Electronic Supplementary Information

One-Step Amino-to-Nitro Transformation of Carbonyl-Containing Fused-Ring Energetic Compounds in Nitric Acid

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1. X-ray crystallography

X-ray of all single crystals were carried out at 150 K or 170 K on a Bruker D8 VENTURE diffractometer using Mo-Kα radiation (λ = 0.71073Å). Integration and scaling of intensity data was performed using the SAINT program. Data were corrected for the effects of absorption using SADABS. The structures were solved by intrinsic phasing and and refined with full-matrix least-squares using ShelXL-2019 software. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were places in calculated positions and refined with riding model.

Table S1 Crystal data of **4**–**6**.

Compound	**4**	**5**	**6**
CCDC	2501547	2501548	2501549
Empirical formula	C5H6ClN9O5	C4H4N6O5	C4H11N7O7
Formula weight	307.64	216.13	269.20
Temperature	150 K	170 K	170 K
Crystal system	Orthorhombic	Monoclinc	Triclinic
Spance group	$P2_12_12_1$	$P2_1$/n	*P*-1
Unit cell dimensions	a = 7.8115 Å α= 90° b = 10.1175 Å β= 90° c = 13.4986 Å γ= 90°	a =11.1923 Å α = 90° b = 5.1853 Å β = 94.830(4)° c = 13.3376 Å γ = 90°	a = 6.5845 Å α = 67.746° b = 8.3838 Å β = 88.999° c = 10.3193 Å γ = 87.729°
Volume	1066.83 Å^3	771.30 Å^3	2843.6 Å^3
Z	4	4	2
Density(calculated)	1.915 g cm^{-3}	1.861 g cm^{-3}	1.697 g cm^{-3}
Crystal size	0.12 × 0.05 × 0.04	0.15 × 0.06 × 0.05	0.12× 0.06 × 0.04
Radiation	MoKα(λ=0.71073)	MoKα(λ=0.71073)	MoKα(λ=0.71073)
2θ range for date collection/°	5.032 to 52.694	4.566 to 52.722	5.254 to 52.73
Index ranges	-8 ⩽ h ⩽ 9, -12 ⩽ k ⩽ 11, -16 ⩽ l ⩽ 16	-13 ⩽ h ⩽ 13, 0 ⩽ k ⩽ 6, 0 ⩽ l ⩽ 16	-8 ⩽ h ⩽ 8, -9 ⩽ k ⩽ 10, -12 ⩽ l ⩽ 12
Reflections collected	8345	1491	5802
Independent reflections	2168 [R_{int} = 0.0837, R_{sigma} = 0.0708]	1491 [R_{int} = 0, R_{sigma} = 0.0971]	2113 [R_{int} = 0.0809, R_{sigma} = 0.1002]
Data/restraints/parameters	2168/55/225	1491/0/142	2113/10/207
Goodness-of-fit on F^2	1.055	1.094	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0429, wR_2 = 0.0886	R_1 = 0.0766, wR_2 = 0.2203	R_1 = 0.0656, wR_2 = 0.1632
Final R indexes [all data]	R_1 = 0.0558, wR_2 = 0.0956	R_1 = 0.1215, wR_2 = 0.2610	R_1 = 0.1332, wR_2 = 0.2157
Largest diff. peak/hole / e Å^{-3}	0.36/-0.39	0.48/-0.47	0.36/-0.40

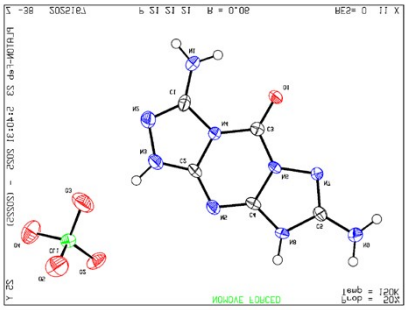


Figure S1. Single-crystal X-ray structures of **4**.

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **4**. *Ueq* is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	*U(eq)*
Cl1	3565(2)	10805(2)	4758(1)	24(1)
O1	6406(6)	3398(4)	2846(3)	23(1)
N6	8077(6)	5260(5)	2765(4)	20(1)
N7	9482(6)	4701(5)	2288(4)	20(1)
N4	5478(6)	5406(5)	3477(4)	20(1)
O2	4387(6)	11006(5)	3823(3)	36(1)
N8	9834(7)	6884(5)	2533(4)	22(1)
O5	4410(8)	11504(6)	5524(4)	51(2)
O3	3370(10)	9458(6)	5002(4)	64(2)
N1	3150(7)	3944(6)	3827(4)	27(1)
N5	7195(7)	7382(5)	3369(4)	24(1)
N3	4480(7)	7155(6)	4169(4)	29(1)
N9	12041(7)	5664(6)	1713(5)	30(1)
N2	3250(7)	6172(6)	4324(4)	31(1)
O4	1854(6)	11347(6)	4705(4)	49(1)
C4	8288(8)	6591(6)	2925(4)	21(1)
C5	10504(7)	5711(6)	2151(4)	22(1)
C2	5800(8)	6729(6)	3656(5)	22(1)
C1	3886(8)	5121(7)	3909(5)	25(1)
C3	6629(7)	4557(6)	3005(4)	19(1)

Table S3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **4**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
Cl1	23(1)	23(1)	24(1)	2(1)	0(1)	-2(1)
O1	23(2)	16(2)	29(2)	-4(2)	-1(2)	0(2)
N6	23(2)	10(2)	26(3)	2(2)	2(2)	2(2)
N7	17(2)	16(3)	26(3)	0(2)	2(2)	1(2)
N4	20(2)	18(3)	21(2)	0(2)	4(2)	0(2)

O2	33(3)	48(3)	25(2)	2(2)	10(2)	-12(2)
N8	23(2)	12(3)	30(3)	1(2)	3(2)	-3(2)
O5	54(3)	62(4)	36(3)	-14(3)	-1(2)	-15(3)
O3	105(5)	26(3)	62(4)	-1(3)	40(4)	-4(3)
N1	22(3)	28(4)	32(3)	0(3)	9(2)	-2(2)
N5	29(3)	16(3)	27(3)	2(2)	4(2)	4(2)
N3	37(3)	18(3)	33(3)	-1(2)	7(2)	2(2)
N9	26(3)	22(3)	42(3)	3(3)	9(2)	0(3)
N2	34(3)	27(3)	33(3)	1(2)	10(2)	3(2)
O4	27(2)	65(4)	56(3)	3(3)	-1(2)	7(2)
C4	26(3)	13(3)	24(3)	1(2)	-3(2)	-1(2)
C5	25(3)	17(3)	24(3)	1(3)	-1(2)	4(3)
C2	27(3)	13(3)	26(3)	-2(3)	-1(2)	3(2)
C1	22(3)	29(4)	24(3)	3(3)	7(2)	6(3)
C3	20(3)	19(3)	18(3)	2(2)	-3(2)	1(2)

Table S4 Bond Lengths for **4**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Cl1	O2	1.432(4)	N8	C5	1.396(8)
Cl1	O5	1.416(5)	N1	C1	1.327(9)
Cl1	O3	1.410(6)	N1	H1A	0.85(3)
Cl1	O4	1.446(5)	N1	H1B	0.87(3)
O1	C3	1.204(7)	N5	C4	1.314(8)
N6	N7	1.393(7)	N5	C2	1.332(8)
N6	C4	1.373(8)	N3	H3	0.8800
N6	C3	1.375(7)	N3	N2	1.398(8)
N7	C5	1.310(8)	N3	C2	1.315(8)
N4	C2	1.384(8)	N9	C5	1.339(8)
N4	C1	1.404(8)	N9	H9A	0.87(3)
N4	C3	1.398(7)	N9	H9B	0.87(3)
N8	H8	0.8800	N2	C1	1.300(8)
N8	C4	1.352(8)			

Table S5 Bond Angles for **4**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
O2	Cl1	O4	108.5(3)	C2	N3	H3	123.7
O5	Cl1	O2	111.3(3)	C2	N3	N2	112.6(5)
O5	Cl1	O4	106.2(4)	C5	N9	H9A	112(5)
O3	Cl1	O2	113.0(3)	C5	N9	H9B	116(5)
O3	Cl1	O5	111.3(4)	H9A	N9	H9B	131(7)
O3	Cl1	O4	106.2(4)	C1	N2	N3	104.8(5)
C4	N6	N7	112.1(5)	N8	C4	N6	105.1(5)
C4	N6	C3	124.7(5)	N5	C4	N6	126.2(6)
C3	N6	N7	123.1(5)	N5	C4	N8	128.7(6)

C5	N7	N6	103.2(5)	N7	C5	N8	112.5(5)
C2	N4	C1	106.7(5)	N7	C5	N9	125.5(6)
C2	N4	C3	123.9(5)	N9	C5	N8	122.0(6)
C3	N4	C1	129.3(5)	N5	C2	N4	125.3(6)
C4	N8	H8	126.5	N3	C2	N4	105.4(5)
C4	N8	C5	107.1(5)	N3	C2	N5	129.3(6)
C5	N8	H8	126.5	N1	C1	N4	122.2(6)
C1	N1	H1A	126(6)	N2	C1	N4	110.4(6)
C1	N1	H1B	119(4)	N2	C1	N1	127.2(6)
H1A	N1	H1B	109(7)	O1	C3	N6	125.6(5)
C4	N5	C2	111.3(5)	O1	C3	N4	125.9(6)
N2	N3	H3	123.7	N6	C3	N4	108.5(5)

Table S6 Torsion Angles for **4**.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
N6	N7	C5	N8	1.0(6)	C2	N4	C1	N1	176.4(6)
N6	N7	C5	N9	-180.0(6)	C2	N4	C1	N2	0.1(7)
N7	N6	C4	N8	0.9(6)	C2	N4	C3	O1	179.1(6)
N7	N6	C4	N5	-179.1(6)	C2	N4	C3	N6	0.1(7)
N7	N6	C3	O1	0.8(9)	C2	N5	C4	N6	-0.1(9)
N7	N6	C3	N4	179.7(5)	C2	N5	C4	N8	179.9(6)
N3	N2	C1	N4	-1.0(7)	C2	N3	N2	C1	1.6(8)
N3	N2	C1	N1	-177.0(6)	C1	N4	C2	N5	179.6(6)
N2	N3	C2	N4	-1.5(7)	C1	N4	C2	N3	0.8(7)
N2	N3	C2	N5	179.8(6)	C1	N4	C3	O1	3.4(10)
C4	N6	N7	C5	-1.2(6)	C1	N4	C3	N6	-175.6(6)
C4	N6	C3	O1	178.0(6)	C3	N6	N7	C5	176.3(5)
C4	N6	C3	N4	-3.1(8)	C3	N6	C4	N8	-176.6(5)
C4	N8	C5	N7	-0.6(7)	C3	N6	C4	N5	3.4(10)
C4	N8	C5	N9	-179.6(6)	C3	N4	C2	N5	3.1(9)
C4	N5	C2	N4	-2.9(9)	C3	N4	C2	N3	-175.7(5)
C4	N5	C2	N3	175.6(6)	C3	N4	C1	N1	-7.4(10)
C5	N8	C4	N6	-0.2(6)	C3	N4	C1	N2	176.4(6)
C5	N8	C4	N5	179.8(6)					

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4**.

Atom	**x**	**y**	**z**	***U(eq)***
H8	10325	7666	2521	26
H3	4381	7970	4391	35
H9A	12280(100)	4880(40)	1480(60)	40(20)
H1A	2280(70)	3680(80)	4160(50)	40(20)

H9B	12590(90)	6410(40)	1670(60)	30(20)
H1B	3780(70)	3260(40)	3670(40)	11(15)

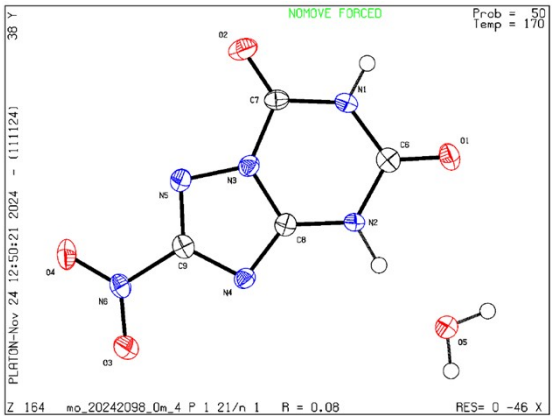


Figure S2. Single-crystal X-ray structures of **5**.

Table S8 Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times10^3$) for **4**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	**x**	**y**	**z**	***U(eq)***
O3	7810(3)	3872(6)	4551(3)	27(1)
O5	3761(3)	11196(6)	5936(3)	24(1)
O2	5633(3)	569(6)	8547(2)	27(1)
O1	3154(3)	7471(6)	7878(2)	24(1)
O4	8412(3)	688(6)	5514(3)	29(1)
N4	6236(3)	5456(7)	5855(3)	18(1)
N3	5935(3)	3287(7)	7234(3)	18(1)
N2	4663(3)	6819(7)	6869(3)	18(1)
N6	7800(3)	2596(7)	5316(3)	20(1)
N5	6833(4)	1958(7)	6829(3)	21(1)
N1	4395(4)	4022(7)	8216(3)	23(1)
C6	4003(4)	6205(9)	7675(3)	19(1)
C8	5587(4)	5323(8)	6637(3)	18(1)
C9	6946(4)	3362(9)	6034(3)	19(1)
C7	5341(4)	2438(9)	8064(3)	19(1)

Table S9 Anisotropic Displacement Parameters ($Å^2\times10^3$) for **5**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U11**	**U22**	**U33**	**U23**	**U13**	**U12**
O3	27(2)	32(2)	23(2)	3(2)	6(2)	3(2)
O5	24(2)	24(2)	26(2)	5(2)	6(2)	4(2)
O2	27(2)	27(2)	27(2)	10(2)	-2(2)	-1(2)
O1	19(2)	26(2)	28(2)	-3(2)	7(2)	2(2)

O4	27(2)	26(2)	34(2)	-5(2)	7(2)	10(2)
N4	17(2)	18(2)	18(2)	3(2)	0(2)	1(2)
N3	16(2)	19(2)	20(2)	3(2)	0(2)	1(2)
N2	19(2)	20(2)	15(2)	4(2)	4(2)	2(2)
N6	22(2)	21(2)	19(2)	-5(2)	4(2)	1(2)
N5	21(2)	20(2)	21(2)	1(2)	2(2)	4(2)
N1	24(2)	26(2)	21(2)	7(2)	9(2)	3(2)
C6	15(2)	22(2)	19(2)	-4(2)	-3(2)	-5(2)
C8	16(2)	16(2)	21(2)	-2(2)	0(2)	-2(2)
C9	16(2)	20(2)	20(2)	-4(2)	1(2)	-3(2)
C7	20(2)	20(2)	16(2)	2(2)	-1(2)	-3(2)

Table S10 Bond Lengths for **5**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
O3	N6	1.217(5)	N3	C7	1.408(6)
O5	H5A	0.8700	N2	C6	1.392(6)
O5	H5B	0.8699	N2	C8	1.349(6)
O2	C7	1.194(5)	N2	H2	0.98(6)
O1	C6	1.204(5)	N6	C9	1.464(6)
O4	N6	1.220(5)	N5	C9	1.301(6)
N4	C8	1.323(5)	N1	H1	0.8800
N4	C9	1.354(6)	N1	C6	1.394(6)
N3	N5	1.367(5)	N1	C7	1.369(6)
N3	C8	1.359(6)			

Table S11 Bond Angles for **5**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
H5A	O5	H5B	104.5	C7	N1	C6	128.7(4)
C8	N4	C9	99.9(4)	O1	C6	N2	121.9(4)
N5	N3	C7	124.4(4)	O1	C6	N1	123.1(4)
C8	N3	N5	110.1(3)	N2	C6	N1	114.9(4)
C8	N3	C7	124.9(4)	N4	C8	N3	110.7(4)
C6	N2	H2	121(3)	N4	C8	N2	129.3(4)
C8	N2	C6	120.8(4)	N2	C8	N3	120.0(4)
C8	N2	H2	118(3)	N4	C9	N6	120.5(4)
O3	N6	O4	125.3(4)	N5	C9	N4	119.7(4)
O3	N6	C9	117.0(4)	N5	C9	N6	119.7(4)
O4	N6	C9	117.7(4)	O2	C7	N3	123.6(4)
C9	N5	N3	99.5(4)	O2	C7	N1	125.9(4)
C6	N1	H1	115.7	N1	C7	N3	110.5(4)
C7	N1	H1	115.7				

Table S12 Torsion Angles for **5**.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**

O3	N6	C9	N4	-2.2(6)	C8	N4	C9	N6	176.4(4)
O3	N6	C9	N5	174.9(4)	C8	N4	C9	N5	-0.7(6)
O4	N6	C9	N4	-179.7(4)	C8	N3	N5	C9	0.9(5)
O4	N6	C9	N5	-2.6(6)	C8	N3	C7	O2	176.3(4)
N3	N5	C9	N4	-0.1(5)	C8	N3	C7	N1	-2.8(6)
N3	N5	C9	N6	-177.3(4)	C8	N2	C6	O1	-177.9(4)
N5	N3	C8	N4	-1.5(5)	C8	N2	C6	N1	1.7(6)
N5	N3	C8	N2	176.4(4)	C9	N4	C8	N3	1.2(5)
N5	N3	C7	O2	6.4(7)	C9	N4	C8	N2	-176.4(5)
N5	N3	C7	N1	-172.8(4)	C7	N3	N5	C9	172.2(4)
C6	N2	C8	N4	173.0(4)	C7	N3	C8	N4	-172.6(4)
C6	N2	C8	N3	-4.5(6)	C7	N3	C8	N2	5.2(7)
C6	N1	C7	O2	-179.3(5)	C7	N1	C6	O1	-179.8(5)
C6	N1	C7	N3	-0.1(7)	C7	N1	C6	N2	0.6(7)

Table S13 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **5**.

Atom	**x**	**y**	**z**	***U(eq)***
H5A	3746	12083	5382	37
H5B	3131	11710	6221	37
H1	3979	3607	8724	28
H2	4400(50)	8190(110)	6400(40)	51(18)

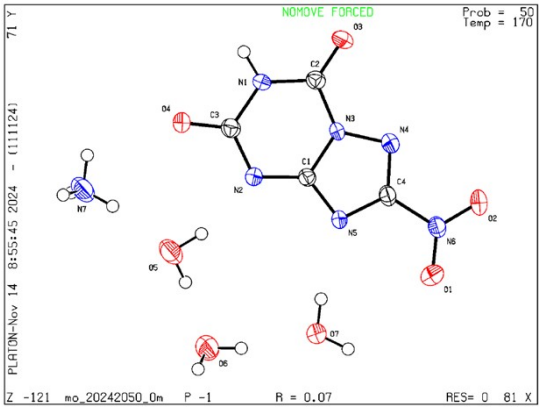


Figure S3. Single-crystal X-ray structures of **6**.

Table S14 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **6**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	**x**	**y**	**z**	***U(eq)***
O4	4370(4)	8148(3)	6407(3)	29(1)
O3	3639(5)	9246(3)	1767(3)	32(1)
O7	1228(5)	842(4)	7267(3)	34(1)
O1	677(5)	1605(4)	3949(3)	34(1)

O6	839(5)	1695(4)	9658(3)	43(1)
N3	2788(5)	6625(4)	3423(3)	22(1)
O5	3372(5)	4425(4)	8817(3)	42(1)
N5	2005(5)	4012(4)	4874(3)	22(1)
O2	1014(6)	3320(4)	1784(3)	46(1)
N1	3954(5)	8682(4)	4108(3)	22(1)
N2	3144(5)	5984(4)	5868(3)	24(1)
N6	1099(5)	2966(4)	3038(3)	26(1)
N4	2214(5)	5830(4)	2558(3)	26(1)
N7	3232(8)	7413(6)	9475(4)	42(1)
C2	3480(6)	8293(5)	2988(4)	23(1)
C1	2655(6)	5523(5)	4808(4)	21(1)
C3	3826(6)	7590(5)	5511(4)	25(1)
C4	1796(6)	4309(5)	3498(4)	24(1)

Table S15 Anisotropic Displacement Parameters ($Å^2×10^3$) for **6**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka*b*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
O4	39(2)	28(2)	23(2)	-12(1)	-1(1)	-7(1)
O3	42(2)	29(2)	20(2)	-3(1)	0(1)	-9(1)
O7	49(2)	29(2)	25(2)	-11(1)	4(1)	-9(1)
O1	38(2)	28(2)	38(2)	-13(1)	1(1)	-6(1)
O6	58(3)	38(2)	32(2)	-12(2)	-4(2)	2(2)
N3	30(2)	22(2)	14(2)	-7(1)	-1(1)	-3(1)
O5	50(2)	50(2)	24(2)	-10(2)	2(2)	-7(2)
N5	30(2)	21(2)	17(2)	-9(1)	-1(1)	-2(1)
O2	73(3)	47(2)	26(2)	-21(2)	-2(2)	-14(2)
N1	28(2)	20(2)	17(2)	-4(1)	2(1)	-5(1)
N2	30(2)	21(2)	20(2)	-9(1)	-1(1)	-3(1)
N6	30(2)	29(2)	21(2)	-11(2)	-1(1)	1(2)
N4	31(2)	26(2)	19(2)	-9(1)	-2(1)	-1(1)
N7	56(3)	43(3)	23(2)	-8(2)	-2(2)	3(2)
C2	24(2)	22(2)	22(2)	-7(2)	1(2)	1(2)
C1	22(2)	21(2)	19(2)	-8(2)	1(2)	0(2)
C3	30(2)	23(2)	23(2)	-9(2)	4(2)	1(2)
C4	29(2)	26(2)	19(2)	-10(2)	-3(2)	2(2)

Table S16 Bond Lengths for **6**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O4	C3	1.247(5)	N5	C4	1.354(5)
O3	C2	1.216(5)	O2	N6	1.216(4)
O7	H7E	0.872(19)	N1	C2	1.359(5)
O7	H7F	0.87(2)	N1	C3	1.392(5)
O1	N6	1.210(4)	N1	H1	0.88(5)

O6	H6A	0.90(2)	N2	C1	1.339(5)
O6	H6B	0.89(2)	N2	C3	1.348(5)
N3	N4	1.366(4)	N6	C4	1.469(5)
N3	C2	1.390(5)	N4	C4	1.313(5)
N3	C1	1.380(5)	N7	H7A	0.882(19)
O5	H5A	0.898(19)	N7	H7B	0.88(2)
O5	H5B	0.88(2)	N7	H7C	0.88(2)
N5	C1	1.330(5)	N7	H7D	0.87(2)

Table S17 Bond Angles for **6**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
H7E	O7	H7F	109(5)	H7A	N7	H7D	98(5)
H6A	O6	H6B	91(6)	H7B	N7	H7C	118(8)
N4	N3	C2	125.4(3)	H7B	N7	H7D	109(5)
N4	N3	C1	110.8(3)	H7C	N7	H7D	104(8)
C1	N3	C2	123.8(3)	O3	C2	N3	123.7(4)
H5A	O5	H5B	95(5)	O3	C2	N1	125.6(4)
C1	N5	C4	101.1(3)	N1	C2	N3	110.7(3)
C2	N1	C3	126.3(4)	N5	C1	N3	109.2(3)
C2	N1	H1	119(3)	N5	C1	N2	128.0(3)
C3	N1	H1	115(3)	N2	C1	N3	122.7(3)
C1	N2	C3	116.1(3)	O4	C3	N1	117.8(4)
O1	N6	O2	126.3(4)	O4	C3	N2	121.9(4)
O1	N6	C4	116.7(3)	N2	C3	N1	120.3(3)
O2	N6	C4	117.0(3)	N5	C4	N6	121.2(3)
C4	N4	N3	99.5(3)	N4	C4	N5	119.4(3)
H7A	N7	H7B	102(5)	N4	C4	N6	119.4(3)
H7A	N7	H7C	124(8)				

Table S18 Torsion Angles for **6**.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
O1	N6	C4	N5	1.7(5)	C2	N1	C3	N2	-1.2(6)
O1	N6	C4	N4	-177.9(4)	C1	N3	N4	C4	-0.4(4)
N3	N4	C4	N5	0.7(5)	C1	N3	C2	O3	178.3(4)
N3	N4	C4	N6	-179.7(3)	C1	N3	C2	N1	-1.3(5)
O2	N6	C4	N5	-177.8(4)	C1	N5	C4	N6	179.7(3)
O2	N6	C4	N4	2.6(6)	C1	N5	C4	N4	-0.6(5)
N4	N3	C2	O3	0.5(6)	C1	N2	C3	O4	-178.3(4)
N4	N3	C2	N1	-179.0(3)	C1	N2	C3	N1	1.2(6)
N4	N3	C1	N5	0.0(4)	C3	N1	C2	O3	-178.4(4)
N4	N3	C1	N2	179.6(3)	C3	N1	C2	N3	1.2(5)
C2	N3	N4	C4	177.6(4)	C3	N2	C1	N3	-1.4(6)
C2	N3	C1	N5	-178.0(3)	C3	N2	C1	N5	178.0(4)
C2	N3	C1	N2	1.6(6)	C4	N5	C1	N3	0.3(4)

C2	N1	C3	O4	178.3(4)	C4	N5	C1	N2	-179.2(4)\

Table S19 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **6**.

Atom	x	y	z	*U(eq)*
H7E	940(70)	90(50)	6900(50)	42(14)
H5A	2540(60)	3540(40)	9020(40)	29(12)
H7A	4330(50)	7140(60)	10000(40)	40(14)
H7B	3200(90)	6570(50)	9170(60)	68(19)
H1	4460(80)	9700(70)	3960(50)	44(14)
H7F	1510(90)	1820(50)	6590(50)	80(20)
H6A	1050(100)	1250(80)	9000(50)	90(20)
H7C	2080(90)	7770(140)	9720(120)	200(50)
H6B	1660(80)	880(60)	10240(50)	80(20)
H7D	3690(70)	8330(40)	8810(40)	49(15)
H5B	3340(100)	4680(90)	7900(20)	90(20)

2. Experimental

Caution! Proper safety precautions should be taken during the preparation, characterization, and handling of energetic materials. Lab personnel should be properly grounded. All the reactions and performance testing of the prepared materials were conducted in a protected fume hood and behind a safety shield. Face shields and leather gloves must be used.

General methods

All reagents were purchased from Energy Chemical or Aladdin in analytical grade. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE 400 nuclear magnetic resonance spectrometer. DMSO-d6 was employed as a solvent and locking solvent. The onset decomposition temperature was measured using a TA Instruments DSC25 differential scanning calorimeter at a heating rate of 10 °C min^{-1} under dry nitrogen atmosphere. Infrared (IR) spectra were recorded on an FT-IR spectrometer (Thermo Nicolet AVATAR 370). Elemental analyses (C, H, N) were performed on a Vario Micro cube Elementar Analyzer. Impact and friction sensitivity measurements were made using a standard BAM Fallhammer and a BAM friction tester.

4,6-dihydrazineyl-1,3,5-triazin-2(1H)-one (2): Compound **1** (2.0 g, 15.7 mmol) was

added dropwise to a solution of 85% hydrazine hydrate (24 mL). The mixture was stirred for 12 h at 120 ℃. The precipitate was filtered off, washed with MeOH, and dried to afford compound **2** as white solid. (1.62 g, 65.9%). IR (KBr): $\tilde{\nu}$ = 2917(s), 1682(s), 1619(s), 1514(s), 1381(s), 1184(s), 1127(w), 1061(m), 974(s), 941(s), 869(w), 975(m) cm^{-1}; Anal. calcd. For C3H7N7O: C 22.93; H 4.49; N 62.40; found: C 23.07; H 4.55; N 62.23.

3,8-diamino-1H,5H-bis([1,2,4]triazolo)[1,5-a:3',4'-d][1,3,5]triazin-5-one (3): Compound **2** (1.57 g, 10 mmol) was dissolved in 1M HCl (80 mL), and cyanogen bromide (5.4 g, 50 mmol) was added. The mixture was stirred for 24 h. The precipitate was filtered off, washed with ethanol (20 mL) and dried in the air to yield **3** (white solid, 1.2 g, 60%). T_d (onset): 276 ℃. 1H NMR (400 MHz, DMSO-d6): δ = 12.36 (br, 1H), 6.71 (s, 2H), 6.00 (s, 2H) ppm; 13C NMR (100 MHz, DMSO-d6): δ = 166.44, 159.19, 149.24, 146.24, 140.02 ppm; IR (KBr): $\tilde{\nu}$ = 3213(s), 1644(s), 1537(w), 1513(m), 1429 (w), 1082(w), 798(w) cm^{-1}; Anal. calcd. For C5H5N9O: C 28.99; H 2.43; N 60.85; found: C 29.00; H 2.50; N 59.99.

Perchlorate 3,8-diamino-5-oxo-1H,5H-bis([1,2,4]triazolo)[1,5-a:3',4'-d][1,3,5]triazin-9-ium (4): A suspension of **3** (0.206 g, 1.0 mmol) in deionized water (6 mL) and perchloric acid (70 wt %, 6 mL) was mixed in portions. The solution was stirred for another 1 h at room temperature and filtered to obtain a white solid **4** (0.122 g, 30%). T_d (onset): 182 ℃. 1H NMR of **4** (400 MHz, DMSO-d6): δ = 12.68 (s, 1H), 9.86 (s, 1H), 8.60 (s, 2H), 8.84 (s, 2H) ppm; 13C NMR of **4** (100 MHz, DMSO-d6): δ = 166.45, 159.20, 149.24,1146.25,140.01 ppm; IR (KBr): $\tilde{\nu}$ = 3152(s), 1767(w), 1662(s), 1646(s), 1498(s), 1269(m), 1051(s), 953(w), 834(s) cm^{-1}; Anal. calcd. For C5H6ClN9O5: C 19.52; H 1.97; N 40.98; found: C 20.20; H 2.01; N 40.62.

2-nitro-[1,2,4]triazolo[1,5-a][1,3,5]triazine-5,7(4H,6H)-dione (5): Compound **3** (0.41 g, 2 mmol) was added into fuming nitric acid (4 mL) in the ice bath. Then the reaction solution was slowly restored to environment temperature and continued to stir for 24 h. The yellow rreaction solution was quenched with ice water and stirred at room temperature for 1 h. At the end of the reaction, the mixed solution was extracted with ethyl acetate, the ethyl acetate phase was dried over $MgSO_4$, and ethyl acetate was

removed by rotary evaporation to get solid **5** (0.21 g, 52%). T_d (onset): 265 °C. 1H NMR of **5** (400 MHz, DMSO-d6): δ = 12.45 (s, H) ppm; 13C NMR of **5** (100 MHz, DMSO-d6): δ = 162.50, 156.66, 145.47, 143.98 ppm; IR (KBr): ῡ = 3088(s), 1714(w), 1645(s), 1512(s), 1080(w), 985(s), 894(w), 852(s) cm^{-1}; Anal. calcd. For C4H2N6O4: C 24.25; H 1.02; N 42.42; found: C 24.10; H 1.09; N 42.44.

Ammonium 2-nitro-5,7-dioxo-6,7-dihydro-5H-[1,2,4]triazolo[1,5-a][1,3,5]triazin-4-ide (6): A clear solution was obtained by adding compound **5** (0.20 g, 1 mmol) to methanol. Next, 2 mL of ammonium hydroxide was added to the reaction solution. With the addition of ammonium hydroxide, solids precipitate from the reaction solution. The solid was collected by simply filtration and subsequently washed with 4 mL of ether to acquire the compound **6** (0.18 g, 85%). T_d (onset): 237 °C. 1H NMR of **6** (400 MHz, DMSO-d6): δ = 10.84 (br, 1H), 7.08 (s, 4H) ppm; 13C NMR of **6** (100 MHz, DMSO-d6): δ = 162.93, 156.51, 152.64, 146.53 ppm; IR (KBr): ῡ = 2979(s), 1729(m), 1646(m), 1551(s), 1508(w), 1392(s), 1311(s), 1193(w), 871(s), 837(w) cm^{-1}; Anal. calcd. For C4H5N7O4: C 22.33; H 2.34; N 45.58; found: C 23.10; H 2.58; N 45.30.

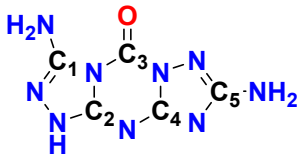
3. Theoretical calculations

3.1 Aromaticity

NICS[1] and ICSS[2] were computed at B3LYP-D3(BJ)/6-31G**[3]level by Gaussian 09 E.01 program[4]. All other wavefunction analyses were finished by Multiwfn 3.8(dev)[5], and isosurface maps were rendered by VMD 1.9.3 program[6] based on the outputs of Multiwfn.

3.2 ^{13}C NMR chemical shifts

^{13}C NMR chemical shifts were predicted with a literature method [7]. The geometry was optimized at B3LYP/6-31+G(d,p) level of theory in gas phase. Isotropic magnetic shielding constants were calculated at mPW1PW91/6-311+G(2d,p) level of theory with GIAO method in gas phase.



δ = (intercept – σ_{isot})/(-k)

(intercept = 182.2853, k = -1.0267)

Item	C1	C2	C3	C4	C5
σ_{isot}	41.83	36.72	30.76	72.13	46.77
Calculated δ_C	143.0	152.0	150.3	148.9	162.3
Measured δ_C	140.0	159.2	149.2	146.2	166.4

3.3 Enthalpy of Formation

The calculations of the heats of formation were carried out using Gaussian 09 (Revision E.01) suite of programs. All the compounds were determined using isodesmic reactions (Scheme S1). The geometry optimization and frequency analyses of the structures were calculated using B3LYP/6-31+G** level. Gas phase heats of formation of the title compounds were computed based on an isodesmic reaction. The enthalpy of reaction was carried out by combining the M062X/6-311++G** energy difference for the reactions, the scaled zero-point energies (ZPE), values of thermal correction (HT), and other thermal factors.[1,2] The solid-state heats of formation were obtained by employing Trouton's rule according to equation 1 (T represents either melting point or decomposition temperature when no melting occurs prior to decomposition).

$$\Delta Hsub = 188/J\ mol - 1\ K - 1 \times T \quad (1)$$

For energetic salts, the solid-phase heat of formation is calculated on basis of a Born-Haber energy cycle (Scheme S2). The number is simplified by equation 2:

$$\Delta H_f(\text{salt, 298 K}) = \Delta H_f(\text{cation, 298K}) + \Delta H_f(\text{anion, 298K}) - \Delta H_L \quad (2)$$

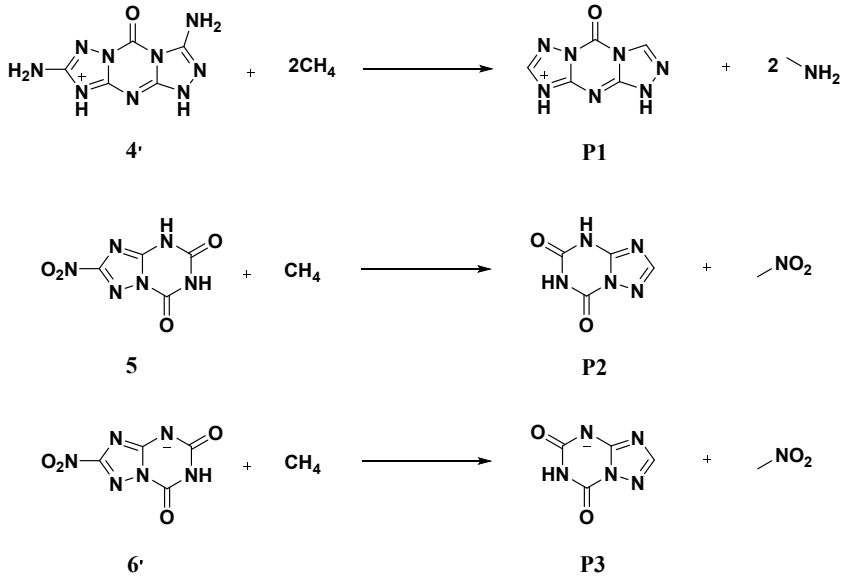
in which ΔH_L can be predicted by using the formula suggested by Jenkins, etal.(equation 3):

$$\Delta H_L = U_{pot} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (3)$$

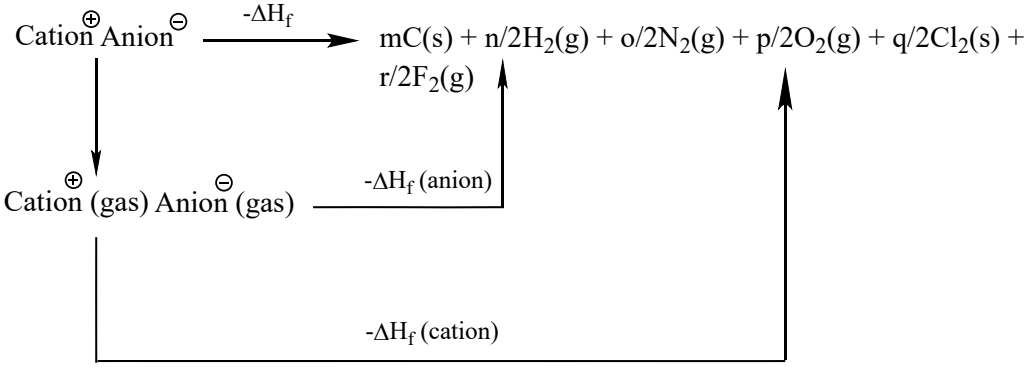
In this equation, n_M and n_X depend on the nature of the ions Mp^+ and Xq^-, respectively. The equation for lattice potential energy U_{pot}(equation 4) has the form:

$$U_{POT}\ [\text{kJ mol}^{-1}] = \gamma(\rho m/Mm)^{1/3} + \delta \quad (4)$$

where ρ_m [g cm^{-3}] is the density of the salt, Mm is the chemical formula mass of the ionic material, and values for g and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.



Scheme S1. Isodesmic reactions.



Scheme S7. Born−Haber Cycle for the formation of energetic salts.

Table S20 The scaled zero point energies (*ZPE*), values of thermal correction (H_{corr}), total energy (E_0) and heats of formation (*HOF*).

Species	*ZEP*	H^{corr}	E_0	*Corrected* E_0	*HOF(kJ* mol^{-1}*)*
4'	0.148576	0.16164	-762.0957815	-761.94008	427.95
5	0.095037	0.106385	-782.9762336	-782.87365	-122.23
6'	0.08058	0.091801	-782.3065141	-782.21794	108.01
P1	0.114124	0.124672	-651.3632546	-651.24315	484.26
P2	0.09312	0.101779	-578.4892665	-578.39121	-132.01
P3	0.078942	0.087402	-577.824815	-577.74057	84.92
CH_4	0.045214	0.049022	-40.5203022	-40.47309	-74.6
CH_3NH_2	0.064435	0.068758	-95.8575523	-95.79137	-23.5

Table S21 Calculated heat of formation for energetic salts.

Compound	ΔH_L(kJ mol^{-1})	ΔH_f^{cation}(kJ mol^{-1})	ΔH_f^{anion}(kJ mol^{-1})	ΔH_f^{298}(kJ mol^{-1})
4	473.2043244	427.9528833	307.7135581	262.462117
6	474.7406739	190.6349708	108.0140451	-176.0916581

Table S22 Cartesian coordinates of compound **4'**.

Atom	X	Y	Z
N	0.943665	0.456464	-0.21887
C	1.10784	-0.96258	-0.41604
N	0.105879	-1.83234	-0.05862
C	-1.05794	-1.26686	-0.02677
N	-1.30281	0.11109	-0.21799
C	-0.25411	1.078137	-0.10116
N	2.168343	1.105489	-0.00617
C	3.019129	0.119686	0.085849
N	2.462178	-1.13448	-0.01277
O	-0.47739	2.265567	0.085559
N	4.356424	0.300877	0.356442
N	-2.30501	-1.79174	0.146242
N	-3.2936	-0.79527	0.264844
C	-2.66318	0.318432	0.019386
N	-3.2119	1.561545	-0.09657
H	2.982868	-1.95917	-0.27449
H	4.988982	-0.31822	-0.13655
H	4.630503	1.273136	0.273062
H	-2.48144	-2.68162	0.586157
H	-2.54981	2.313717	0.075404
H	-4.1246	1.655279	0.328607

Table S23 Cartesian coordinates of compound **5**.

Atom	X	Y	Z
C	-2.71856	-0.77063	0.000005
N	-2.58214	0.624816	0.000174
C	-1.4311	1.411043	-0.000009
N	-0.28255	0.581175	-0.00116
C	-0.30032	-0.79201	-0.00056
N	-1.4986	-1.44398	-0.00051
N	1.009434	1.021238	-0.00071
C	1.652075	-0.12534	-0.00022
N	0.918197	-1.27631	-0.000029
O	-3.79019	-1.3289	0.000718
O	-1.41354	2.61074	0.000602
N	3.117854	-0.15669	0.000202
O	3.636335	-1.26626	0.00073
O	3.691021	0.925444	0.000245

H	-3.45641	1.137787	0.000853
H	-1.52056	-2.45609	-0.00033

Table S24 Cartesian coordinates of compound **6'**.

Atom	X	Y	Z
C	-2.66253	-0.83512	0.000433
N	-2.59578	0.580267	-0.00113
C	-1.47946	1.391422	-0.001036
N	-0.31255	0.563178	-0.00119
C	-0.35654	-0.84365	0.000167
N	-1.45747	-1.55095	0.000555
N	0.941045	1.004104	-0.000893
C	1.622814	-0.16558	-0.000089
N	0.928888	-1.29093	0.000641
O	-3.74214	-1.38703	0.001711
O	-1.45619	2.591053	-0.000438
N	3.094414	-0.14262	0.00025
O	3.651619	-1.22973	-0.00354
O	3.615988	0.965255	0.004307
H	-3.48981	1.059856	-0.000782

4. DSC spectra of all products

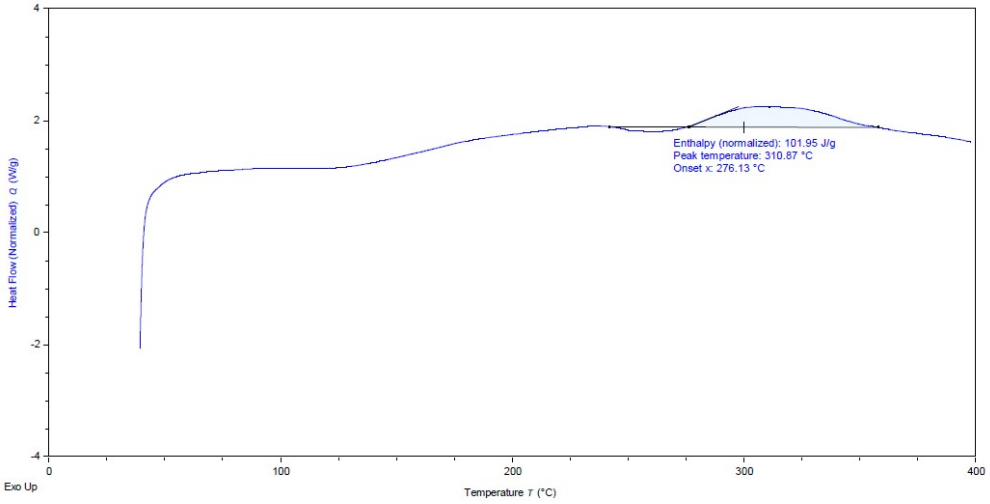


Figure S4. DSC curve of **3**.

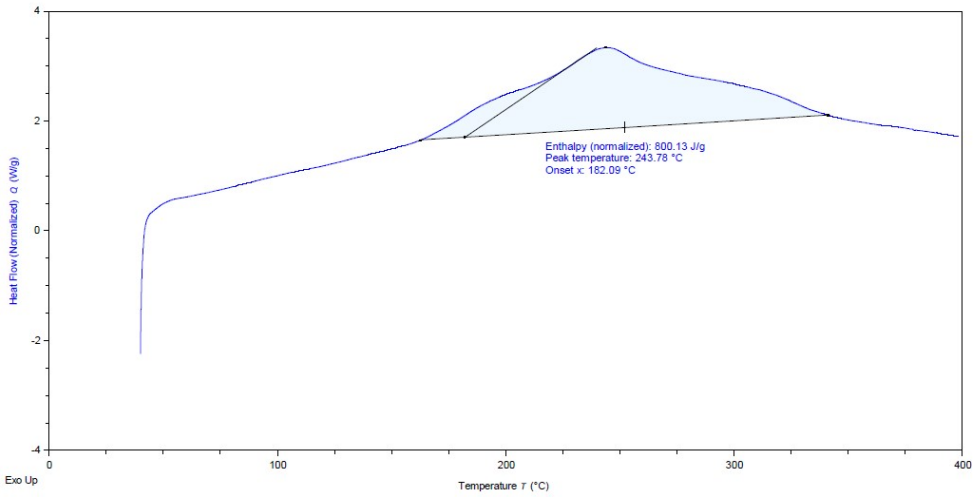


Figure S5. DSC curve of **4**.

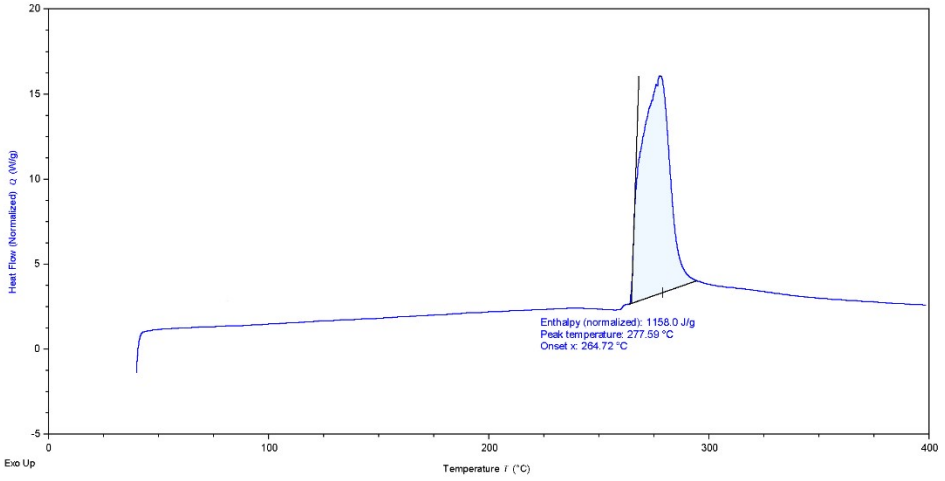


Figure S6. DSC curve of **5**.

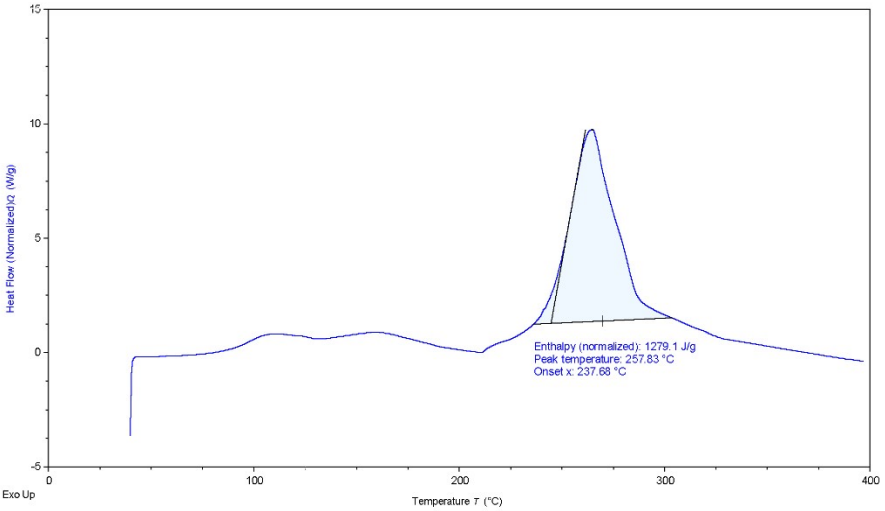


Figure S7. DSC curve of **6**.

5. ^{1}H and ^{13}C NMR spectra of all products

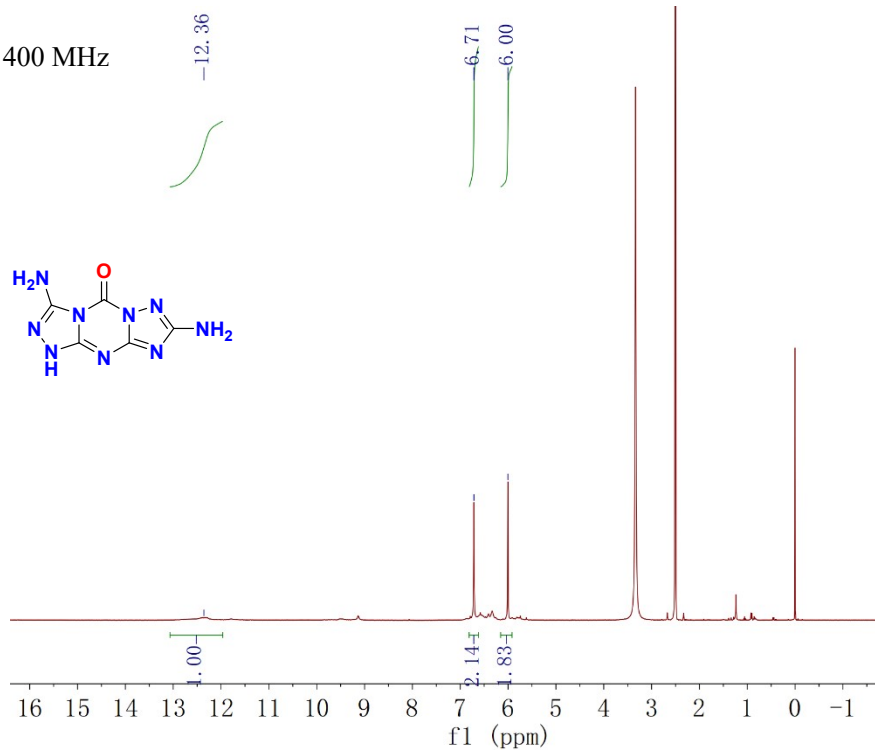


Figure S8. ^{1}H NMR of **3** in d_6-DMSO.

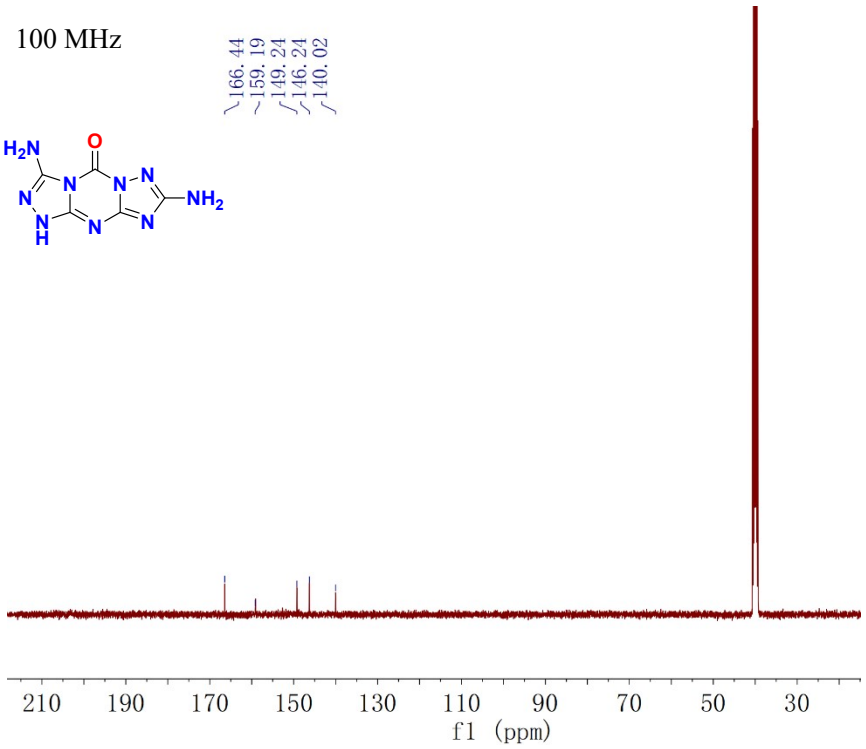


Figure S9. ^{13}C NMR of **3** in d_6-DMSO.

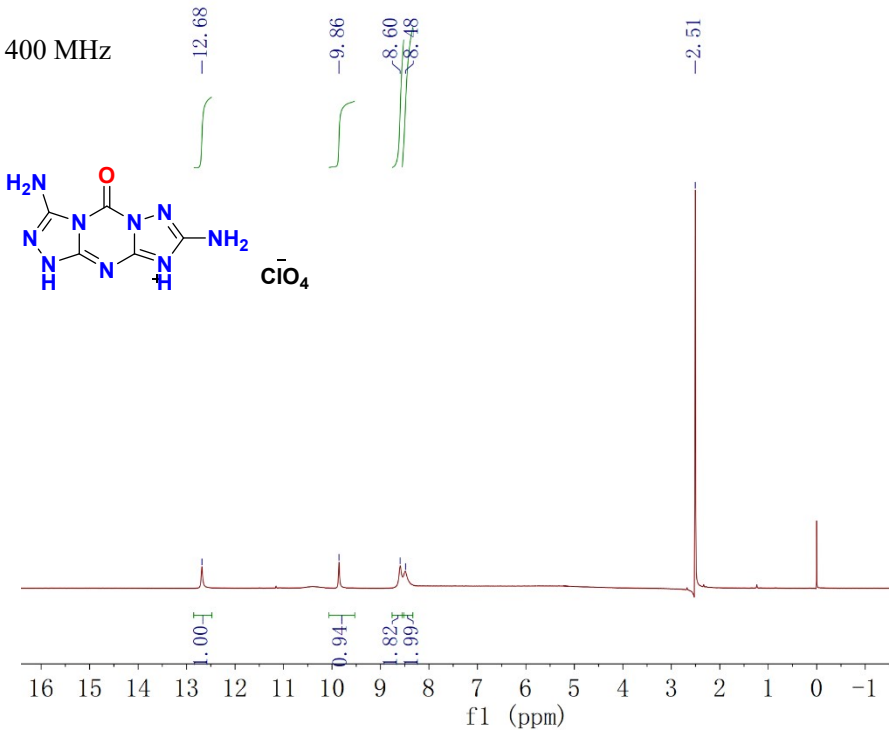


Figure S10. ^{1}H NMR of **4** in d_6-DMSO.

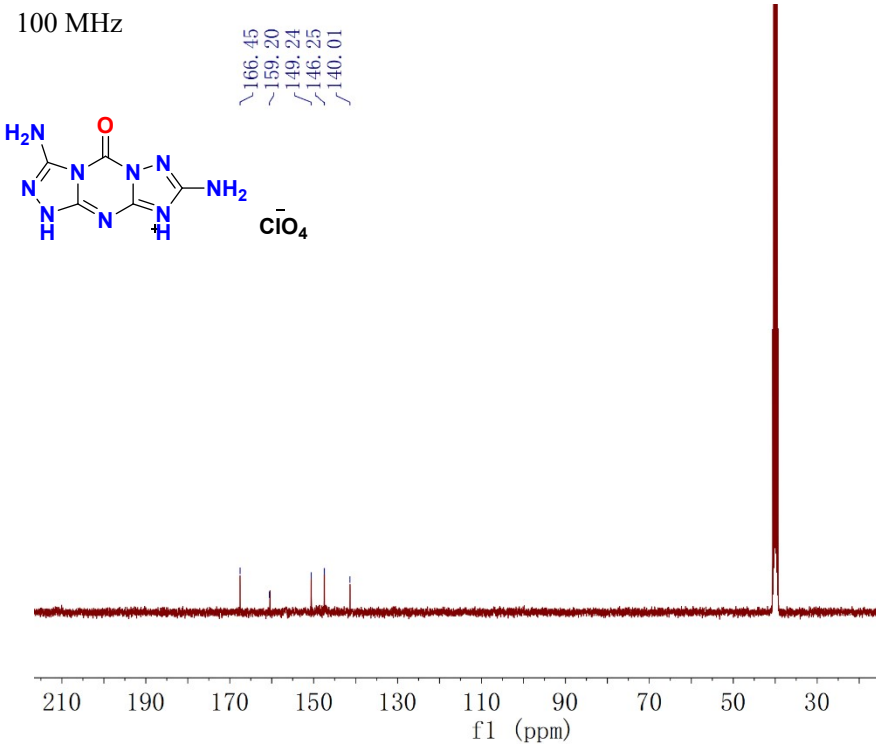


Figure S11. ^{13}C NMR of **4** in d_6-DMSO.

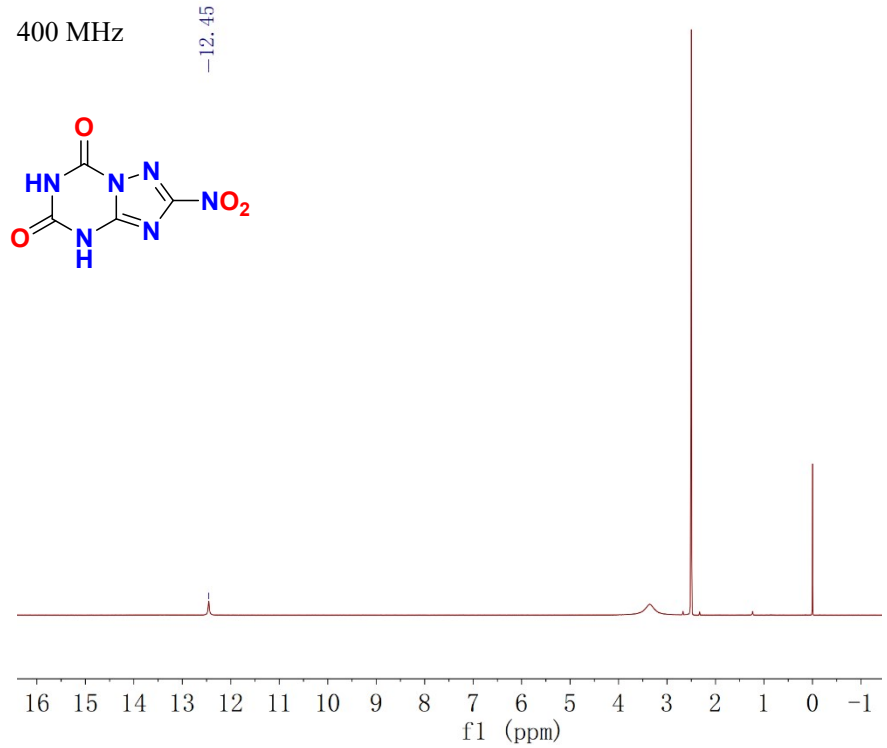


Figure S12. ^{1}H NMR of **5** in d_6-DMSO.

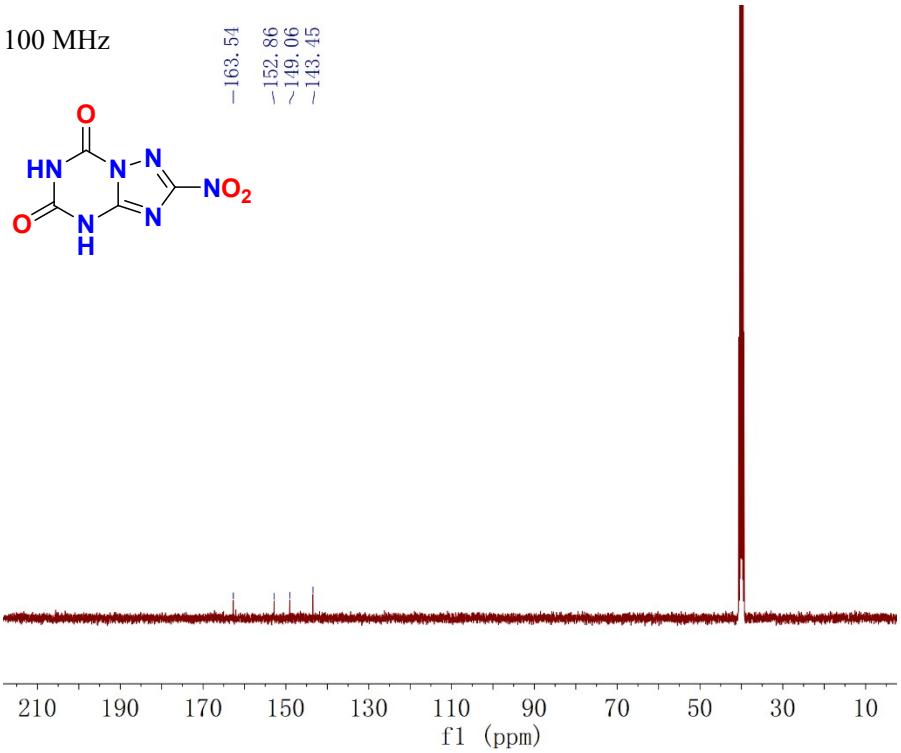


Figure S13. ^{13}C NMR of **5** in d_6-DMSO.

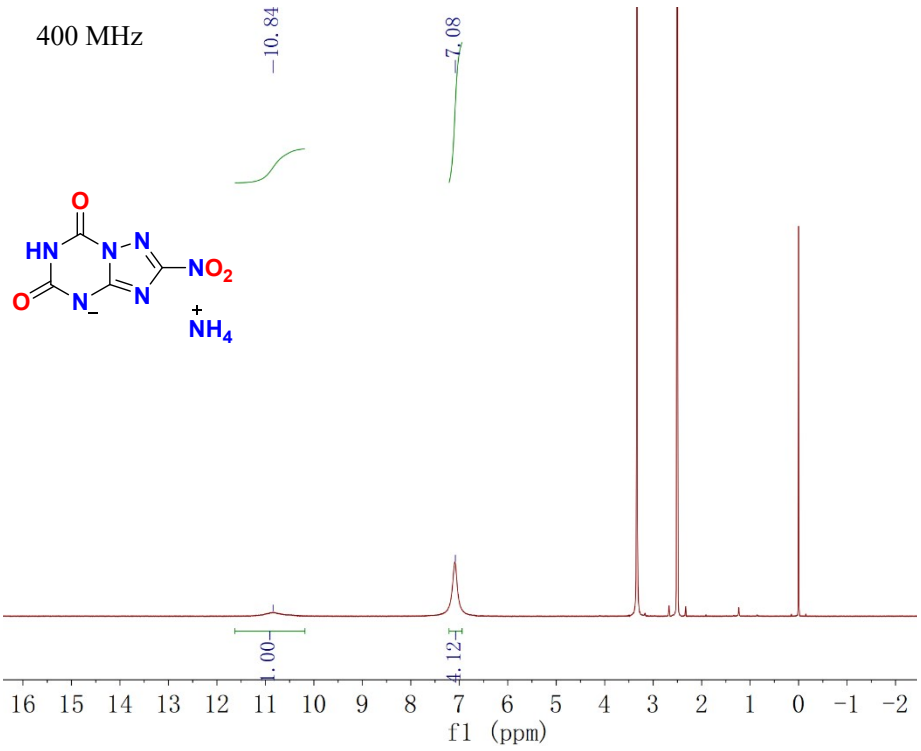


Figure S14. ^{1}H NMR of **6** in d_6-DMSO.

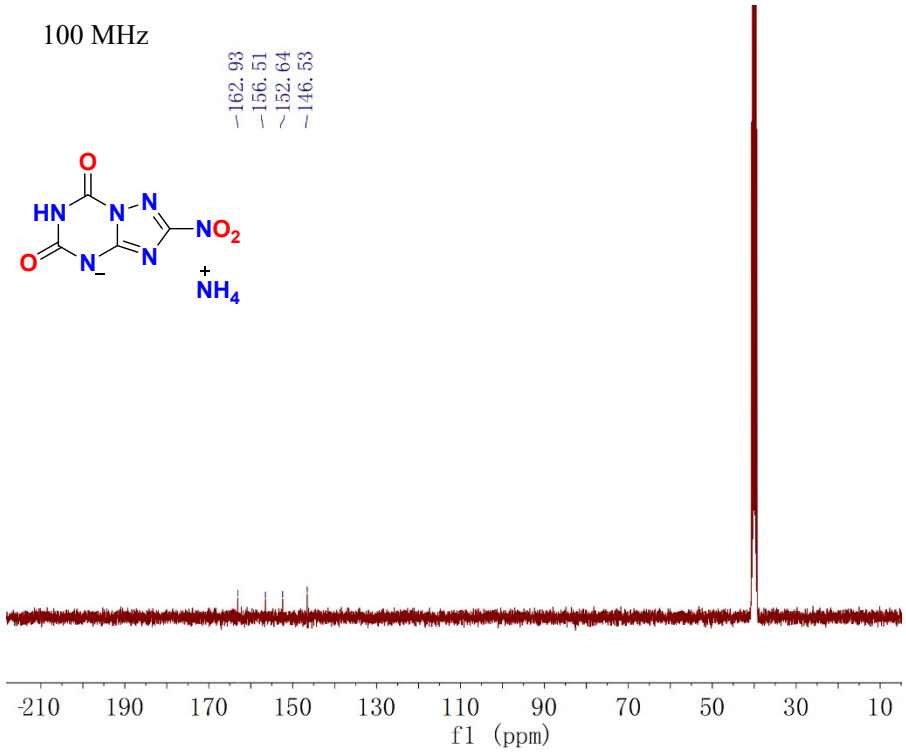


Figure S15. ^{13}C NMR of **6** in d_6-DMSO.

6. ESP of all products

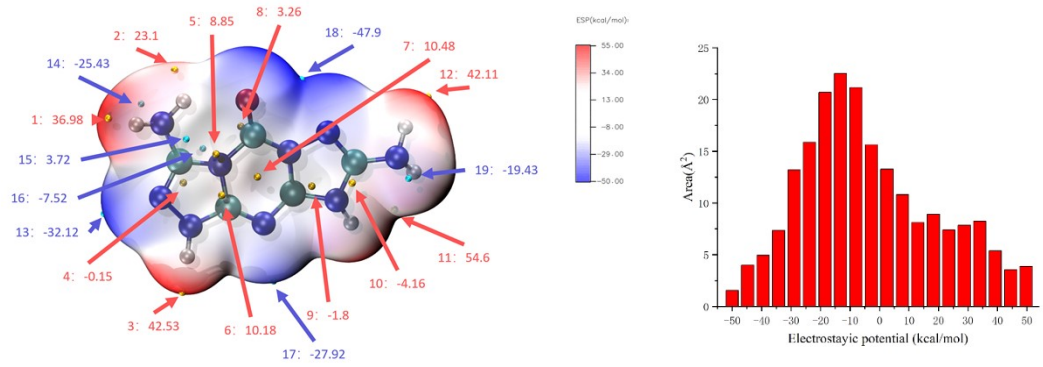


Figure S16. ESP of **4**.

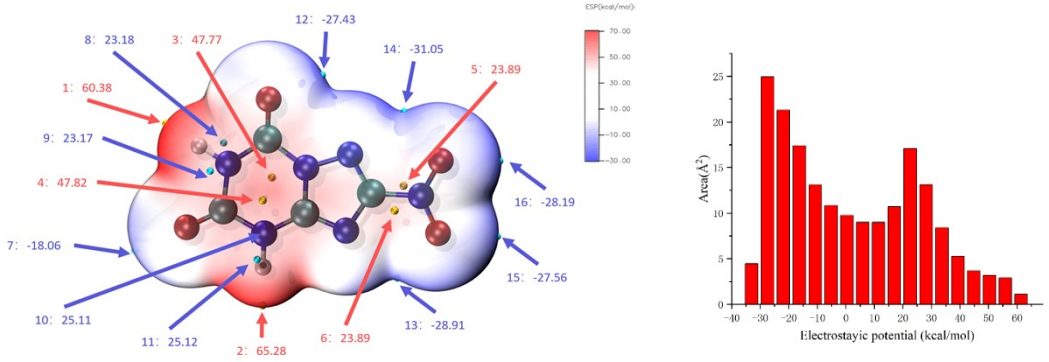


Figure S17. ESP of **5**.

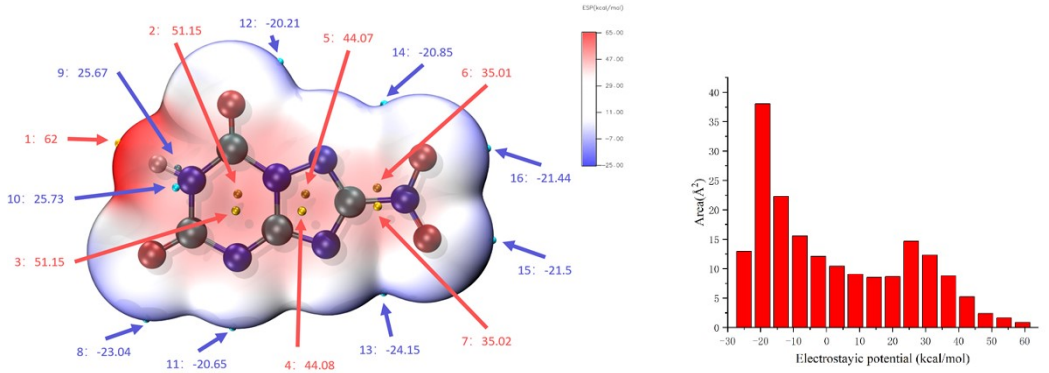


Figure S18. ESP of **6**.

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