)	0.000	0.001(3)	0.000
N4	0.062(4)	0.055(4)	0.042(3)	0.000	0.000(3)	0.000
C3	0.051(5)	0.056(4)	0.040(4)	0.000	−0.003(3)	0.000
C6	0.060(5)	0.058(5)	0.032(4)	0.000	0.003(3)	0.000

N10	0.061(4)	0.118(6)	0.029(3)	0.000	−0.009(3)	0.000
C1	0.055(5)	0.047(4)	0.040(4)	0.000	−0.006(4)	0.000
N8	0.060(4)	0.073(4)	0.028(3)	0.000	0.000(3)	0.000
N2	0.061(5)	0.072(5)	0.036(3)	0.000	0.003(3)	0.000
N11	0.053(4)	0.058(4)	0.042(3)	0.000	−0.001(3)	0.000
C2	0.062(5)	0.060(5)	0.035(3)	0.000	0.002(3)	0.000
O5	0.054(3)	0.120(5)	0.035(3)	0.000	−0.001(3)	0.000
C7	0.067(5)	0.055(5)	0.033(4)	0.000	0.005(4)	0.000
N9	0.062(5)	0.066(4)	0.042(4)	0.000	0.000(3)	0.000
N7	0.057(4)	0.079(5)	0.033(3)	0.000	0.001(3)	0.000
N5	0.055(4)	0.078(5)	0.047(4)	0.000	0.002(3)	0.000
O4	0.078(4)	0.114(6)	0.029(3)	0.000	0.000(3)	0.000
N6	0.057(4)	0.073(5)	0.036(3)	0.000	0.004(3)	0.000
O2	0.068(4)	0.105(5)	0.044(3)	0.000	0.004(3)	0.000
O3	0.074(4)	0.113(6)	0.046(3)	0.000	−0.007(3)	0.000

Table S6. Torsion angles [°] for **2c**$^{-}$·NO_3^+·H_2O.

C(4)-N(1)-N(3)-C(1)	180.0(1)	N(10)-N(8)-C(6)-N(5)	180.00(1)
C(4)-N(1)-N(3)-C(3)	0(1)	N(10)-N(8)-C(6)-C(4)	0.00(1)
N(3)-N(1)-C(4)-N(4)	0(1)	C(7)-N(8)-C(6)-N(5)	0.00(1)
N(3)-N(1)-C(4)-C(6)	-180.0(1)	C(7)-N(8)-C(6)-C(4)	-180.00(1)
C(2)-N(2)-N(12)-C(1)	-149.9(2)	N(1)-N(8)-C(7)-N(6)	-180.00(1)
N(12)-N(2)-C(2)N(11)	0.00(1)	N(10)-N(8)-C(7)-N(7)	0.00(1)
N(1)-N(3)-C(1)-N(11)	180.00(1)	C(6)-N(8)-C(7)-N(6)	0.00(1)
N(1)-N(3)-C(1)N(12)	0.00(1)	C(6)-N(8)-C(7)-N(7)	180.00(1)
C(3)-N(3)-C(1)-N(11)	0.00(1)	C(2)-N(11)-C(1)-N(3)	180.00(1)
C(4)-N(4)-C(3)-N(3)	180.00(1)	C(2)-N(11)-C(1)N(12)	0.00(1)
C(3)-N(4)-C(4)-N(1)	0.00(1)	C(1)-N(11)-C(2)-N(2)	0.00(1)
C(3)-N(4)-C(4)-C(6)	180.00(1)	N(2)-N(12)-C(1)-N(3)	180.00(1)
C(6)-N(5)-N(6)-C(7)	0.00(1)	N(2)-N(12)-C(1)-N(11)	0.00(1)
N(6)-N(5)-C(6)-N(8)	0.00(1)	N(1)-C(4)-C(6)-N(5)	-180.00(1)
N(6)-N(5)-C(6)-C(4)	180.00(1)	N(1)-C(4)-C(6)-N(8)	0.00(1)
N(5)-N(6)-C(7)-N(7)	180.00(1)	N(4)-C(4)-C(6)-N(5)	0.00(1)
N(5)-N(6)-C(7)-N(8)	0.00(1)	N(4)-C(4)-C(6)-N(8)	-180.00(1)

Table S7. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **3c**. Ueq is defined as 1/3 of of the trace of the orthogonalised Uij tensor.

	x	y	z	U(eq)
C1	9014(5)	2546(2)	6941(2)	36.1(6)
C2	7175(4)	3004(2)	6378.9(19)	33.5(6)
C3	7524(4)	2835(2)	5485.2(19)	34.0(6)
C4	3858(4)	3077(2)	4325(2)	38.3(7)
C5	5471(4)	3725(2)	3331.3(18)	31.1(6)
C6	5645(4)	4144(2)	2452.1(18)	30.9(6)
C7	6868(5)	4885(2)	1345.7(19)	37.9(7)
N1	5378(4)	3539.1(19)	6697.0(17)	41.3(6)
N2	10289(4)	2145.7(18)	6389.4(15)	37.3(6)
N3	9428(4)	2306.0(19)	5492.1(16)	37.2(6)
N4	6189(4)	3142.2(18)	4644.7(15)	34.5(6)
N5	7258(3)	3563.2(18)	3995.1(15)	33.7(5)
N6	3310(3)	3436.9(19)	3497.1(16)	37.8(6)
N7	4060(4)	4045.6(19)	1727.1(15)	37.5(6)
N8	4774(4)	4510(2)	999.1(16)	44.3(6)
N9	8209(5)	5425(3)	889(2)	55.3(8)
N10	7496(4)	4662.5(17)	2243.0(15)	31.5(5)
N11	9539(4)	5027(2)	2809.1(17)	36.1(6)
O1	5376(4)	3534.1(19)	7515.6(16)	59.2(7)
O2	3929(4)	3971.5(17)	6127.6(15)	52.0(6)

Table S8. Bond lengths [Å] and angles [°] for **3c**.

C1-C2	1.377(4)	**N2-C1-C2**	105.7(2)
C1-N2	1.325(4)	**C1-C2-C3**	105.5(2)
C2-C3	1.404(4)	**C1-C2-N1**	124.3(3)
C2-N1	1.427(4)	**C3-C2-N1**	130.2(3)
C3-N3	1.321(3)	**C2-C3-N4**	129.9(2)
C3-N4	1.406(4)	**N3-C3-C2**	110.8(2)
C4-N4	1.348(3)	**N3-C3-N4**	119.3(2)
C4-N6	1.311(4)	**N6-C4-N4**	110.8(2)
C5-C6	1.452(4)	**N5-C5-C6**	124.6(2)
C5-N5	1.308(3)	**N5-C5-N6**	115.6(2)
C5-N6	1.452(4)	**N6-C5-C6**	119.7(2)
C6-N7	1.286(3)	**N7-C6-C5**	123.7(2)
C6-N10	1.373(3)	**N7-C6-N10**	109.2(2)
C7-N8	1.330(4)	**N10-C6-C5**	127.0(2)
C7-N9	1.348(4)	**N8-C7-N9**	126.0(3)
C7-N10	1.352(4)	**N8-C7-N10**	110.6(2)
N1-O1	1.220(3)	**N9-C7-N10**	123.4(3)

N1-O2	1.228(3)	**O1-N1-C2**	117.9(2)
N2-N3	1.353(3)	**O1-N1-O2**	124.3(2)
N4-N5	1.372(3)	**O2-N1-C2**	117.8(2)
N7-N8	1.388(3)	**C1-N2-N3**	113.6(2)
N10-N11	1.409(3)	**C3-N3-N2**	104.4(2)
		C4-N4-C3	129.8(2)

Table S9. Anisotropic displacement parameters ($Å^2$ x 10^3) for **3c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2a^{*2}U^{11}$+ ... + 2 h k a* b* U^{12}].

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	42.1(14)	39.2(17)	28.0(15)	1.9(12)	9.1(11)	-3.6(12)
C(2)	36.4(13)	33.0(15)	33.3(16)	2.8(12)	11.7(11)	0.1(11)
C(3)	31.4(12)	38.9(17)	32.9(15)	5.9(13)	9.0(10)	-1.1(11)
C(4)	31.6(13)	50.9(19)	33.6(16)	5.4(13)	9.3(11)	-3.0(12)
C(5)	28.7(12)	36.3(16)	28.6(14)	-0.2(12)	6.1(10)	-0.3(11)
C(6)	30.1(12)	33.9(16)	29.0(14)	2.4(12)	6.6(10)	1.2(11)
C(7)	39.9(14)	44.6(18)	30.6(15)	4.6(13)	10.3(12)	-1.0(12)
N(1)	47.9(13)	41.7(16)	36.5(14)	-0.1(12)	14.0(11)	5.5(11)
N(2)	34.3(11)	47.2(16)	30.4(13)	5.9(11)	5.9(9)	3.8(10)
N(3)	32.8(11)	48.5(16)	31.0(13)	6.4(11)	7.7(9)	4.4(10)
N(4)	28.4(10)	46.5(15)	28.9(12)	7.0(11)	6.4(9)	-0.2(10)
N(5)	33.6(11)	42.1(14)	26.4(12)	5.9(10)	8.1(9)	-1.6(10)
N(6)	30.8(11)	52.7(17)	31.2(13)	4.7(12)	9.2(9)	-3.3(10)
N(7)	37.6(11)	48.0(16)	26.4(13)	2.0(11)	4.9(10)	-3.5(10)
N(8)	45.1(13)	60.1(18)	27.3(13)	7.9(12)	5.6(10)	-12.1(12)
N(9)	51.5(16)	78(2)	36.6(16)	15.2(15)	7.5(13)	-17.2(15)
N(10)	31.1(10)	37.7(14)	25.6(12)	2.5(10)	5.2(9)	-1.0(9)
N(11)	31.6(11)	41.2(16)	35.4(14)	-1.2(12)	5.7(10)	-3.8(11)
O(1)	81.4(15)	63.5(17)	38.5(13)	1.7(12)	26.2(11)	21.9(13)
O(2)	57.4(12)	53.3(15)	45.1(13)	1.3(11)	9.1(10)	21.9(11)

Table S10. Torsion angles [°] for **3c**.

C(1)-C(2)-C(3)-N(3)	0.4(3)	**N(2)-C(1)-C(2)-N(1)**	-179.3(3)
C(1)-C(2)-C(3)-N(4)	-179.4(3)	**N(3)-C(3)-N(4)-C(4)**	130.3(3)
C(1)-C(2)-N(1)-O(1)	-5.4(4)	**N(3)-C(3)-N(4)-N(5)**	-48.1(4)
C(1)-C(2)-N(1)-O(2)	174.9(3)	**N(4)-C(3)-N(3)-N(2)**	179.5(2)
C(1)-N(2)-N(3)-C(3)	0.2(3)	**N(4)-C(4)-N(6)-C(5)**	0.2(3)
C(2)-C(1)-N(2)-N(3)	0.1(3)	**N(5)-C(5)-C(6)-N(7)**	159.1(3)
C(2)-C(3)-N(3)-N(2)	-0.4(3)	**N(5)-C(5)-C(6)-N(10)**	-18.2(5)
C(2)-C(3)-N(4)-C(4)	-49.9(5)	**N(5)-C(5)-N(6)-C(4)**	0.0(3)
C(2)-C(3)-N(4)-N(5)	131.6(3)	**N(6)-C(4)-N(4)-C(3)**	-178.9(3)
C(3)-C(2)-N(1)-O(1)	175.8(3)	**N(6)-C(4)-N(4)-N(5)**	-0.3(4)

C(3)-C(2)-N(1)-O(2)	-3.9(5)	**N(6)-C(5)-C(6)-N(7)**	-18.7(4)
C(3)-N(4)-N(5)-C(5)	179.1(3)	**N(6)-C(5)-C(6)-N(10)**	164.0(3)
C(4)-N(4)-N(5)-C(5)	0.3(3)	**N(6)-C(5)-N(5)-N(4)**	-0.2(3)
C(5)-C(6)-N(7)-N(8)	-178.6(3)	**N(7)-C(6)-N(10)-C(7)**	1.4(3)
C(5)-C(6)-N(10)-C(7)	179.0(3)	**N(7)-C(6)-N(10)-N(11)**	173.9(3)
C(5)-C(6)-N(10)-N(11)	-8.5(5)	**N(8)-C(7)-N(10)-C(6)**	-1.5(3)
C(6)-C(5)-N(5)-N(4)	-178.1(3)	**N(8)-C(7)-N(10)-N(11)**	-174.6(3)
C(6)-C(5)-N(6)-C(4)	178.0(3)	**N(9)-C(7)-N(8)-N(7)**	-178.1(3)
C(6)-N(7)-N(8)-C(7)	0.0(3)	**N(9)-C(7)-N(10)-C(6)**	177.7(3)
N(1)-C(2)-C(3)-N(3)	179.4(3)	**N(9)-C(7)-N(10)-N(11)**	4.5(5)
N(1)-C(2)-C(3)-N(4)	-0.4(5)	**N(10)-C(6)-N(7)-N(8)**	-0.9(3)
N(2)-C(1)-C(2)-C(3)	-0.3(3)	**N(10)-C(7)-N(8)-N(7)**	1.0(3)

Table S11. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3c**

Atom	x	y	z	U(eq)
H1	9307.49	2521.58	7590.24	43
H(4)	2761.49	2806.36	4654.76	46
H(2)	11573.8	1807.73	6587.48	45
H(9A)	9660(40)	5560(20)	1190(20)	46(9)
H(9B)	7680(60)	5420(30)	296(13)	54(10)
H(11A)	9100(60)	5340(30)	3280(20)	61(11)
H(11B)	10270(70)	4530(30)	3040(30)	66(12)

Table S12. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **4c**. Ueq is defined as 1/3 of the trace of the orthogonalised Uij tensor.

	x	y	z	U(eq)
C1	3998(6)	2494(3)	6606(2)	45(1)
C2	2388(6)	3350(2)	6379(2)	42(1)
C3	716(6)	2709(3)	5949(2)	45(1)
C4	1030(7)	5133(3)	6937(2)	54(1)
C5	3279(6)	6320(2)	6522(2)	44(1)
C6	4351(6)	7438(2)	6373(2)	44(1)
C7	6655(7)	8752(3)	5968(2)	47(1)
N1	6193(6)	2595(3)	7075(2)	58(1)
N2	3372(6)	1449(2)	6337(1)	52(1)
N3	1277(6)	1574(2)	5930(1)	53(1)
N4	-1398(6)	3112(3)	5533(1)	62(1)
N5	2410(5)	4558(2)	6540(1)	44(1)
N6	3905(5)	5316(2)	6261(1)	48(1)
N7	1484(6)	6258(2)	6940(2)	57(1)
N8	6243(5)	7587(2)	5992(1)	43(1)

N9	5078(6)	9238(2)	6323(1)	54(1)
N10	3602(6)	8437(2)	6579(2)	54(1)
N11	7444(6)	6780(2)	5618(2)	59(1)
N12	8309(6)	9253(2)	5640(2)	64(1)
O1	7499(6)	1746(3)	7142(2)	84(1)
O2	6522(6)	3526(2)	7381(2)	79(1)
O3	-2630(6)	2379(3)	5203(2)	99(1)
O4	-1812(7)	4145(3)	5521(2)	100(1)

Table S13. Bond lengths [Å] and angles [°] for **4c.**

C1-N2	1.336(4)	**N2-C1-C2**	112.4(3)
C1-C2	1.374(4)	**N2-C1-N1**	118.8(3)
C1-N1	1.451(5)	**C2-C1-N1**	128.9(3)
C2-C3	1.392(4)	**C1-C2-C3**	101.0(3)
C2-N5	1.419(4)	**C1-C2-N5**	129.7(3)
C3-N3	1.339(4)	**C3-C2-N5**	129.3(3)
C3-N4	1.435(5)	**N3-C3-C2**	112.5(3)
C4-N7	1.315(4)	**N3-C3-N4**	118.8(3)
C4-N5	1.328(4)	**C2-C3-N4**	128.7(3)
C4-H4	0.9300	**N7-C4-N5**	111.2(3)
C5-N6	1.321(4)	**N7-C4-H4**	124.4
C5-N7	1.366(5)	**N5-C4-H4**	124.4
C5-C6	1.459(4)	**N6-C5-N7**	115.4(3)
C6-N10	1.299(4)	**N6-C5-C6**	123.7(3)
C6-N8	1.374(4)	**N7-C5-C6**	121.0(3)
C7-N9	1.308(4)	**N10-C6-N8**	110.7(3)
C7-N12	1.317(4)	**N10-C6-C5**	123.8(3)
C7-N8	1.358(4)	**N8-C6-C5**	125.4(3)
N1-O1	1.219(4)	**N9-C7-N12**	129.0(3)
N1-O2	1.223(4)	**N9-C7-N8**	105.7(3)
N2-N3	1.349(4)	**N12-C7-N8**	125.3(3)
N4-O4	1.206(4)	**O1-N1-O2**	126.0(4)
N4-O3	1.221(4)	**O1-N1-C1**	117.8(3)
N5-N6	1.363(3)	**O2-N1-C1**	116.2(3)
N8-N11	1.394(4)	**C1-N2-N3**	107.7(3)
N9-N10	1.368(4)	**C3-N3-N2**	106.4(2)
N9-H9	0.8600	**O4-N4-O3**	124.5(4)
N11-H11A	0.8600	**O4-N4-C3**	118.3(3)
N11-H11B	0.8600	**O3-N4-C3**	117.1(3)
N12-H12A	0.8600	**C4-N5-N6**	110.0(2)
N12-H12B	0.8600	**C4-N5-C2**	128.2(3)
		N6-N5-C2	121.7(3)

C5-N6-N5	101.5(2)
C4-N7-C5	101.9(3)
C7-N8-C6	106.7(3)
C7-N8-N11	122.6(3)
C6-N8-N11	130.3(2)
C7-N9-N10	112.5(3)
C7-N9-H9	123.7
N10-N9-H9	123.7
C6-N10-N9	104.3(3)
N8-N11-H11A	120.0
N8-N11-H11B	120.0
H11A-N11-H11B	120.0
C7-N12-H12A	120.0
C7-N12-H12B	120.0
H12A-N12-H12B	120.0

Table S14. Anisotropic displacement parameters ($Å^2$ x 10^3) for **4c.** The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2a^{*2}U^{11}$+ ... + 2 h k a* b* U^{12}].

Atom	**U^{11}**	**U22**	**U^{33}**	**U23**	**U^{13}**	**U^{12}**
C(1)	58(2)	30(2)	44(2)	2(1)	0(1)	-1(1)
C(2)	64(2)	20(1)	41(2)	-1(1)	4(1)	-4(1)
C(3)	62(2)	32(2)	40(2)	-4(1)	-2(1)	-4(2)
C(4)	80(3)	30(2)	54(2)	-3(1)	19(2)	-5(2)
C(5)	63(2)	22(2)	45(2)	-2(1)	-3(2)	-2(1)
C(6)	61(2)	26(2)	44(2)	-4(1)	-5(2)	2(1)
C(7)	70(2)	22(2)	45(2)	-3(1)	-5(2)	-1(2)
N(1)	63(2)	50(2)	61(2)	8(1)	1(2)	-6(2)
N(2)	75(2)	22(1)	56(2)	-3(1)	2(1)	0(1)
N(3)	76(2)	29(1)	51(2)	-9(1)	-1(1)	-5(1)
N(4)	71(2)	65(2)	48(2)	-8(1)	-7(2)	6(2)
N(5)	65(2)	21(1)	47(1)	-2(1)	6(1)	-4(1)
N(6)	66(2)	21(1)	58(2)	-2(1)	8(1)	-5(1)
N(7)	83(2)	29(1)	60(2)	-7(1)	19(2)	-2(1)
N(8)	55(2)	23(1)	48(1)	-3(1)	-3(1)	-1(1)
N(9)	75(2)	20(1)	64(2)	-2(1)	2(2)	-4(1)
N(10)	71(2)	24(1)	66(2)	-3(1)	6(2)	-3(1)
N(11)	70(2)	26(1)	84(2)	-5(1)	25(2)	-2(1)
N(12)	89(2)	28(2)	77(2)	-4(1)	15(2)	-12(2)
O(1)	68(2)	81(2)	99(2)	8(2)	-4(2)	23(2)
O(2)	89(2)	52(2)	88(2)	0(1)	-24(2)	-22(2)
O(3)	94(2)	107(3)	85(2)	-9(2)	-38(2)	-22(2)
O(4)	118(3)	71(2)	100(2)	-22(2)	-35(2)	46(2)

Table S15. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4c**.

Atom	x	y	z	U(eq)
H(4)	-109	4784	7182	64
H(9)	4979	9977	6389	65
H(11A)	8494	7015	5360	70
H(11B)	7134	6048	5646	70
H(12A)	8449	10000	5643	77
H(12B)	9248	8832	5422	77

Table S16. Torsion angles [°] for **4c.**

N(2)-C(1)-C(2)-C(3)	0.4(4)	**N(7)-C(4)-N(5)-C(2)**	-176.9(3)
N(1)-C(1)-C(2)-C(3)	179.9(3)	**C(1)-C(2)-N(5)-C(4)**	-107.9(4)
N(2)-C(1)-C(2)-N(5)	-179.9(3)	**C(3)-C(2)-N(5)-C(4)**	71.8(5)
N(1)-C(1)-C(2)-N(5)	-0.3(6)	**C(1)-C(2)-N(5)-N(6)**	74.7(4)
C(1)-C(2)-C(3)-N(3)	0.6(4)	**C(3)-C(2)-N(5)-N(6)**	-105.6(4)
N(5)-C(2)-C(3)-N(3)	-179.1(3)	**N(7)-C(5)-N(6)-N(5)**	-0.6(4)
C(1)-C(2)-C(3)-N(4)	-177.8(3)	**C(6)-C(5)-N(6)-N(5)**	-179.2(3)
N(5)-C(2)-C(3)-N(4)	2.4(6)	**C(4)-N(5)-N(6)-C(5)**	-0.1(3)
N(6)-C(5)-C(6)-N(10)	173.8(3)	**C(2)-N(5)-N(6)-C(5)**	177.7(3)
N(7)-C(5)-C(6)-N(10)	-4.7(5)	**N(5)-C(4)-N(7)-C(5)**	-1.0(4)
N(6)-C(5)-C(6)-N(8)	-5.2(5)	**N(6)-C(5)-N(7)-C(4)**	1.0(4)
N(7)-C(5)-C(6)-N(8)	176.3(3)	**C(6)-C(5)-N(7)-C(4)**	179.6(3)
N(2)-C(1)-N(1)-O(1)	7.9(5)	**N(9)-C(7)-N(8)-C(6)**	0.4(3)
C(2)-C(1)-N(1)-O(1)	-171.6(3)	**N(12)-C(7)-N(8)-C(6)**	-178.9(3)
N(2)-C(1)-N(1)-O(2)	-170.2(3)	**N(9)-C(7)-N(8)-N(11)**	174.3(3)
C(2)-C(1)-N(1)-O(2)	10.3(5)	**N(12)-C(7)-N(8)-N(11)**	-5.0(5)
C(2)-C(1)-N(2)-N(3)	-1.3(4)	**N(10)-C(6)-N(8)-C(7)**	0.0(4)
N(1)-C(1)-N(2)-N(3)	179.2(3)	**C(5)-C(6)-N(8)-C(7)**	179.1(3)
C(2)-C(3)-N(3)-N(2)	-1.4(4)	**N(10)-C(6)-N(8)-N(11)**	-173.2(3)
N(4)-C(3)-N(3)-N(2)	177.2(3)	**C(5)-C(6)-N(8)-N(11)**	5.9(5)
C(1)-N(2)-N(3)-C(3)	1.6(4)	**N(12)-C(7)-N(9)-N(10)**	178.6(3)
N(3)-C(3)-N(4)-O(4)	-175.6(4)	**N(8)-C(7)-N(9)-N(10)**	-0.6(3)
C(2)-C(3)-N(4)-O(4)	2.8(6)	**N(8)-C(6)-N(10)-N(9)**	-0.4(3)
N(3)-C(3)-N(4)-O(3)	2.8(5)	**C(5)-C(6)-N(10)-N(9)**	-179.5(3)
C(2)-C(3)-N(4)-O(3)	-178.8(3)	**C(7)-N(9)-N(10)-C(6)**	0.6(4)
N(7)-C(4)-N(5)-N(6)	0.7(4)		

Table S17. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **5c**$^-\cdot NO_3^+ \cdot H_2O$. Ueq is defined as 1/3 of the trace of the orthogonalised Uij tensor.

	x	y	z	U(eq)
C1	1735(3)	-765(2)	5307.0(17)	22.6(4)
C2	3344(3)	829(2)	5647.7(16)	21.7(4)
C3	3698(3)	1206(2)	4605.1(16)	21.2(4)
C4	6550(3)	4054(2)	5046.1(17)	26.0(4)
C5	6470(3)	4007(2)	3332.4(16)	23.1(4)
C6	7015(3)	4539(2)	2341.4(16)	23.6(4)
C7	7266(3)	4524(2)	590.9(17)	26.1(4)
N1	804(3)	-1741(2)	5908.2(15)	27.2(4)
N2	1278(3)	-1186(2)	4162.7(14)	25.5(4)
N3	2452(3)	-2(2)	3714.9(14)	24.7(4)
N4	4373(3)	1654(2)	6785.4(14)	28.7(4)
N5	5084(3)	2603(2)	4370.1(13)	22.1(4)
N6	5025(3)	2568(2)	3246.0(14)	25.0(4)
N7	7455(3)	4978(2)	4420.1(14)	26.6(4)
N8	8181(3)	6044(2)	2386.9(14)	27.5(4)
N9	8332(3)	6028(2)	1284.7(14)	28.2(4)
N10	6407(3)	3552(2)	1243.9(14)	24.5(4)
N11	5285(3)	1857(2)	777.3(15)	30.5(4)
N12	7054(3)	4024(2)	-505.7(15)	36.7(5)
O1	3748(3)	1020.3(19)	7536.3(13)	37.8(4)
O2	5872(3)	2971(2)	7022.4(14)	53.8(6)
N13	628(3)	2607(2)	1653.6(17)	33.7(4)
O3	789(3)	3850(2)	2345(2)	72.0(7)
O4	1782(3)	2733(3)	1005.6(17)	57.7(6)
O5	-683(3)	1251(2)	1624.9(15)	41.7(4)
O6	1237(3)	-1090.8(19)	1267.8(13)	38.1(4)

Table S18. Bond lengths [Å] and angles [°] for **5c**$^{-}\cdot NO_3^{+}\cdot H_2O$.

C1-C2	1.418(3)	**N1-C1-C2**	131.70(18)
C1-N1	1.326(3)	**N1-C1-N2**	123.34(18)
C1-N2	1.339(3)	**N2-C1-C2**	104.95(17)
C2-C3	1.427(3)	**C1-C2-C3**	104.97(16)
C2-N4	1.388(2)	**N4-C2-C1**	123.01(18)
C3-N3	1.312(2)	**N4-C2-C3**	131.74(18)
C3-N5	1.415(2)	**N3-C3-C2**	111.18(17)
C4-N5	1.355(3)	**N3-C3-N5**	116.33(17)
C4-N7	1.316(3)	**N5-C3-C2**	132.48(17)
C5-C6	1.455(3)	**N7-C4-N5**	110.48(18)
C5-N6	1.315(2)	**N6-C5-C6**	122.66(17)
C5-N7	1.366(2)	**N6-C5-N7**	115.67(17)
C6-N8	1.301(3)	**N7-C5-C6**	121.67(18)
C6-N10	1.381(2)	**N8-C6-C5**	123.36(18)
C7-N9	1.334(3)	**N8-C6-N10**	110.77(17)
C7-N10	1.354(3)	**N10-C6-C5**	125.87(18)
C7-N12	1.312(3)	**N9-C7-N10**	106.41(17)
N2-N3	1.374(2)	**N12-C7-N9**	128.7(2)
N4-O1	1.239(2)	**N12-C7-N10**	124.91(19)
N4-O2	1.229(2)	**C1-N2-N3**	113.78(16)
N5-N6	1.371(2)	**C3-N3-N2**	105.12(16)
N8-N9	1.380(2)	**O1-N4-C2**	118.24(17)
N10-N11	1.403(2)	**O2-N4-C2**	119.81(18)
N13-O3	1.240(3)	**O2-N4-O1**	121.95(17)
N13-O4	1.246(3)	**C4-N5-C3**	133.09(17)
N13-O5	1.240(2)	**C4-N5-N6**	109.30(16)
		N6-N5-C3	117.61(15)
		C5-N6-N5	102.01(15)
		C4-N7-C5	102.53(17)
		C6-N8-N9	105.20(16)
		C7-N9-N8	110.82(17)
		C6-N10-N11	132.55(17)
		C7-N10-C6	106.80(16)
		C7-N10-N11	120.47(16)
		O3-N13-O4	119.9(2)
		O3-N13-O5	119.0(2)
		O5-N13-O4	121.0(2)

Table S19. Anisotropic displacement parameters (Å^2 x 10^3) for **5c**$^-$·NO_3^+·H_2O. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2a^{*2}U^{11}$+ ... + 2 h k a* b* U^{12}].

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	21.5(9)	21.6(9)	23.6(10)	4.3(8)	6.8(7)	7.4(8)
C2	21.6(9)	18.8(9)	18.8(9)	2.7(7)	3.4(7)	3.1(7)
C3	20.4(9)	20.1(9)	20.4(9)	4.0(7)	5.6(7)	5.2(7)
C4	29.2(10)	21.3(9)	20.4(10)	4.0(8)	5.6(8)	2.8(8)
C5	23.0(9)	22.3(10)	20.2(10)	4.3(8)	5.6(7)	5.2(8)
C6	24.0(10)	22.2(10)	19.2(9)	3.4(8)	4.3(7)	4.4(8)
C7	27.8(10)	24.5(10)	20.9(10)	5.0(8)	5.8(8)	4.9(8)
N1	29.6(9)	22.0(8)	22.8(9)	4.8(7)	6.4(7)	2.5(7)
N2	25.4(9)	19.5(8)	22.3(9)	2.5(7)	4.5(7)	0.0(7)
N3	24.2(8)	22.0(8)	21.0(8)	3.5(7)	4.4(7)	2.7(7)
N4	31.1(9)	24.6(9)	20.2(8)	4.7(7)	7.0(7)	-0.6(7)
N5	23.4(8)	21.7(8)	17.0(8)	3.8(6)	4.5(6)	5.0(7)
N6	26.9(9)	24.0(9)	18.2(8)	5.3(7)	5.3(7)	3.3(7)
N7	30.4(9)	22.0(8)	21.2(8)	4.2(7)	6.9(7)	3.7(7)
N8	33.4(10)	23.0(9)	19.8(8)	4.6(7)	7.8(7)	3.8(7)
N9	36.3(10)	22.5(8)	19.1(8)	6.0(7)	9.5(7)	2.2(7)
N10	27.2(9)	20.0(8)	18.1(8)	2.6(6)	5.0(7)	1.2(7)
N11	34.2(10)	19.9(8)	25.8(9)	0.5(7)	7.1(8)	0.1(7)
N12	50.4(12)	26.8(9)	19.1(9)	2.1(7)	10.2(8)	0.2(9)
O1	46.0(10)	33.9(9)	21.6(8)	7.8(6)	11.6(7)	-0.2(7)
O2	58.7(12)	38.3(10)	22.1(8)	1.2(7)	4.6(8)	-24.4(9)
N13	27.1(9)	30.9(10)	39.9(11)	14.5(8)	5.4(8)	7.4(8)
O3	54.0(13)	33.4(11)	105.0(19)	-12.9(11)	4.0(12)	12.6(9)
O4	41.3(10)	92.6(16)	54.8(12)	47.5(12)	23.5(9)	25.9(11)
O5	41.3(10)	28.7(8)	47.1(10)	12.0(7)	13.5(8)	2.5(7)
O6	47.9(10)	30.1(8)	25.9(8)	7.6(7)	5.3(7)	5.3(7)

Table S20. Torsion angles [°] for **5c**$^-$·NO_3^+·H_2O.

C(1)-C(2)-C(3)-N(3)	0.3(2)	**N(3)-C(3)-N(5)-C(4)**	179.5(2)
C(1)-C(2)-C(3)-N(5)	179.6(2)	**N(3)-C(3)-N(5)-N(6)**	-0.7(3)
C(1)-C(2)-N(4)-O(1)	-5.6(3)	**N(4)-C(2)-C(3)-N(3)**	174.2(2)
C(1)-C(2)-N(4)-O(2)	173.8(2)	**N(4)-C(2)-C(3)-N(5)**	-6.5(4)
C(1)-N(2)-N(3)-C(3)	0.2(2)	**N(5)-C(3)-N(3)-N(2)**	-179.75(16)
C(2)-C(1)-N(2)-N(3)	0.0(2)	**N(5)-C(4)-N(7)-C(5)**	-0.4(2)
C(2)-C(3)-N(3)-N(2)	-0.3(2)	**N(6)-C(5)-C(6)-N(8)**	168.3(2)
C(2)-C(3)-N(5)-C(4)	0.2(4)	**N(6)-C(5)-C(6)-N(10)**	-12.3(3)
C(2)-C(3)-N(5)-N(6)	180.0(2)	**N(6)-C(5)-N(7)-C(4)**	0.5(2)
C(3)-C(2)-N(4)-O(1)	-178.6(2)	**N(7)-C(4)-N(5)-C(3)**	180.00(19)
C(3)-C(2)-N(4)-O(2)	0.8(4)	**N(7)-C(4)-N(5)-N(6)**	0.2(2)

C(3)-N(5)-N(6)-C(5)	-179.74(17)	**N(7)-C(5)-C(6)-N(8)**	-12.4(3)
C(4)-N(5)-N(6)-C(5)	0.1(2)	**N(7)-C(5)-C(6)-N(10)**	167.04(19)
C(5)-C(6)-N(8)-N(9)	179.48(18)	**N(7)-C(5)-N(6)-N(5)**	-0.4(2)
C(5)-C(6)-N(10)-C(7)	-179.34(19)	**N(8)-C(6)-N(10)-C(7)**	0.1(2)
C(5)-C(6)-N(10)-N(11)	-4.3(3)	**N(8)-C(6)-N(10)-N(11)**	175.2(2)
C(6)-C(5)-N(6)-N(5)	179.04(18)	**N(9)-C(7)-N(10)-C(6)**	-0.2(2)
C(6)-C(5)-N(7)-C(4)	-178.93(19)	**N(9)-C(7)-N(10)-N(11)**	-175.96(18)
C(6)-N(8)-N(9)-C(7)	-0.1(2)	**N(10)-C(6)-N(8)-N(9)**	0.0(2)
N(1)-C(1)-C(2)-C(3)	178.7(2)	**N(10)-C(7)-N(9)-N(8)**	0.2(2)
N(1)-C(1)-C(2)-N(4)	4.1(4)	**N(12)-C(7)-N(9)-N(8)**	-179.4(2)
N(1)-C(1)-N(2)-N(3)	-178.98(18)	**N(12)-C(7)-N(10)-C6)**	179.5(2)
N(2)-C(1)-C(2)-C(3)	-0.2(2)	**N(12)-C(7)-N(10)-N(11)**	3.7(3)
N(2)-C(1)-C(2)-N(4)	-174.73(19)		

Table S21. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **5c**$^-$·NO_3^+·H_2O.

Atom	x	y	z	U(eq)
H(4)	6878.68	4360.76	5858.06	31
H(1A)	-167.96	-2721.1	5555.22	33
H(1B)	1158.01	-1409.44	6660.09	33
H(2)	315.53	-2132.27	3736.66	31
H(9)	9035.82	6893.67	1068.95	34
H(11A)	5959.24	1306.94	1099.63	37
H(11B)	4041.24	1552.44	902.81	37
H(12A)	7664.21	4724.27	-876	44
H(12B)	6300.9	2988.04	-871.12	44
H(6A)	1841.21	-580.48	1986.35	57
H(6B)	523.63	-540.94	1021.12	57

4. NMR Spectra

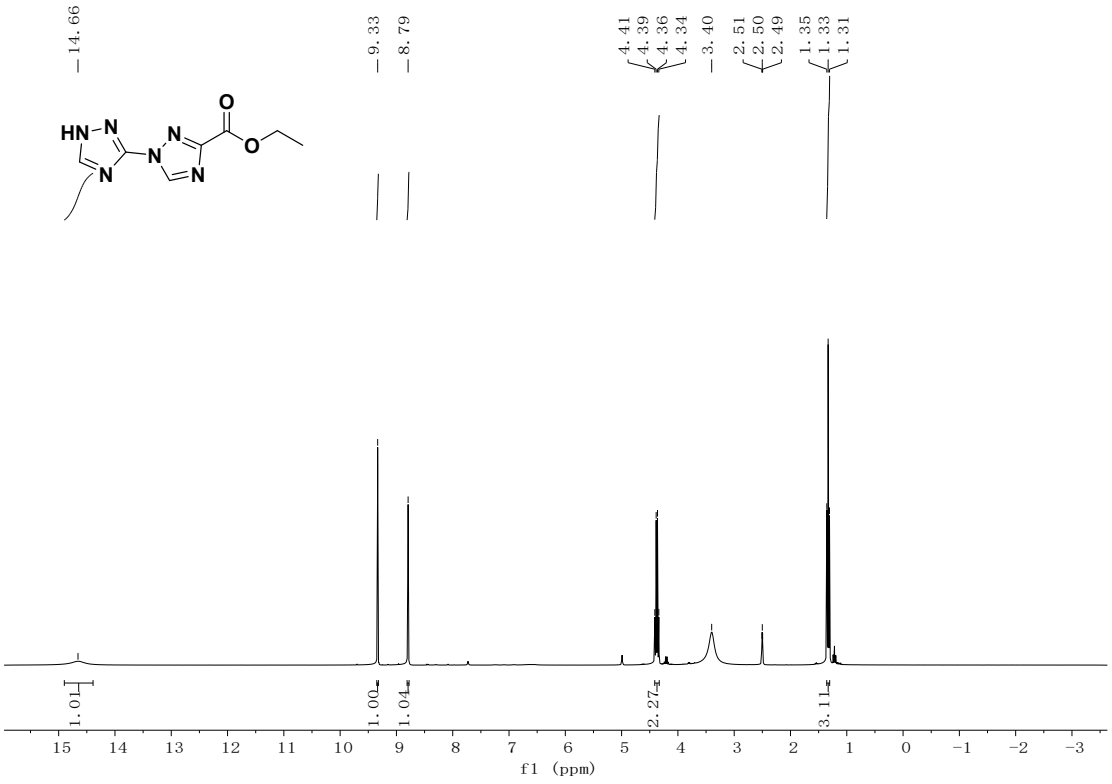


Fig. S1 ^{1}H NMR spectrum of **2a**.

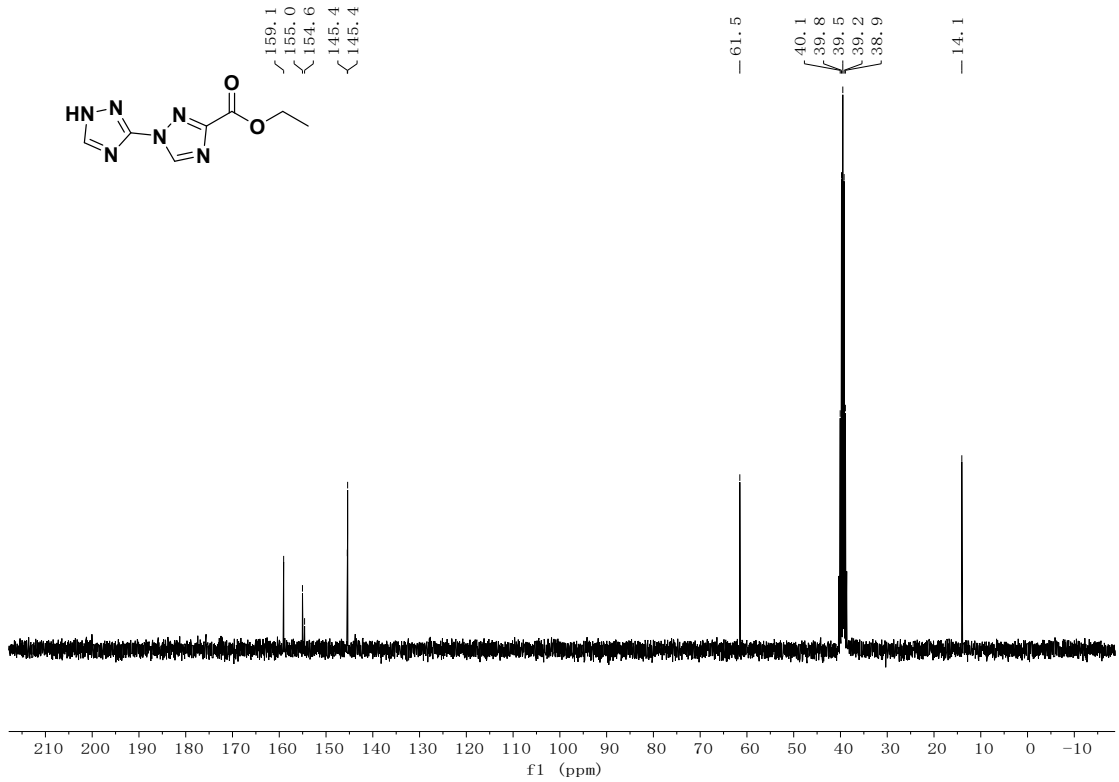


Fig. S2 ^{13}C NMR spectrum of **2a**.

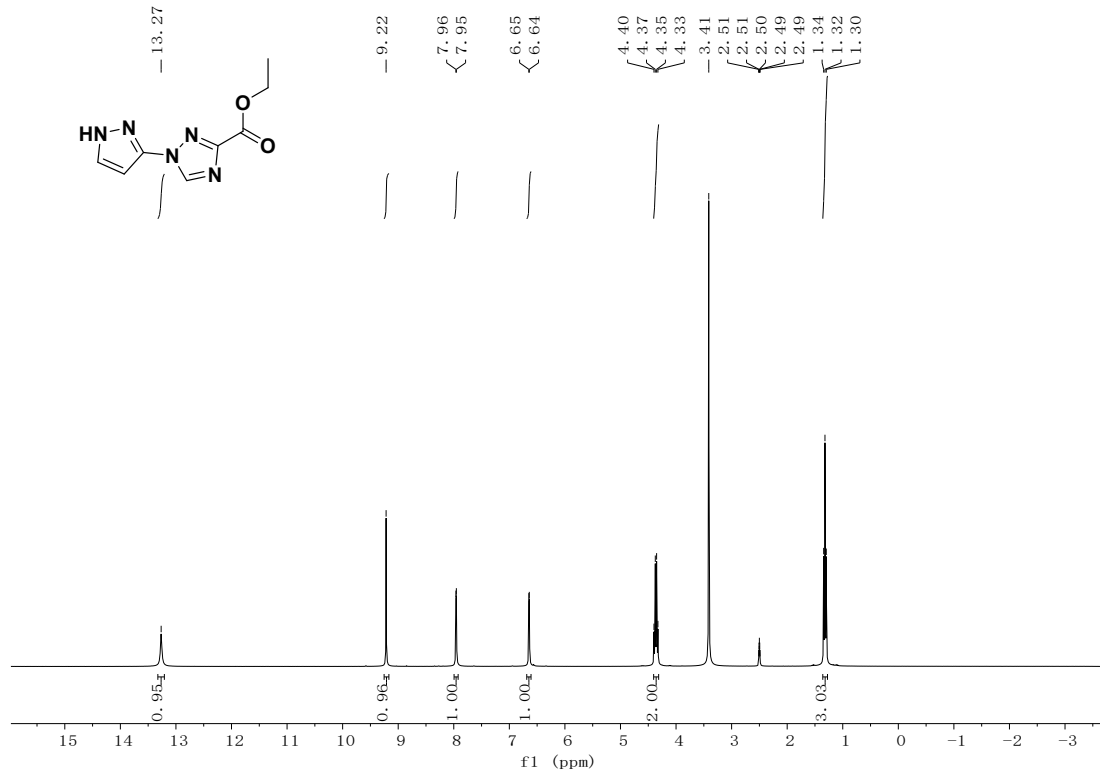


Fig. S3 ^{1}H NMR spectrum of **3a**.

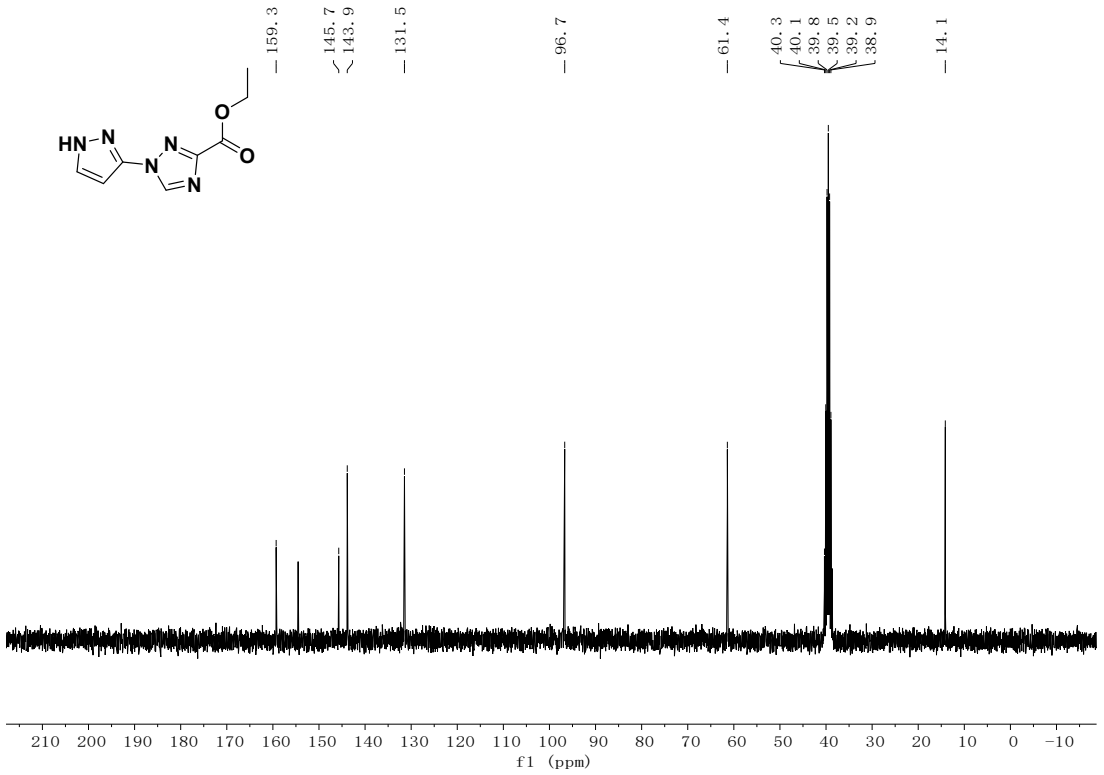


Fig. S4 ^{13}C NMR spectrum of **3a**.

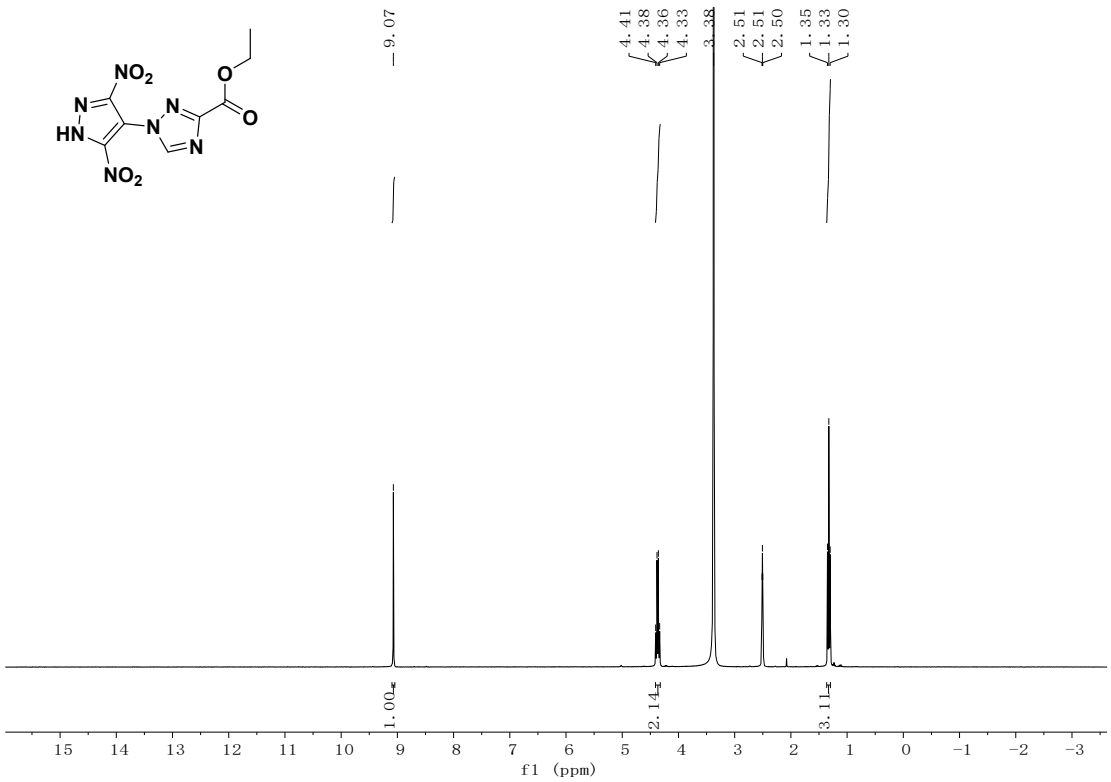


Fig. S5 ^{1}H NMR spectrum of **4a**.

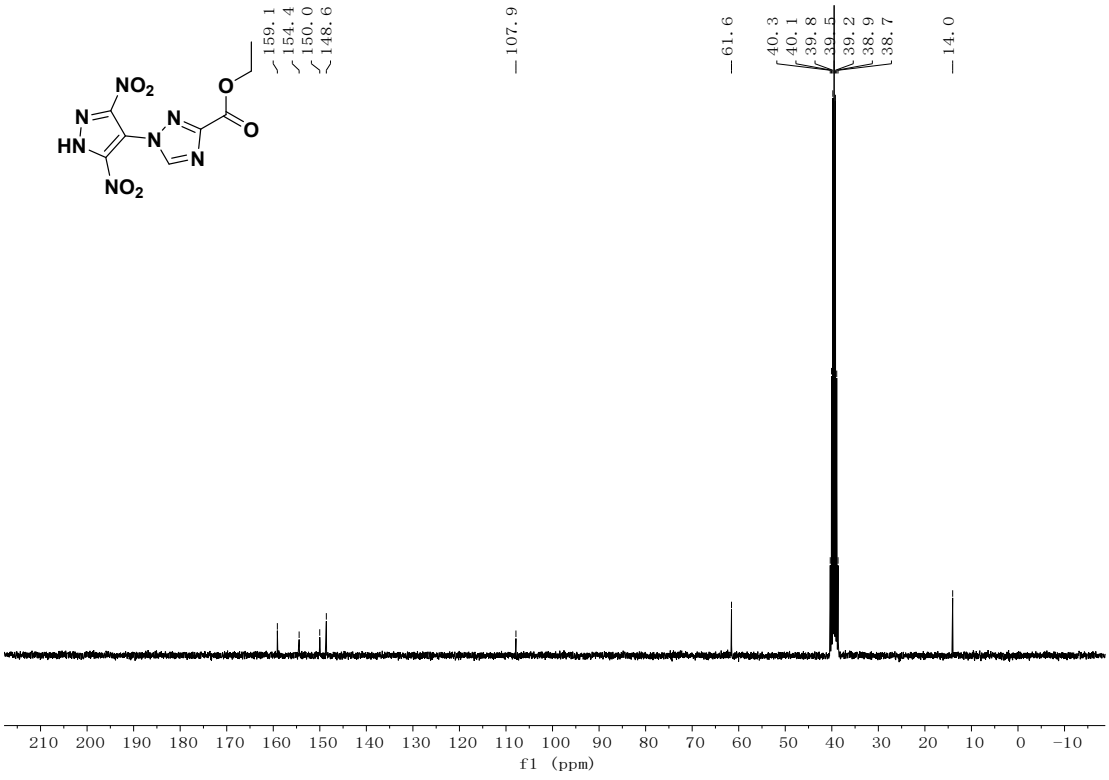


Fig. S6 ^{13}C NMR spectrum of **4a**.

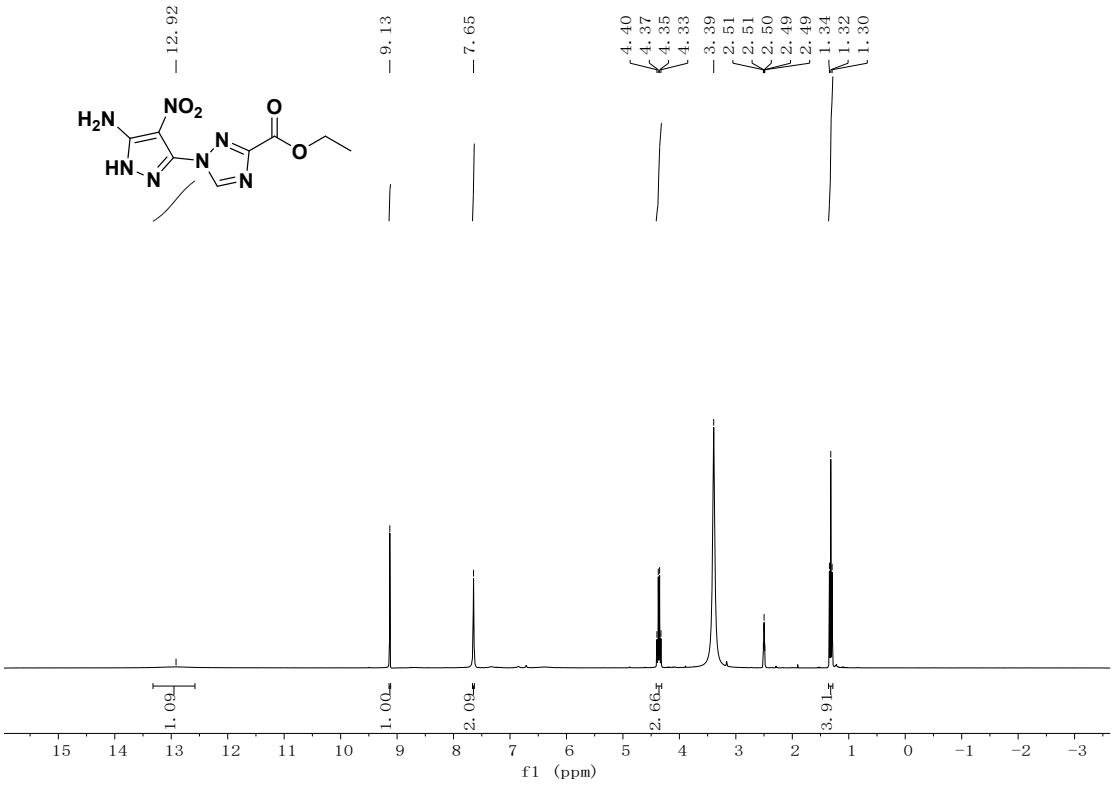


Fig. S7 ^{1}H NMR spectrum of **5a**.

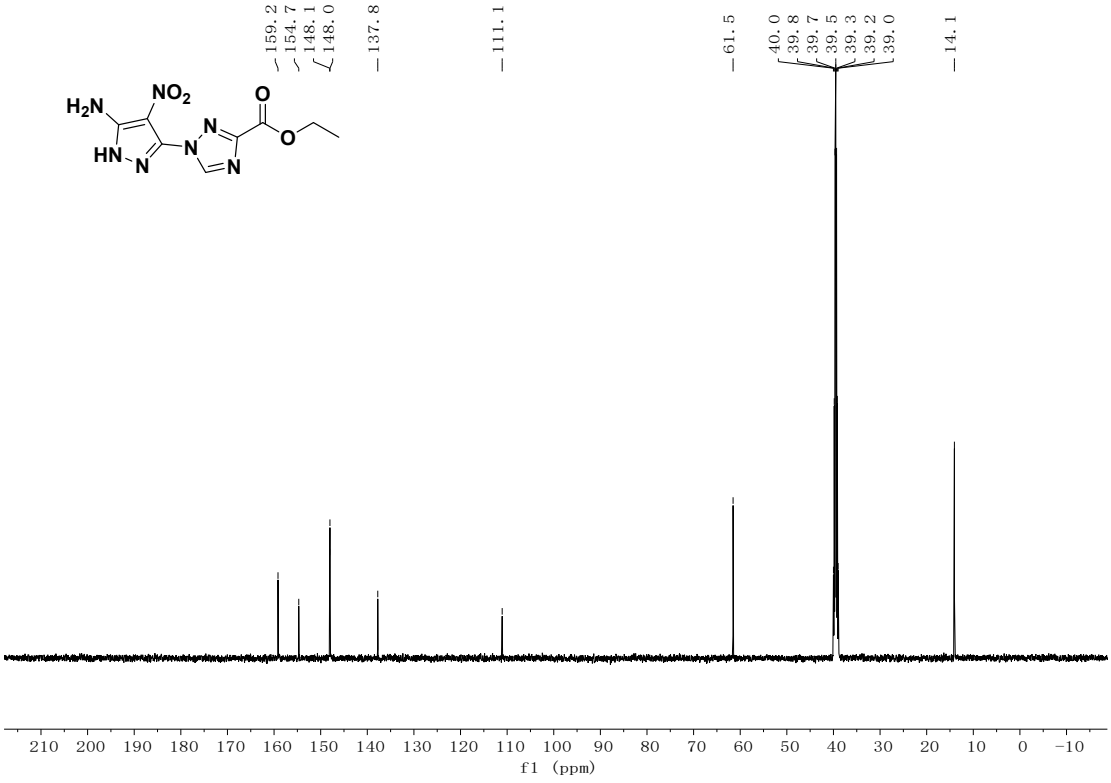


Fig. S8 ^{13}C NMR spectrum of **5a**.

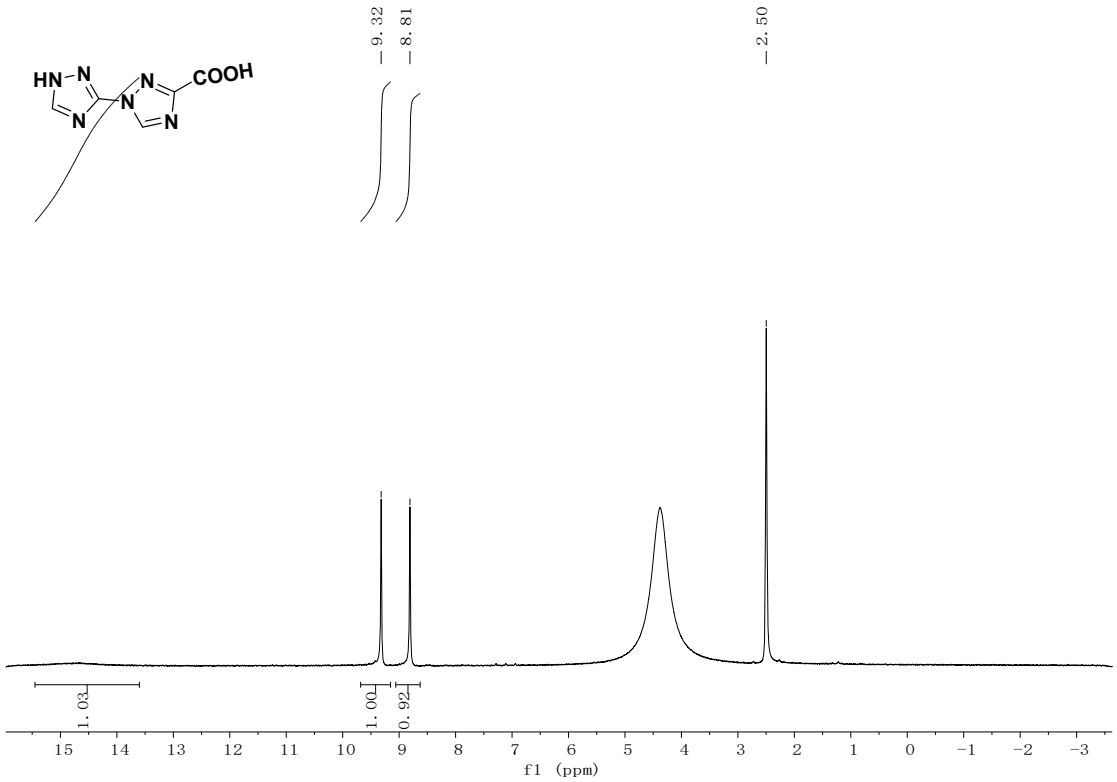


Fig. S9 ^{1}H NMR spectrum of **2b**.

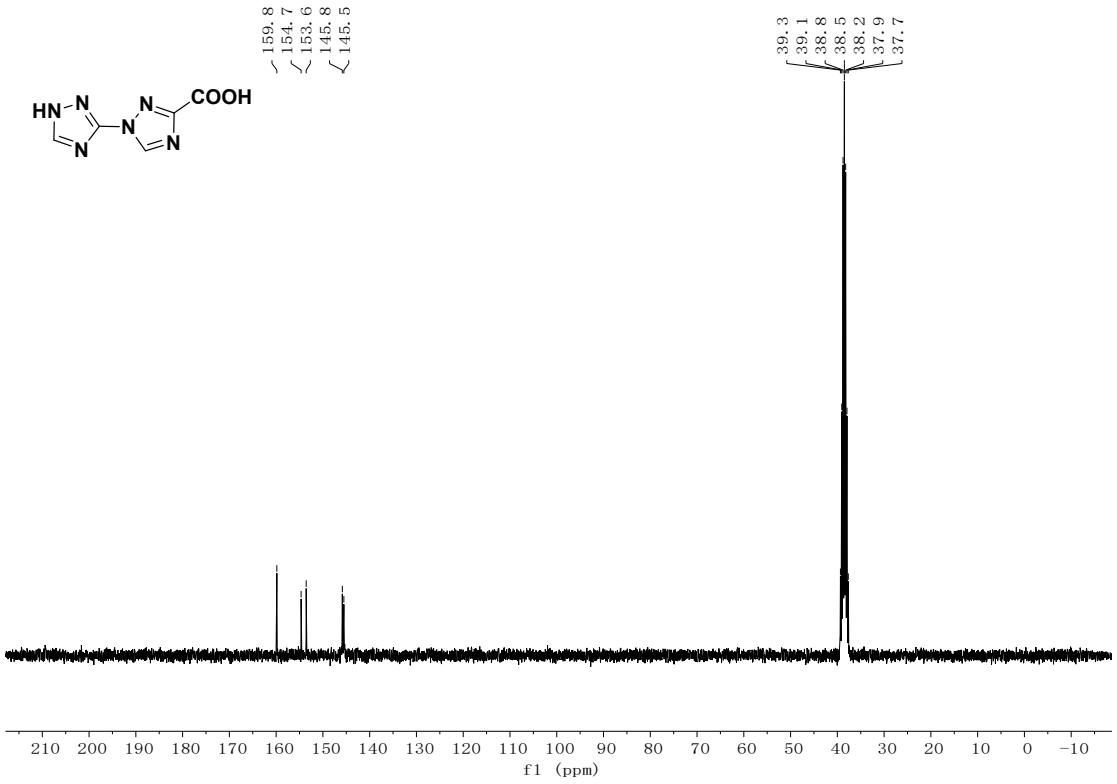


Fig. S10 ^{13}C NMR spectrum of **2b**.

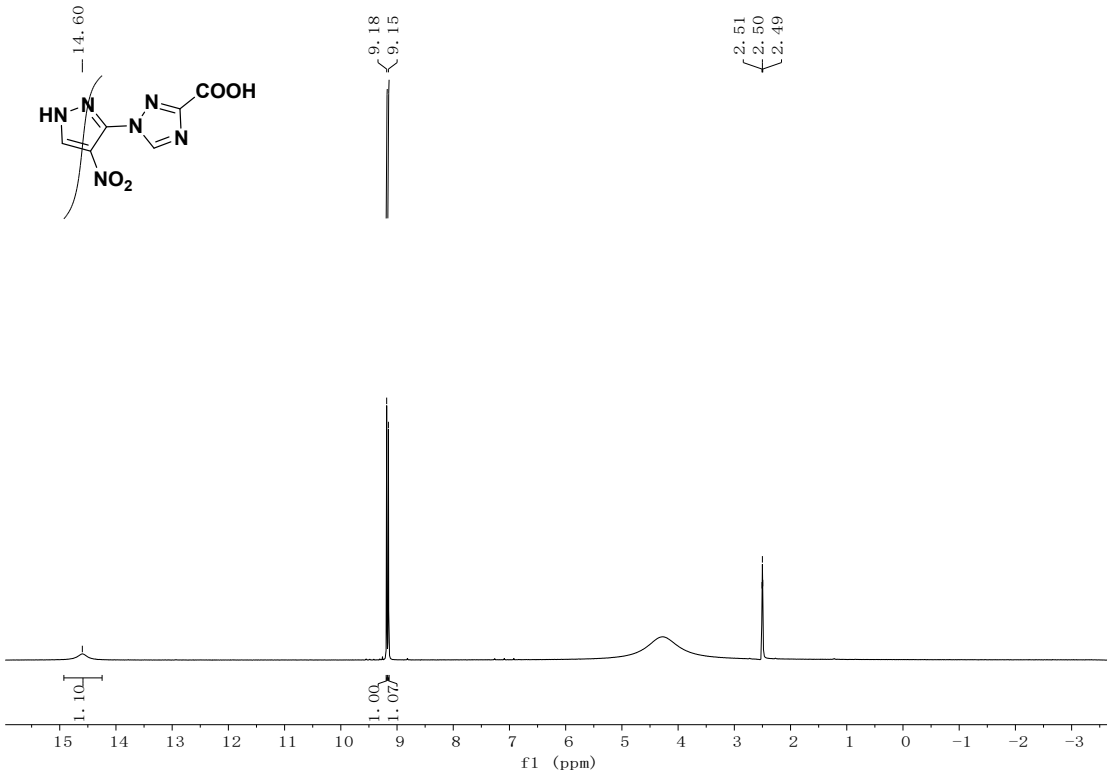


Fig. S11 ^{1}H NMR spectrum of **3b**.

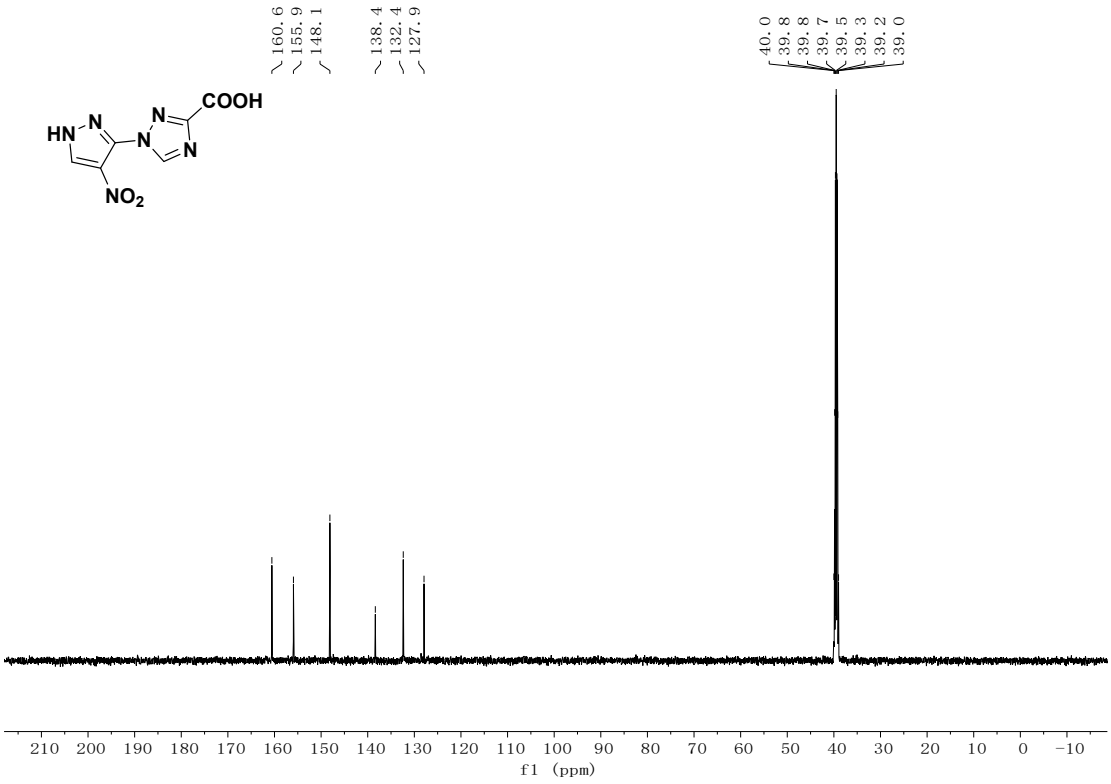


Fig. S12 ^{13}C NMR spectrum of **3b**.

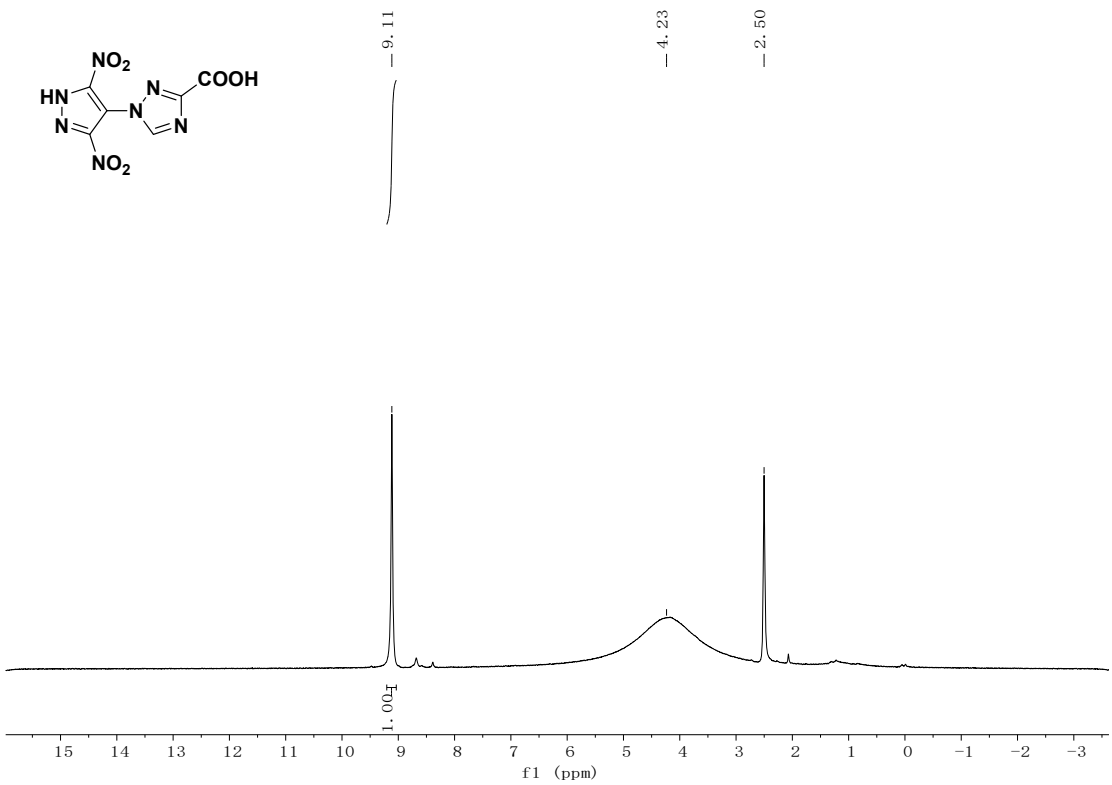


Fig. S13 ^{1}H NMR spectrum of **4b**.

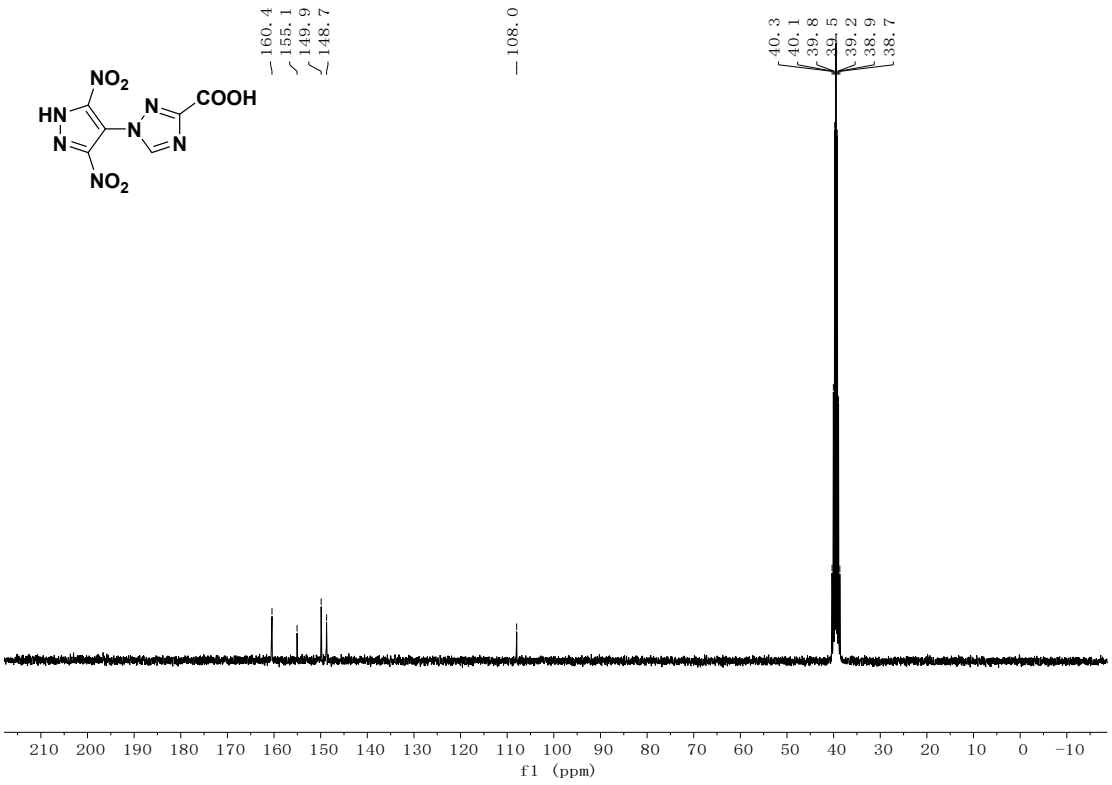


Fig. S14 ^{13}C NMR spectrum of **4b**.

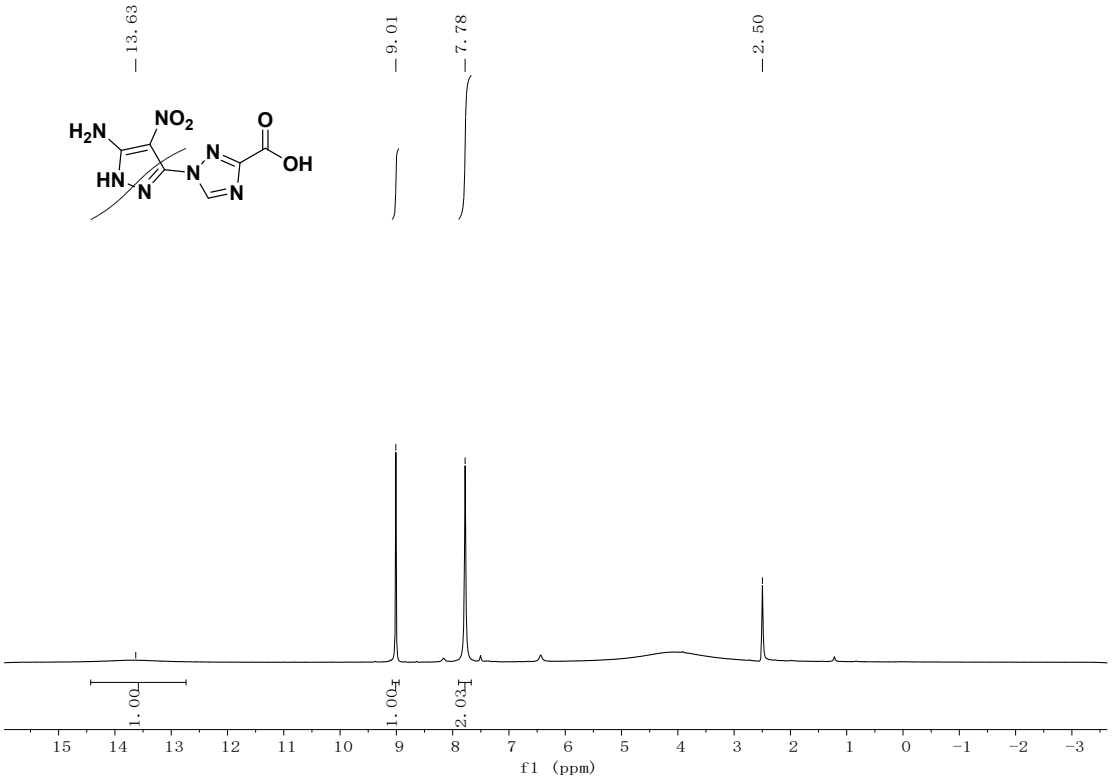


Fig. S15 ^{1}H NMR spectrum of **5b**.

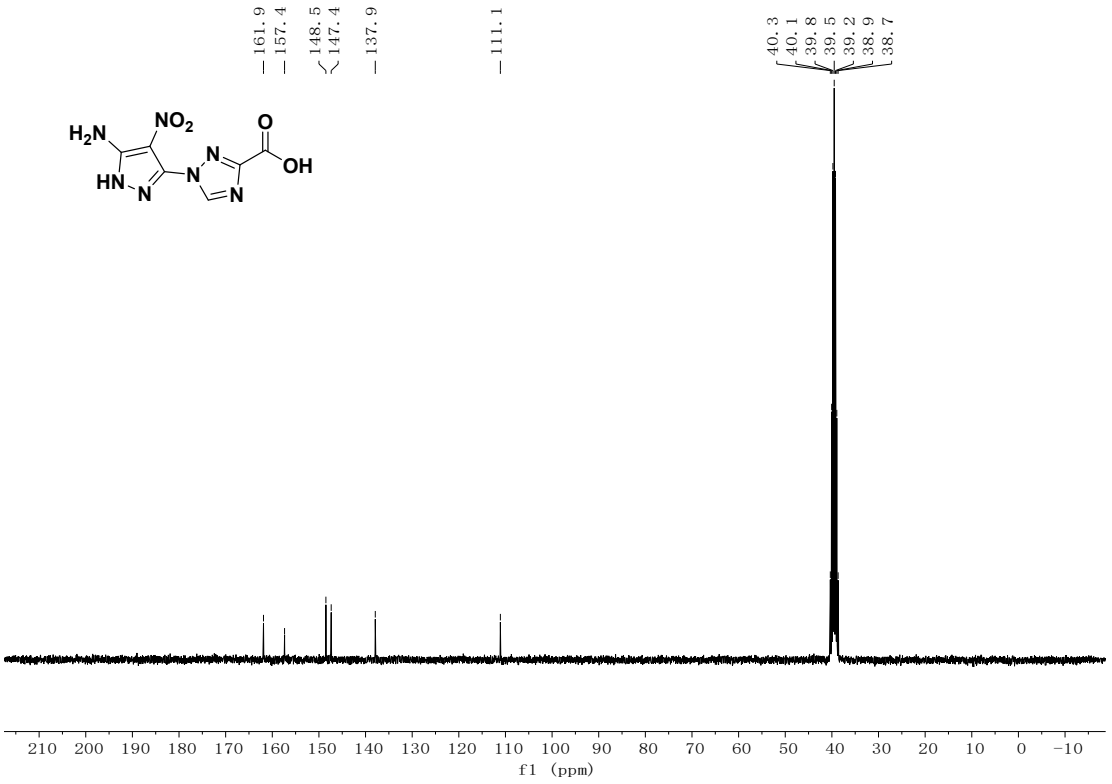


Fig. S16 ^{13}C NMR spectrum of **5b**.

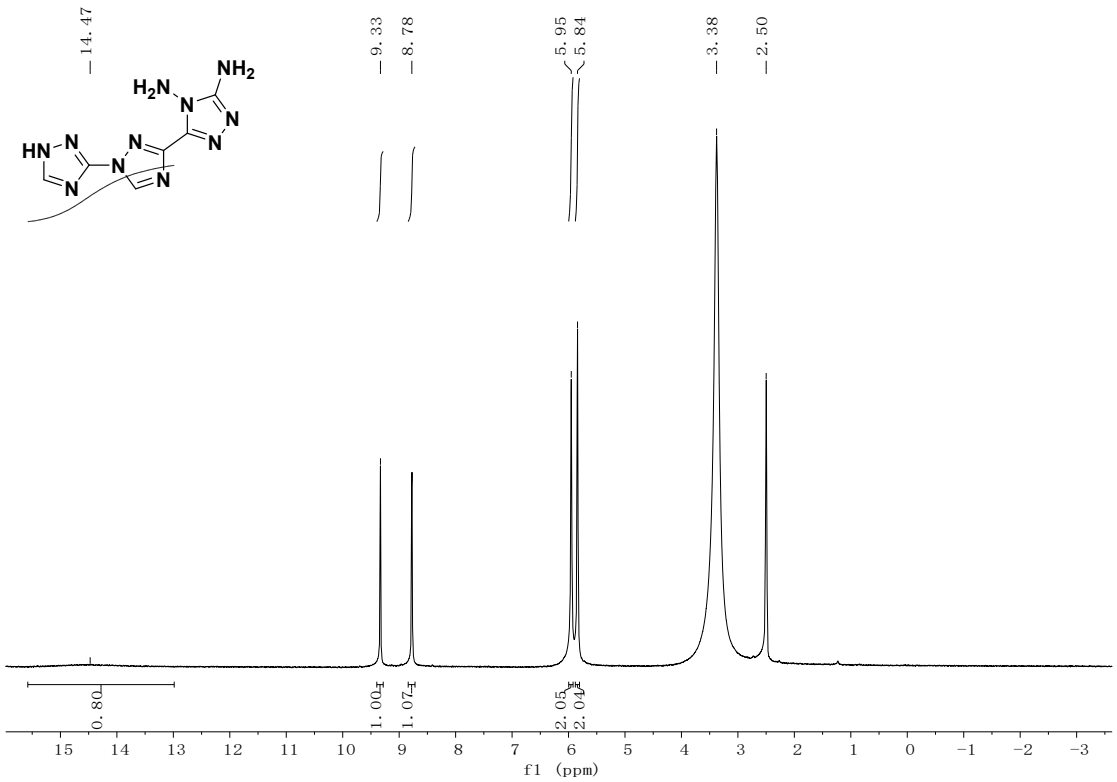


Fig. S17 ^{1}H NMR spectrum of **2c**.

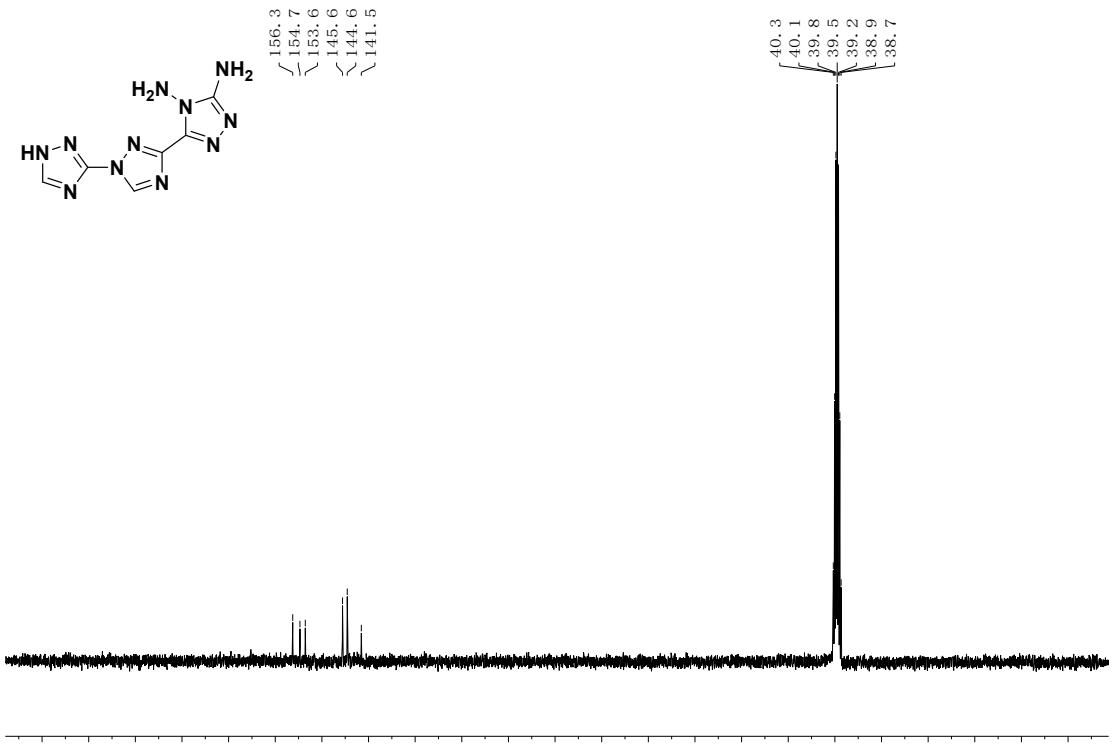


Fig. S18 ^{13}C NMR spectrum of **2c**.

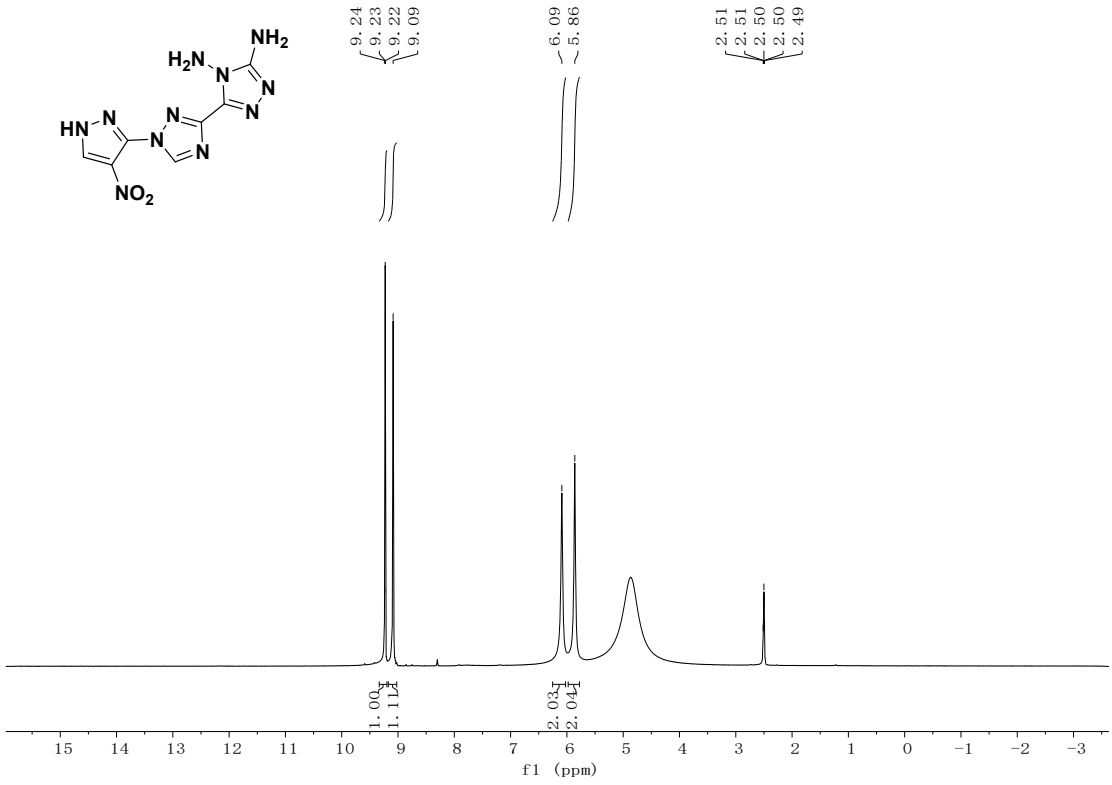


Fig. S19 ^{1}H NMR spectrum of **3c**.

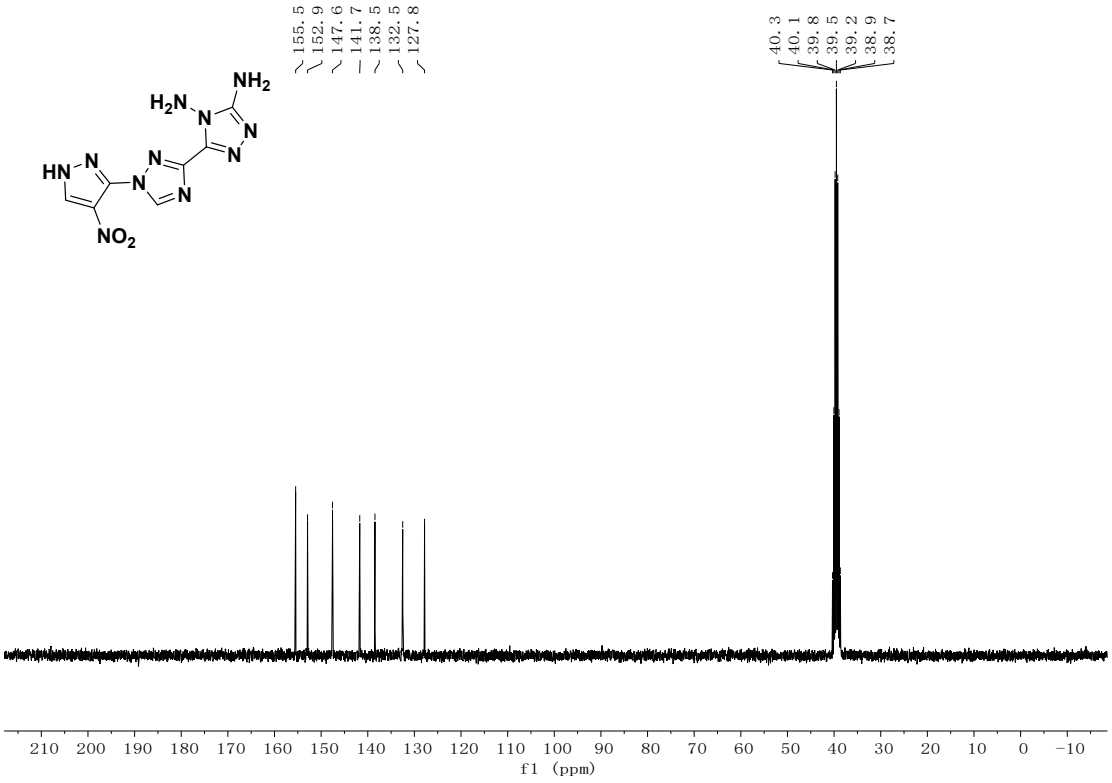


Fig. S20 ^{13}C NMR spectrum of **3c**.

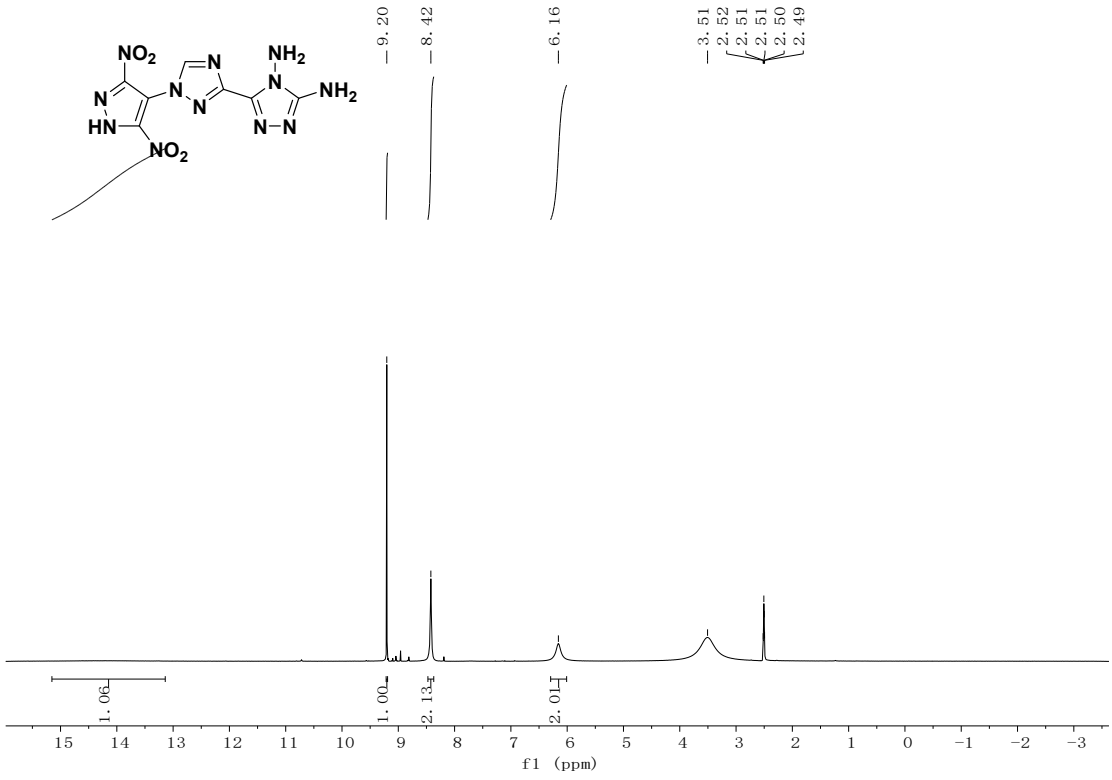


Fig. S21 ^{1}H NMR spectrum of **4c**.

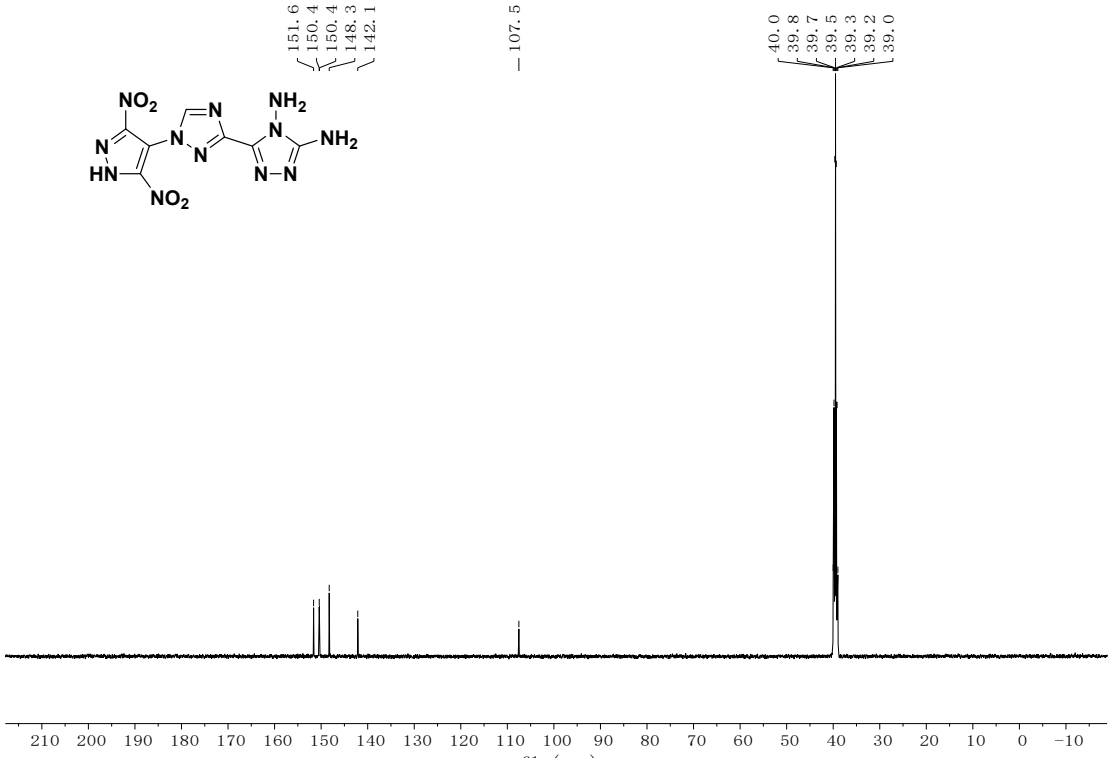


Fig. S22 ^{13}C NMR spectrum of **4c**.

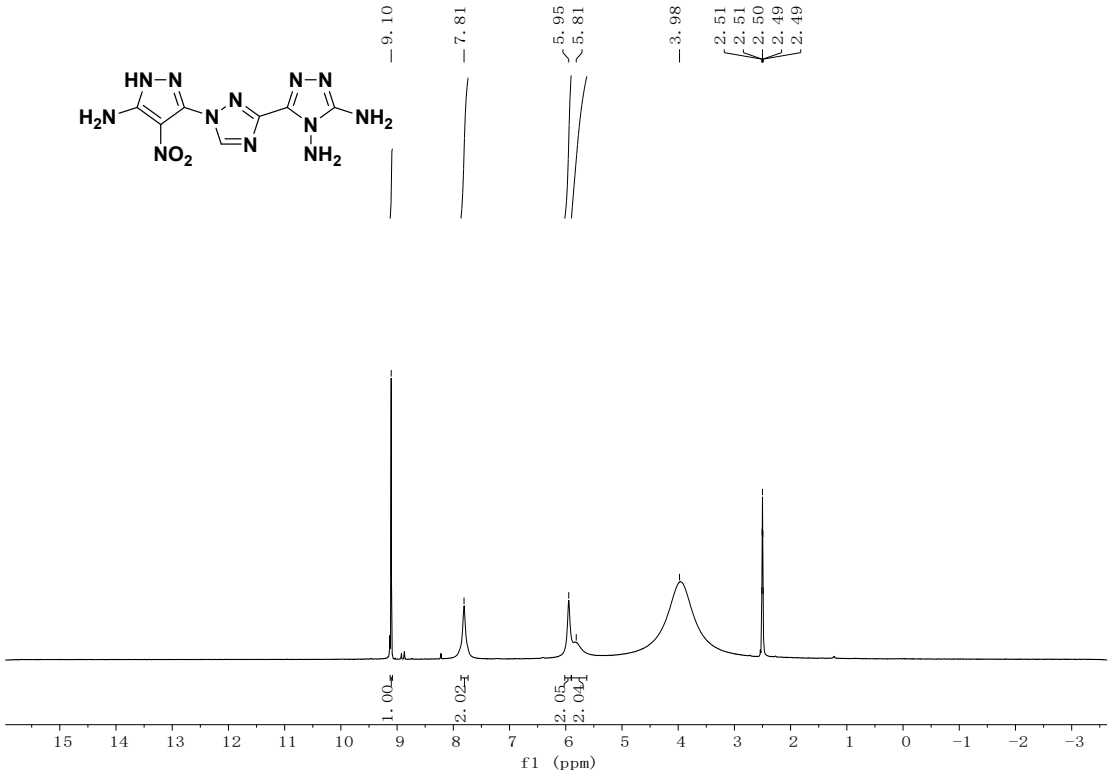


Fig. S23 ^{1}H NMR spectrum of **5c**.

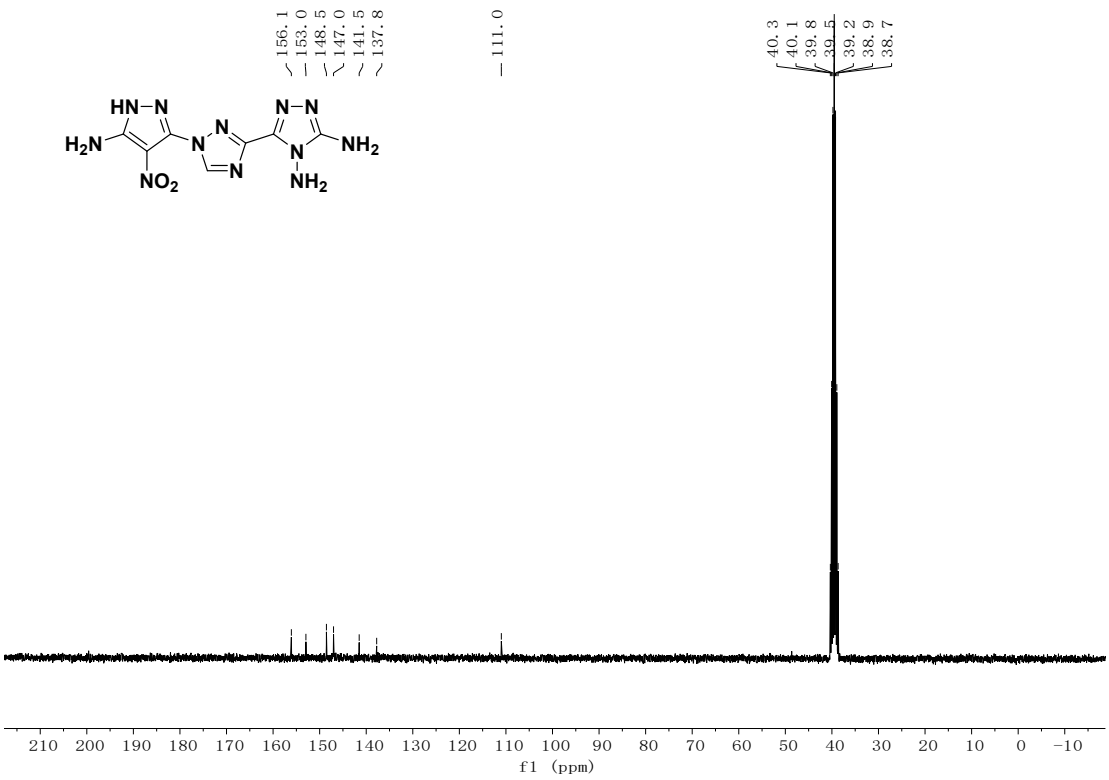


Fig. S24 ^{13}C NMR spectrum of **5c**.

5. The test of five-second (5s) delay exploding point

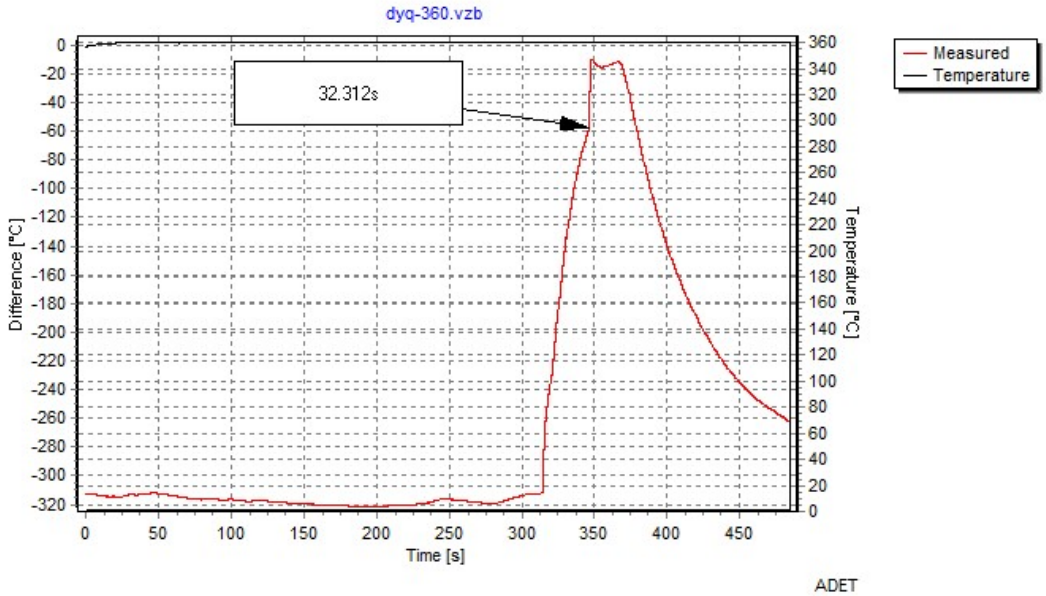


Fig. S25 The delay time of explosion of **4c** at 360 ° C.

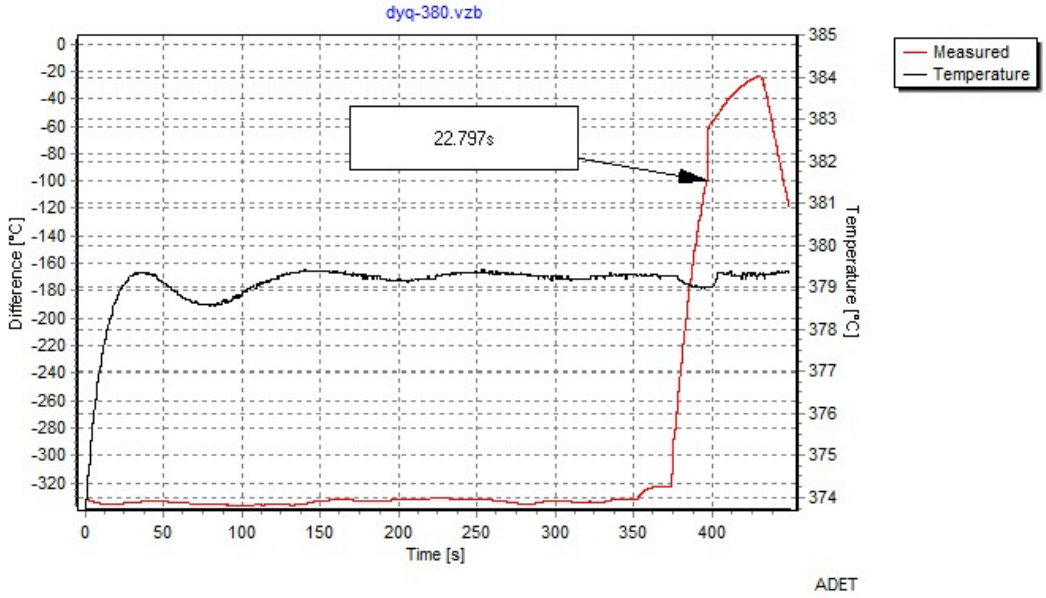


Fig. S26 The delay time of explosion of **4c** at 380 ° C.

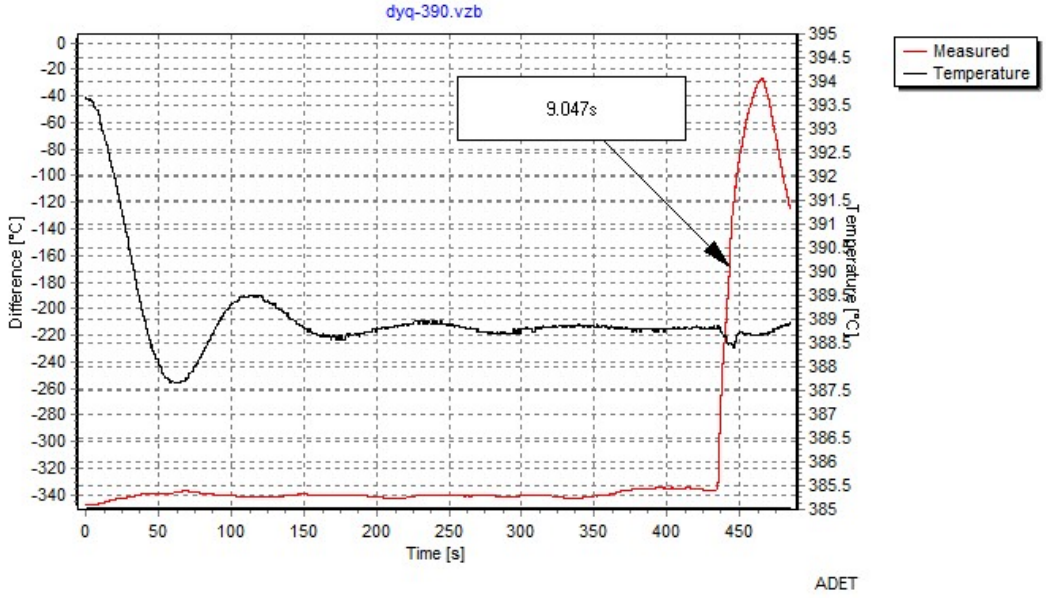


Fig. S27 The delay time of explosion of **4c** at 390 ° C.

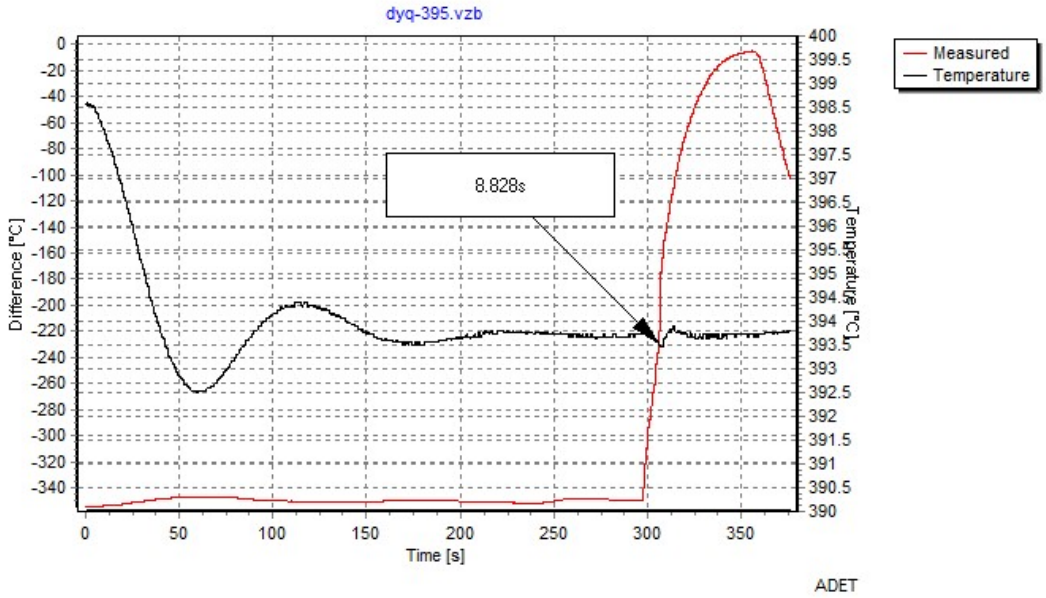


Fig. S28 The delay time of explosion of **4c** at 395 ° C.

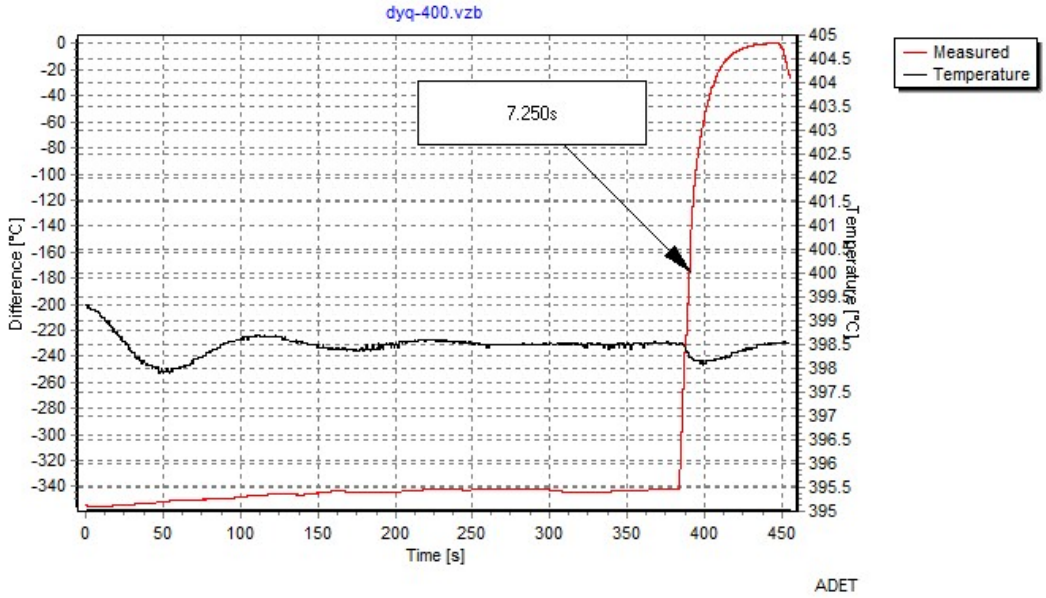


Fig. S29 The delay time of explosion of **4c** at 400 ° C.

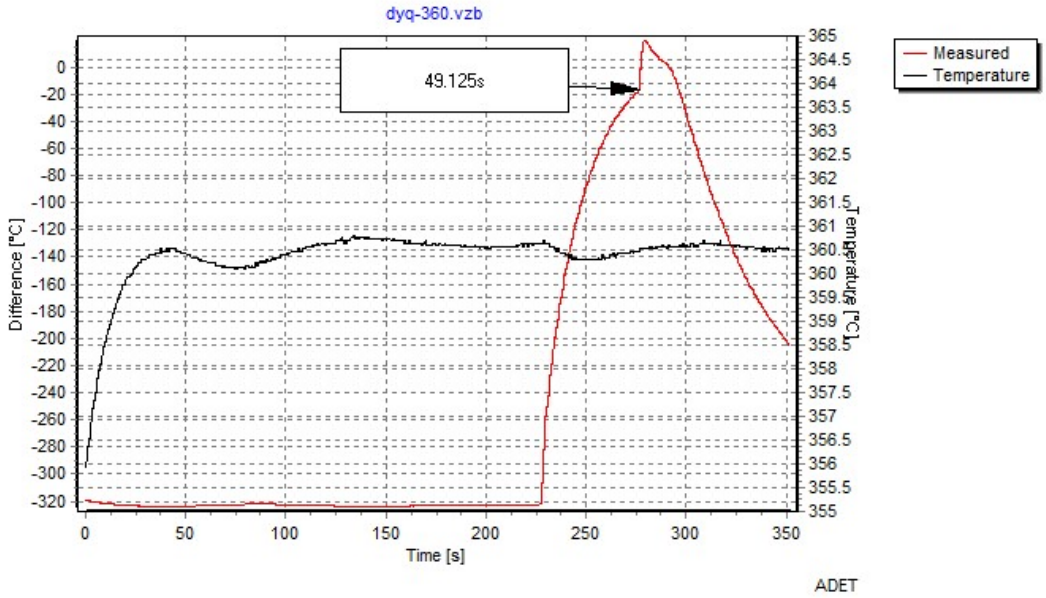


Fig. S30 The delay time of explosion of **5c** at 360 ° C.

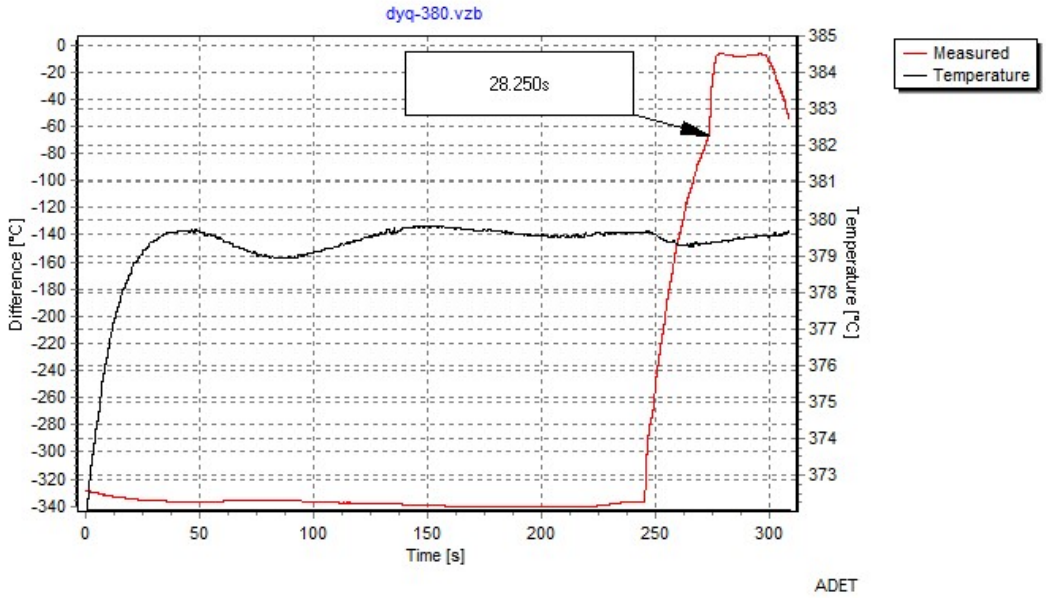


Fig. S31 The delay time of explosion of **5c** 380 ° C.

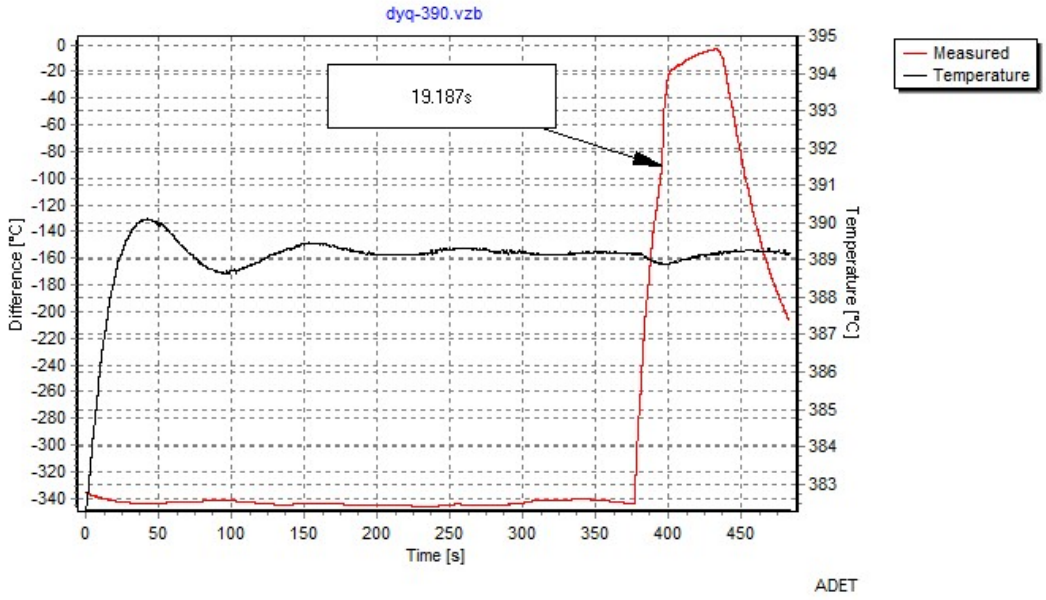


Fig. S32 The delay time of explosion of **5c** at 390 ° C.

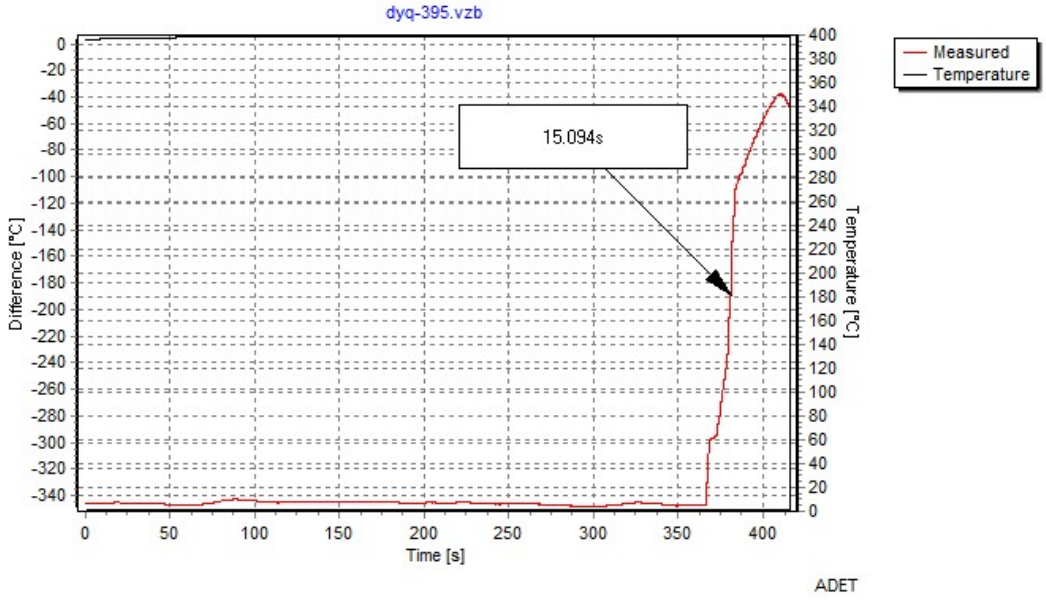


Fig. S33 The delay time of explosion of **5c** 395 ° C.

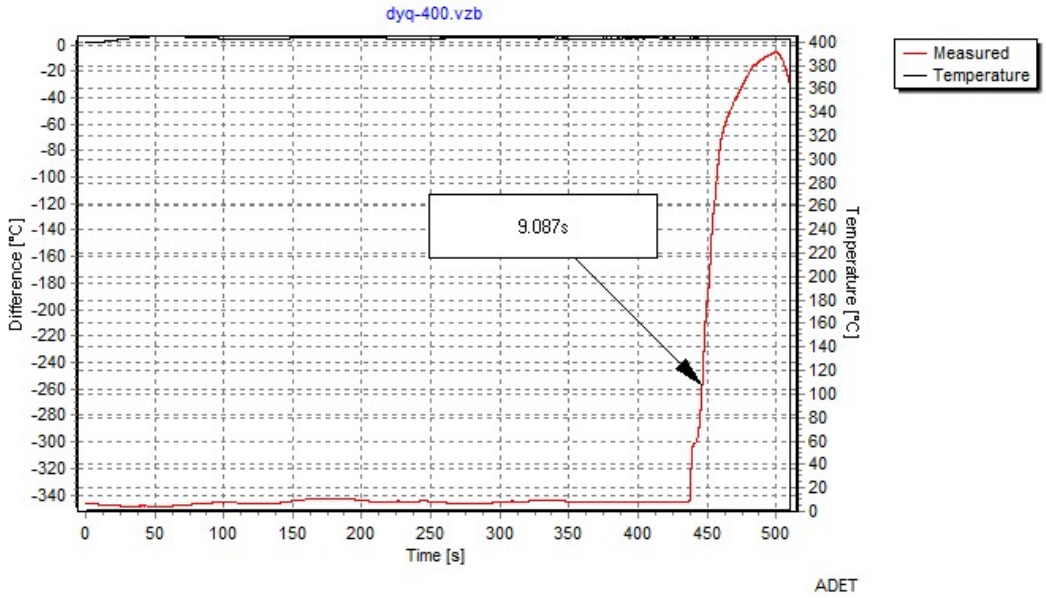


Fig. S34 The delay time of explosion of **5c** at 400 ° C.

6. DSC plots

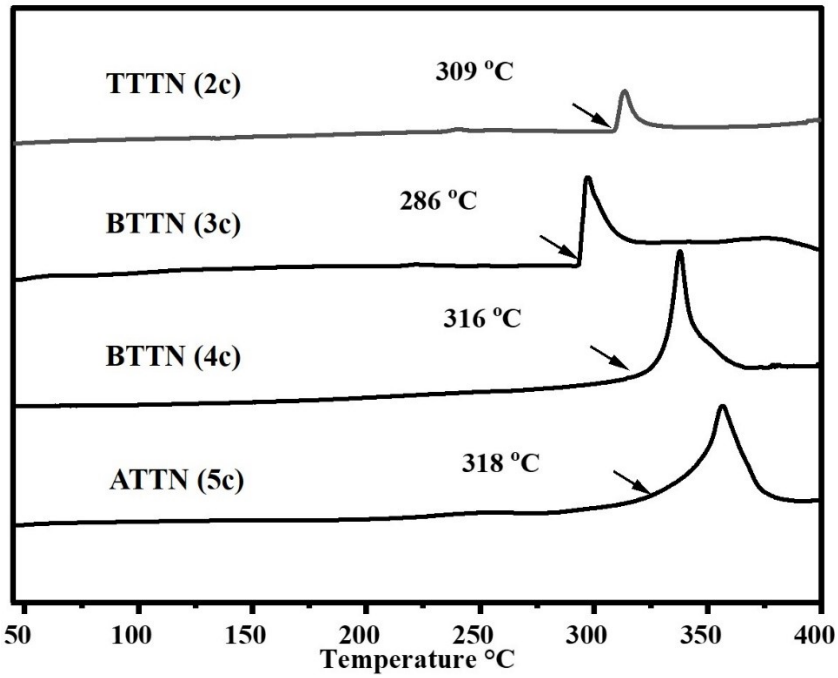


Fig. S35 DSC plots of TTTN (**2c**), BTTN (**3c**), DTTN (**4c**) and ATTN (**5c**)

7. The device image of the 5 s bursting point

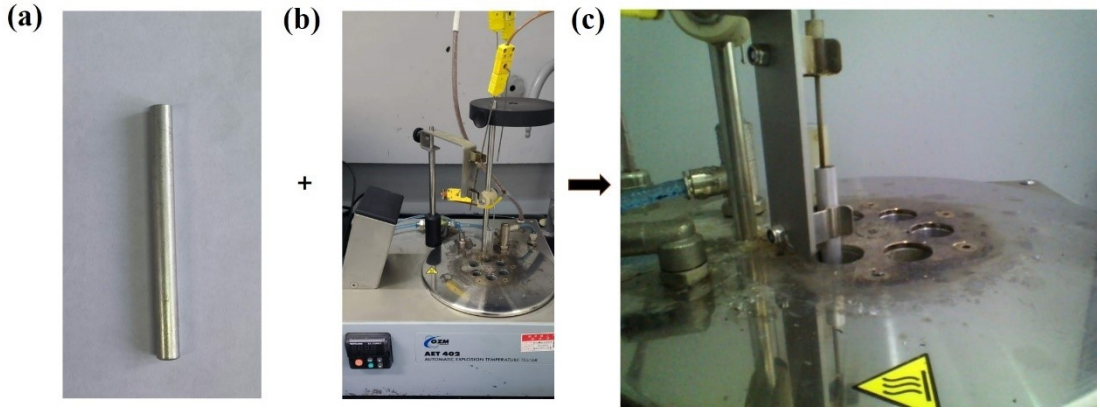


Fig. S36 (a) Aluminum tube for holding samples; (b) Heating module; (c) Diagram of the device before the sample was decomposed