Supporting Information

Structure-performance relationship in thermally stable energetic materials: tunable physical properties of benzopyridotetraazapentalene by incorporating amino groups, hydrogen bonding and π-π interactions

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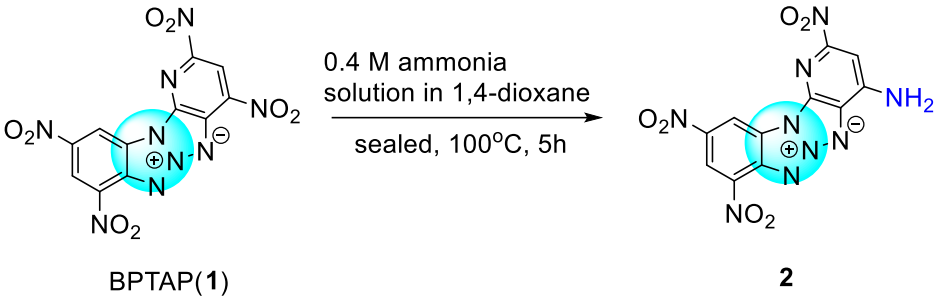
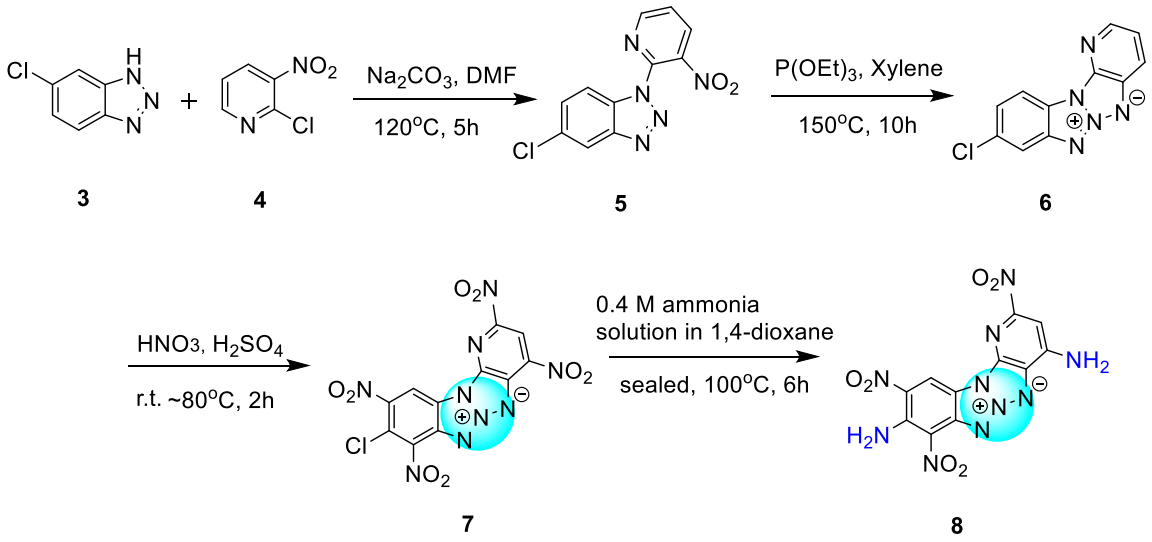
1. Experimental Section



Scheme 1 The synthetic pathway of compound **2**



Scheme 2 The synthetic pathway of compound **8**

4-diamino-2,8,10-trinitrobenzo-[4',5'][1,2,3]triazolo-[2',1':2,3][1,2,3]triazolo-[4,5-b] pyridin-6-ium-5-ide (2). As shown in Scheme 1, BPTAP (**1**)[1] (0.5g,1.285 mmol) was dissolved in 10 mL 0.4 M ammonia solution in 1,4-dioxane, the mixture was sealed and stirred at 100 °C for 5 h. Then it was cooled to room temperature and poured into the ice water (20 mL). The precipitate was collected by filtration. 0.381 g of **5** as a brick red solid was obtained in a yield of 82.5 %. ^{1}H NMR (400 MHz,

d_6-DMSO): δ=9.18 (d, 1H), 9.01(d, 1H), 8.39 (s, 2H), 7.69 (s, 1H) ppm; ^{13}C NMR (101 MHz, d_6-DMSO): δ=154.79, 148.73, 142.00, 139.52, 135.61, 132.36, 128.31, 123.55, 119.87, 111.88, 99.51 ppm. FT-IR (KBr): v=3349, 3093, 1560, 1540, 1451, 1417, 1336, 1243, 781, 726cm^{-1}. HRMS (ESI) m/z [M]$^-$calcd for $C_{11}H_4N_9O_6$: 358.2103, found: 358.22933. Elemental analysis calcd: C 36.78, H 1.40, N 35.09, found: C 35.99, H 1.85, N 33.36.

5-chloro-1-(3-nitropyridin-2-yl)-1H-benzo[d]-[1,2,3]-triazole(5). As shown in Scheme 2, 5-chlorobenzotriazole (**3**) (1.15 g, 7.5 mmol), 2-chloro-3-nitro-pyridine (**4**) (1.187 g, 7.5 mmol) and anhydrous sodium carbonate (0.794 g, 7.5 mmol) were dissolved in DMF. The solution became syrup, and then it was heated to 120 ℃ for 5 h. The cooled reaction solution was poured into ice water and filtered to obtain a brown product. After drying, it was dissolved with ethyl acetate, and then decolorized with activated carbon to remove the impurities, the precipitate was collected by filtration. Isolated as white solid (1.074 g, yield 52%) by column chromatography (ethyl acetate: petroleum ether=1:5). ^{1}H NMR (400 MHz, DMSO-d_6): δ=9.01 (s,1 H), 8.81 (d, 1H), 8.79 (d, 1H), 8.45 (s, 1H), 8.24 (d, 1H), 7.96 (m,1H) ppm; ^{13}C NMR(101MHz, DMSO-d_6): δ=152.26, 145.72, 139.68, 139.37, 135.51, 130.10, 129.93, 129.91, 125.14, 119.03, 113.99 ppm. FT-IR(KBr): v=3095, 1614, 1597, 1526, 1480, 1356, 856, 757,640 cm^{-1}

9-chlorobenzo[4',5'][1,2,3]triazolo[2',1':2,3][1,2,3]triazolo[4,5-b]pyridin-6-ium-5-ide(6). Compound **5** (0.95 g, 0.003.45 mol) was dissolved in 14 ml of xylene, and 2.5 ml of triethyl phosphite was added dropwise with stirring. The solution became

yellow, and it was refluxed at 150 ℃ for 10 h. Then it was cooled to room temperature and petroleum ether was added, collected the precipitate by filtration. Isolated as white solid (0.504 g, yield 60%) by column chromatography (ethyl acetate: petroleum ether=1:5). ^{1}H NMR (400 MHz, DMSO-d_6): δ= 8.57 (s, 1H), 8.35 (s, 1H), 8.24 (s, 1H), 7.96 (s, 1H), 7.69 (s, 2H) ppm.^{13}CNMR (101MHz, DMSO-d_6): δ=170.77, 143.36, 137.12, 127.43, 124.14, 122.85, 117.84, 115.65, 112.18, 110.43 ppm. FT-IR(KBr): v=3095, 1590, 1518, 1459, 1422, 856, 792, 744, 689 cm^{-1}

9-chloro-2,4,8,10-tetranitrobenzo[4',5'][1,2,3]triazolo[2',1':2,3][1,2,3]triazol-o[4,5-b]pyridin-6-ium-5-ide(7). 1.06 mL of concentrated sulfuric acid was added to a three-necked flask with a thermometer and then compound **6** (0.12 g, 0.493 mmol) was added slowly with stirring at room temperature. The solution became yellow. After being completely dissolved, 1.06.ml fuming nitric acid was added slowly at 30 ℃, and the solution turned black immediately. After complete addition, the mixture was stirred at room temperature for 30 min, and the temperature was raised to 80 ℃ for another 2 h. The solution became yellow, subsequently the reaction solution was cooled to the room temperature and poured into ice water for quenching. The product **7** is obtained by suction filtration. Isolated as white solid (0.14 g, yield 71.1%) by column chromatography (ethyl acetate: petroleum ether=1:3). ^{1}H NMR (400MHz, DMSO-d_6): δ=9.64 (s,1H), 9.27 (s,1H) ppm;^{13}C NMR (101MHz, DMSO-d_6): δ=150.02, 144.91, 141.13, 138.62, 137.09, 134.02, 121.81, 119.06, 113.95 ppm. FT-IR(KBr): v=3071, 1596, 1546, 1485, 1360, 858, 819, 753, 637 cm^{-1}

4,9-diamino-2,8,10-trinitrobenzo-[4',5'][1,2,3]-triazolo-[2',1':2,3]-[1,2,3]-tri-azolo [4,5-b]-pyridin-6-ium-5-ide (8). 80 mL of 0.4 M ammonia solution in 1,4-dioxane in a single-necked flask, compound **7** (0.8 g, 0.188 mmol) was added in one portion under stirring at room temperature. Then the mixture was heated to 100 ℃ for 6 h, and poured into ice water for quenching. The precipitate was collected by filtration. It can be further purified by anti-solvent crystallization: the product was dissolved in 10-20 mL DMF and poured slowly into ice water (300 g). 0.424 g of compound **8** as a brick red solid was obtained in a yield of 80%. Its ^{13}C NMR signal can not be obtained because of its weak solubility in DMSO though it was scanned for 24 h. ^{1}H NMR (400 MHz, DMSO-d_6): δ=9.22 (s,2H), 8.92 (s,1H), 8.35 (s,2H), 7.65 (s,1H) ppm. FT-IR(KBr): ν=3351, 1625, 1545, 1517, 1485, 1265, 991, 776 cm^{-1}; HRMS (ESI) m/z $[M]^-$calcd for $C_{11}H_5N_{10}O_6$: 373.2307, found: 373.24019. Elemental analysis calcd: C 35.30, H 1.62, N 37.43; found: C 34.90, H 1.90, N 36.61.

2. Crystalline parameters

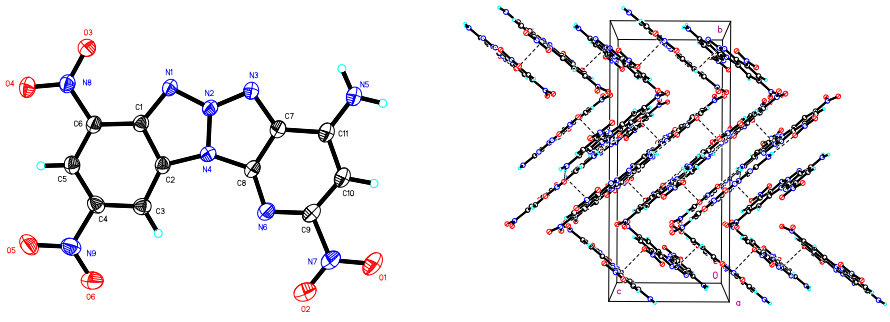


Table S1. Crystal data and structure refinement for compound 2.

Identification code	CCDC 1967657
Empirical formula	C11 H5 N9 O6
Formula weight	359.24

Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P c c n	
Unit cell dimensions	a = 13.1386(7) Å	= 90 °.
	b = 22.6944(13) Å	= 90 °.
	c = 9.7371(5) Å	= 90 °.
Volume	2903.3(3) $Å^3$	
Z	8	
Density (calculated)	1.644 Mg/m^3	
Absorption coefficient	0.138 mm^{-1}	
F(000)	1456	
Crystal size	0.150 x 0.120 x 0.100 mm^3	
Theta range for data collection	2.754 to 25.500 °.	
Index ranges	-14<=h<=15, -27<=k<=27, -10<=l<=11	
Reflections collected	12375	
Independent reflections	2690 [R(int) = 0.0348]	
Completeness to theta = 25.242 °	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6177	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2690 / 0 / 244	
Goodness-of-fit on F^2	1.064	
Final R indices [I>2sigma(I)]	R1 = 0.0486, wR2 = 0.1297	
R indices (all data)	R1 = 0.0678, wR2 = 0.1429	
Extinction coefficient	0.0044(13)	
Largest diff. peak and hole	0.223 and -0.193 e.$Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound 2. aU(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	9340(1)	4246(1)	3848(2)	79(1)
O(2)	8759(2)	3715(1)	5487(3)	89(1)
O(3)	1411(1)	4029(1)	5623(2)	75(1)
O(4)	1083(1)	3419(1)	7254(2)	59(1)
O(5)	3722(2)	2520(1)	9760(2)	68(1)
O(6)	5265(2)	2495(1)	8992(2)	88(1)
N(1)	3367(1)	4230(1)	4734(2)	42(1)
N(2)	4329(1)	4321(1)	4330(2)	40(1)
N(3)	4695(1)	4665(1)	3363(2)	44(1)

N(4)	5036(1)	4006(1)	5039(2)	41(1)
N(5)	6375(2)	5182(1)	1636(2)	54(1)
N(6)	6874(1)	3979(1)	4907(2)	47(1)
N(7)	8643(2)	4046(1)	4533(2)	57(1)
N(8)	1673(1)	3680(1)	6500(2)	47(1)
N(9)	4390(2)	2669(1)	8950(2)	56(1)
C(1)	3484(2)	3833(1)	5780(2)	40(1)
C(2)	4505(2)	3682(1)	6015(2)	39(1)
C(3)	4855(2)	3300(1)	7007(2)	44(1)
C(4)	4100(2)	3072(1)	7835(2)	45(1)
C(5)	3078(2)	3198(1)	7678(2)	44(1)
C(6)	2762(2)	3569(1)	6651(2)	41(1)
C(7)	5728(2)	4563(1)	3459(2)	41(1)
C(8)	5972(2)	4164(1)	4495(2)	41(1)
C(9)	7596(2)	4227(1)	4150(2)	47(1)
C(10)	7497(2)	4621(1)	3084(3)	48(1)
C(11)	6529(2)	4810(1)	2669(2)	44(1)

Table S3 Bond lengths [Å] and angles [ ] for compound 2

Atom	Length/Å	Atom	Length/Å
O(1)-N(7)	1.220(3)	N(6)-C(8)	1.320(3)
O(2)-N(7)	1.205(3)	N(6)-C(9)	1.326(3)
O(3)-N(8)	1.214(3)	N(7)-C(9)	1.483(3)
O(4)-N(8)	1.221(2)	N(8)-C(6)	1.460(3)
O(5)-N(9)	1.227(3)	N(9)-C(4)	1.469(3)
O(6)-N(9)	1.216(3)	C(1)-C(2)	1.404(3)
N(1)-N(2)	1.341(2)	C(1)-C(6)	1.407(3)
N(1)-C(1)	1.369(3)	C(2)-C(3)	1.377(3)
N(2)-N(3)	1.313(2)	C(3)-C(4)	1.379(3)
N(2)-N(4)	1.360(2)	C(3)-H(3)	0.9300
N(3)-C(7)	1.380(3)	C(4)-C(5)	1.382(3)
N(4)-C(8)	1.386(3)	C(5)-C(6)	1.372(3)
N(4)-C(2)	1.389(3)	C(5)-H(5)	0.9300
N(5)-C(11)	1.329(3)	C(7)-C(8)	1.393(3)
N(5)-H(5A)	0.88(3)	C(7)-C(11)	1.418(3)
N(5)-H(5B)	0.86(3)	C(9)-C(10)	1.376(3)
O(1)-N(7)	1.220(3)	C(10)-C(11)	1.402(3)
O(2)-N(7)	1.205(3)	C(10)-H(10)	0.9300

Table S4 Bond angles [ ] for compound 2

Atom	angles [ ]	Atom	angles [ ]
N(2)-N(1)-C(1)	102.33(16)	N(4)-C(2)-C(1)	103.82(18)
N(3)-N(2)-N(1)	130.30(18)	C(2)-C(3)-C(4)	114.0(2)
N(3)-N(2)-N(4)	115.28(16)	C(2)-C(3)-H(3)	123.0
N(1)-N(2)-N(4)	114.42(17)	C(4)-C(3)-H(3)	123.0
N(2)-N(3)-C(7)	102.21(17)	C(3)-C(4)-C(5)	123.8(2)
N(2)-N(4)-C(8)	105.97(17)	C(3)-C(4)-N(9)	118.6(2)
N(2)-N(4)-C(2)	106.49(16)	C(5)-C(4)-N(9)	117.6(2)
C(8)-N(4)-C(2)	147.49(19)	C(6)-C(5)-C(4)	120.1(2)
C(11)-N(5)-H(5A)	118.8(19)	C(6)-C(5)-H(5)	119.9
C(11)-N(5)-H(5B)	113.8(17)	C(4)-C(5)-H(5)	119.9
H(5A)-N(5)-H(5B)	127(3)	C(5)-C(6)-C(1)	119.8(2)
C(8)-N(6)-C(9)	109.7(2)	C(5)-C(6)-N(8)	118.42(19)
O(2)-N(7)-O(1)	123.9(2)	C(1)-C(6)-N(8)	121.8(2)
O(2)-N(7)-C(9)	118.9(2)	N(3)-C(7)-C(8)	112.59(18)
O(1)-N(7)-C(9)	117.2(2)	N(3)-C(7)-C(11)	128.8(2)

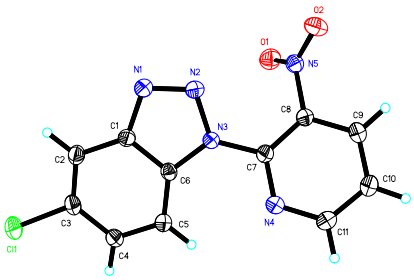
O(3)-N(8)-O(4)	124.0(2)	C(8)-C(7)-C(11)	118.6(2)
O(3)-N(8)-C(6)	117.46(18)	N(6)-C(8)-N(4)	126.7(2)
O(4)-N(8)-C(6)	118.5(2)	N(6)-C(8)-C(7)	129.3(2)
O(6)-N(9)-O(5)	124.4(2)	N(4)-C(8)-C(7)	103.92(18)
O(6)-N(9)-C(4)	118.2(2)	N(6)-C(9)-C(10)	128.9(2)
O(5)-N(9)-C(4)	117.4(2)	N(6)-C(9)-N(7)	114.0(2)
N(1)-C(1)-C(2)	112.94(18)	C(10)-C(9)-N(7)	117.2(2)
N(1)-C(1)-C(6)	130.78(19)	C(9)-C(10)-C(11)	120.1(2)
C(2)-C(1)-C(6)	116.27(19)	C(9)-C(10)-H(10)	120.0
C(3)-C(2)-N(4)	130.2(2)	C(11)-C(10)-H(10)	120.0
C(3)-C(2)-C(1)	125.9(2)	N(5)-C(11)-C(10)	123.4(2)
C(10)-C(11)-C(7)	113.4(2)	N(5)-C(11)-C(7)	123.3(2)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for compound 2.

	x	y	z	U(eq)
H(3)	5539	3204	7109	53
H(5)	2603	3031	8270	52
H(10)	8073	4762	2638	57
H(5A)	5750(30)	5298(13)	1460(30)	71(9)
H(5B)	6930(20)	5284(11)	1210(30)	58(8)

Table S6. Torsion angles [ ] for compound 2

C(1)-N(1)-N(2)-N(3)	-179.4(2)	O(4)-N(8)-C(6)-C(5)	-3.1(3)
C(1)-N(1)-N(2)-N(4)	0.6(2)	O(3)-N(8)-C(6)-C(1)	-2.9(3)
N(1)-N(2)-N(3)-C(7)	179.9(2)	O(4)-N(8)-C(6)-C(1)	177.2(2)
N(4)-N(2)-N(3)-C(7)	-0.1(2)	N(2)-N(3)-C(7)-C(8)	-0.7(2)
N(3)-N(2)-N(4)-C(8)	0.8(2)	N(2)-N(3)-C(7)-C(11)	179.7(2)
N(1)-N(2)-N(4)-C(8)	-179.15(17)	C(9)-N(6)-C(8)-N(4)	-179.6(2)
N(3)-N(2)-N(4)-C(2)	179.07(17)	C(9)-N(6)-C(8)-C(7)	-1.1(3)
N(1)-N(2)-N(4)-C(2)	-0.9(2)	N(2)-N(4)-C(8)-N(6)	177.6(2)
N(2)-N(1)-C(1)-C(2)	0.0(2)	C(2)-N(4)-C(8)-N(6)	0.8(5)
N(2)-N(1)-C(1)-C(6)	178.6(2)	N(2)-N(4)-C(8)-C(7)	-1.1(2)
N(2)-N(4)-C(2)-C(3)	-178.9(2)	C(2)-N(4)-C(8)-C(7)	-178.0(3)
C(8)-N(4)-C(2)-C(3)	-2.1(5)	N(3)-C(7)-C(8)-N(6)	-177.6(2)
N(2)-N(4)-C(2)-C(1)	0.8(2)	C(11)-C(7)-C(8)-N(6)	2.1(4)
C(8)-N(4)-C(2)-C(1)	177.6(3)	N(3)-C(7)-C(8)-N(4)	1.2(2)
N(1)-C(1)-C(2)-C(3)	179.3(2)	C(11)-C(7)-C(8)-N(4)	-179.20(19)
C(6)-C(1)-C(2)-C(3)	0.5(3)	C(8)-N(6)-C(9)-C(10)	0.1(3)
N(1)-C(1)-C(2)-N(4)	-0.5(2)	C(8)-N(6)-C(9)-N(7)	-179.92(19)
C(6)-C(1)-C(2)-N(4)	-179.31(18)	O(2)-N(7)-C(9)-N(6)	-2.1(3)
N(4)-C(2)-C(3)-C(4)	177.8(2)	O(1)-N(7)-C(9)-N(6)	177.9(2)
C(1)-C(2)-C(3)-C(4)	-1.9(3)	O(2)-N(7)-C(9)-C(10)	177.9(2)
C(2)-C(3)-C(4)-C(5)	1.6(3)	O(1)-N(7)-C(9)-C(10)	-2.1(3)
C(2)-C(3)-C(4)-N(9)	-178.5(2)	N(6)-C(9)-C(10)-C(11)	-0.1(4)
O(6)-N(9)-C(4)-C(3)	-9.2(3)	N(7)-C(9)-C(10)-C(11)	179.9(2)
O(5)-N(9)-C(4)-C(3)	172.6(2)	C(9)-C(10)-C(11)-N(5)	-179.0(2)
O(6)-N(9)-C(4)-C(5)	170.8(2)	C(9)-C(10)-C(11)-C(7)	0.9(3)
O(5)-N(9)-C(4)-C(5)	-7.5(3)	N(3)-C(7)-C(11)-N(5)	-2.2(4)
C(3)-C(4)-C(5)-C(6)	0.1(4)	C(8)-C(7)-C(11)-N(5)	178.2(2)
N(9)-C(4)-C(5)-C(6)	-179.8(2)	N(3)-C(7)-C(11)-C(10)	177.8(2)
C(4)-C(5)-C(6)-C(1)	-1.7(3)	C(8)-C(7)-C(11)-C(10)	-1.8(3)
C(4)-C(5)-C(6)-N(8)	178.5(2)	O(4)-N(8)-C(6)-C(5)	-3.1(3)
N(1)-C(1)-C(6)-C(5)	-177.1(2)	O(3)-N(8)-C(6)-C(1)	-2.9(3)
C(2)-C(1)-C(6)-C(5)	1.4(3)	O(4)-N(8)-C(6)-C(1)	177.2(2)
N(1)-C(1)-C(6)-N(8)	2.6(4)	N(2)-N(3)-C(7)-C(8)	-0.7(2)
C(2)-C(1)-C(6)-N(8)	-178.83(19)	N(2)-N(3)-C(7)-C(11)	179.7(2)
O(3)-N(8)-C(6)-C(5)	176.9(2)	C(9)-N(6)-C(8)-N(4)	-179.6(2)



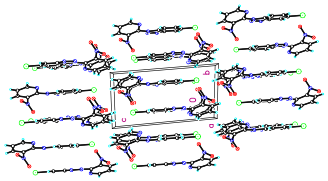


Table S7. Crystal data and structure refinement for compound 5.

Identification code	CCDC 1970939	
Empirical formula	C11 H6 Cl N5 O2	
Formula weight	275.66	
Temperature	192(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.9177(8) Å	= 88.706(4) °.
	b = 7.3512(8) Å	= 78.355(3) °.
	c = 12.8123(14) Å	= 62.367(3) °.
Volume	563.45(11) $Å^3$	
Z	2	
Density (calculated)	1.625 Mg/m^3	
Absorption coefficient	0.345 mm^{-1}	
F(000)	280	
Crystal size	0.160 x 0.130 x 0.100 mm^3	
Theta range for data collection	3.138 to 25.999 °.	
Index ranges	-8<=h<=8, -9<=k<=9, -15<=l<=15	
Reflections collected	7825	
Independent reflections	2159 [R(int) = 0.0457]	
Completeness to theta = 25.242 °	97.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6397	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2159 / 0 / 173	
Goodness-of-fit on F^2	1.085	
Final R indices [I>2sigma(I)]	R1 = 0.0545, wR2 = 0.1389	
R indices (all data)	R1 = 0.0603, wR2 = 0.1424	
Extinction coefficient	0.17(3)	
Largest diff. peak and hole	0.296 and -0.213 e.$Å^{-3}$	

Table S8 Bond lengths [Å] and angles [ ] for compound 5

Atom	Length/Å	Atom	Length/Å
Cl(1)-C(3)	1.744(3)	C(2)-C(3)	1.358(4)
Cl(1)-C(3)	1.744(3)	C(2)-H(2)	0.9500
O(1)-N(5)	1.212(4)	C(3)-C(4)	1.402(4)
O(2)-N(5)	1.218(3)	C(4)-C(5)	1.376(4)
N(1)-N(2)	1.289(3)	C(4)-H(4)	0.9500
N(1)-C(1)	1.377(4)	C(5)-C(6)	1.395(4)
N(2)-N(3)	1.370(3)	C(5)-H(5)	0.9500
N(3)-C(6)	1.377(3)	C(7)-C(8)	1.385(4)
N(3)-C(7)	1.407(4)	C(8)-C(9)	1.379(4)
N(4)-C(7)	1.325(4)	C(9)-C(10)	1.372(4)
N(4)-C(11)	1.332(4)	C(9)-H(9)	0.9500
N(5)-C(8)	1.473(4)	C(10)-C(11)	1.375(5)
C(1)-C(6)	1.387(4)	C(10)-H(10)	0.9500

Table S9 Bond angles [ ] for compound 5

Atom	angles [ ]	Atom	angles [ ]
N(2)-N(1)-C(1)	108.4(2)	C(4)-C(5)-H(5)	122.0
N(1)-N(2)-N(3)	108.7(2)	C(6)-C(5)-H(5)	122.0
N(2)-N(3)-C(6)	110.2(2)	N(3)-C(6)-C(1)	103.0(2)
N(2)-N(3)-C(7)	120.3(2)	N(3)-C(6)-C(5)	134.4(3)
C(6)-N(3)-C(7)	129.3(2)	C(1)-C(6)-C(5)	122.5(3)
C(7)-N(4)-C(11)	118.0(3)	N(4)-C(7)-C(8)	121.9(3)
O(1)-N(5)-O(2)	124.7(3)	N(4)-C(7)-N(3)	114.9(3)
O(1)-N(5)-C(8)	118.6(3)	C(8)-C(7)-N(3)	123.2(3)
O(2)-N(5)-C(8)	116.6(3)	C(9)-C(8)-C(7)	119.7(3)
N(1)-C(1)-C(6)	109.7(2)	C(9)-C(8)-N(5)	116.9(3)
N(1)-C(1)-C(2)	129.3(3)	C(7)-C(8)-N(5)	123.3(2)
C(6)-C(1)-C(2)	121.1(3)	C(10)-C(9)-C(8)	118.2(3)
C(3)-C(2)-C(1)	115.8(3)	C(10)-C(9)-H(9)	120.9
C(3)-C(2)-H(2)	122.1	C(8)-C(9)-H(9)	120.9
C(1)-C(2)-H(2)	122.1	C(9)-C(10)-C(11)	118.6(3)
C(2)-C(3)-C(4)	123.4(3)	C(9)-C(10)-H(10)	120.7
C(2)-C(3)-Cl(1)	118.6(2)	C(11)-C(10)-H(10)	120.7
C(4)-C(3)-Cl(1)	117.9(2)	N(4)-C(11)-C(10)	123.5(3)
C(5)-C(4)-C(3)	121.2(3)	N(4)-C(11)-H(11)	118.2
C(5)-C(4)-H(4)	119.4	C(10)-C(11)-H(11)	118.2
C(3)-C(4)-H(4)	119.4	C(4)-C(5)-C(6)	116.0(3)

Table S10. Torsion angles [ ] for compound 5

C(1)-N(1)-N(2)-N(3)	0.5(3)	C(4)-C(5)-C(6)-C(1)	-0.1(4)
N(1)-N(2)-N(3)-C(6)	-1.2(3)	C(11)-N(4)-C(7)-C(8)	-0.5(5)
N(1)-N(2)-N(3)-C(7)	-176.2(3)	C(11)-N(4)-C(7)-N(3)	-178.1(3)
N(2)-N(1)-C(1)-C(6)	0.4(3)	N(2)-N(3)-C(7)-N(4)	152.4(3)
N(2)-N(1)-C(1)-C(2)	-179.7(3)	C(6)-N(3)-C(7)-N(4)	-21.5(4)
N(1)-C(1)-C(2)-C(3)	-179.3(3)	N(2)-N(3)-C(7)-C(8)	-25.1(4)
C(6)-C(1)-C(2)-C(3)	0.6(4)	C(6)-N(3)-C(7)-C(8)	160.9(3)
C(1)-C(2)-C(3)-C(4)	-0.6(5)	N(4)-C(7)-C(8)-C(9)	-2.5(5)
C(1)-C(2)-C(3)-Cl(1)	179.1(2)	N(3)-C(7)-C(8)-C(9)	174.9(3)
C(2)-C(3)-C(4)-C(5)	0.3(5)	N(4)-C(7)-C(8)-N(5)	174.3(3)
Cl(1)-C(3)-C(4)-C(5)	-179.4(2)	N(3)-C(7)-C(8)-N(5)	-8.3(5)
C(3)-C(4)-C(5)-C(6)	0.0(4)	O(1)-N(5)-C(8)-C(9)	120.8(3)
N(2)-N(3)-C(6)-C(1)	1.4(3)	O(2)-N(5)-C(8)-C(9)	-56.1(4)
C(7)-N(3)-C(6)-C(1)	175.8(3)	O(1)-N(5)-C(8)-C(7)	-56.1(4)
N(2)-N(3)-C(6)-C(5)	-179.5(3)	O(2)-N(5)-C(8)-C(7)	127.0(3)
C(7)-N(3)-C(6)-C(5)	-5.0(5)	C(7)-C(8)-C(9)-C(10)	3.1(5)
N(1)-C(1)-C(6)-N(3)	-1.1(3)	N(5)-C(8)-C(9)-C(10)	-173.9(3)
C(2)-C(1)-C(6)-N(3)	179.0(3)	C(8)-C(9)-C(10)-C(11)	-0.9(5)
N(1)-C(1)-C(6)-C(5)	179.6(3)	C(7)-N(4)-C(11)-C(10)	2.8(5)
C(2)-C(1)-C(6)-C(5)	-0.2(4)	C(9)-C(10)-C(11)-N(4)	-2.2(6)
C(4)-C(5)-C(6)-N(3)	-179.1(3)	C(1)-N(1)-N(2)-N(3)	0.5(3)

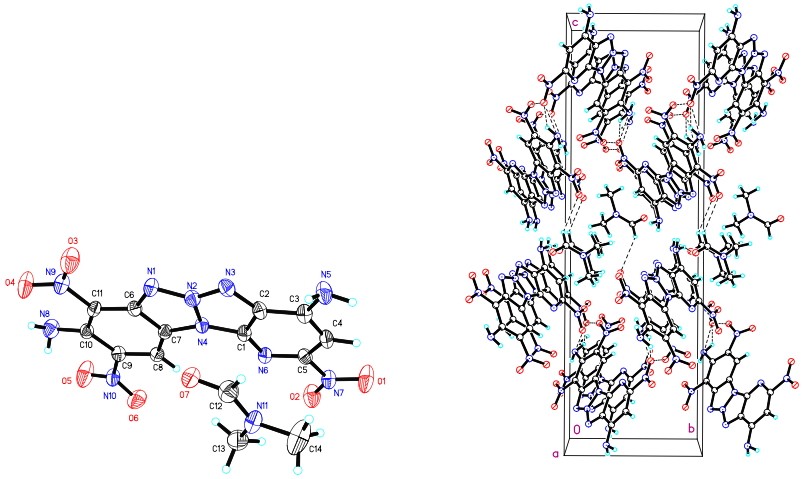


Table S11. Crystal data and structure refinement for compound 8.

Identification code	CCDC 1967658	
Empirical formula	C14 H13 N11 O7	
Formula weight	447.35	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.2893(5) Å	= 90 °.
	b = 8.7871(9) Å	= 90 °.
	c = 28.116(2) Å	= 90 °.
Volume	1800.9(3) $Å^3$	
Z	4	
Density (calculated)	1.650 Mg/m^3	
Absorption coefficient	0.136 mm^{-1}	
F(000)	920	
Crystal size	0.160 x 0.130 x 0.080 mm^3	
Theta range for data collection	2.428 to 25.997 °.	
Index ranges	-8<=h<=8, -10<=k<=7, -34<=l<=28	
Reflections collected	8972	
Independent reflections	3508 [R(int) = 0.0581]	
Completeness to theta = 25.242 °	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6348	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3508 / 0 / 294	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0558, wR2 = 0.1083	
R indices (all data)	R1 = 0.1100, wR2 = 0.1330	
Absolute structure parameter	1.3(10)	

Largest diff. peak and hole	0.216 and -0.189 e.Å^{-3}

Table S12 Bond lengths [Å] and angles [ ] for compound 8

Atom	Length/Å	Atom	Length/Å
O(1)-N(7)	1.223(5)	C(1)-C(2)	1.408(6)
O(2)-N(7)	1.198(5)	C(2)-C(3)	1.399(7)
O(3)-N(9)	1.207(6)	C(3)-C(4)	1.401(7)
O(4)-N(9)	1.230(6)	C(4)-C(5)	1.361(7)
O(5)-N(10)	1.199(6)	C(4)-H(4)	0.9300
O(6)-N(10)	1.201(6)	C(6)-C(11)	1.400(7)
N(1)-N(2)	1.320(6)	C(6)-C(7)	1.407(7)
N(1)-C(6)	1.374(6)	C(7)-C(8)	1.373(7)
N(2)-N(3)	1.328(5)	C(8)-C(9)	1.390(6)
N(2)-N(4)	1.379(5)	C(8)-H(8)	0.9300
N(3)-C(2)	1.369(7)	C(9)-C(10)	1.421(7)
N(4)-C(1)	1.374(6)	C(10)-C(11)	1.433(7)
N(4)-C(7)	1.379(6)	O(7)-C(12)	1.212(7)
N(5)-C(3)	1.341(6)	N(11)-C(12)	1.308(8)
N(5)-H(5A)	0.8599	N(11)-C(13)	1.436(7)
N(5)-H(5B)	0.8599	N(11)-C(14)	1.455(8)
N(6)-C(1)	1.323(6)	C(12)-H(12)	0.9300
N(6)-C(5)	1.335(6)	C(13)-H(13A)	0.9600
N(7)-C(5)	1.480(7)	C(13)-H(13B)	0.9600
N(8)-C(10)	1.358(6)	C(13)-H(13C)	0.9600
N(8)-H(8A)	0.8602	C(14)-H(14A)	0.9600
N(8)-H(8B)	0.8599	C(14)-H(14B)	0.9600
N(9)-C(11)	1.425(7)	C(14)-H(14C)	0.9600
N(10)-C(9)	1.463(6)	C(1)-C(2)	1.408(6)

Table S13 Bond angles [ ] for compound 8

Atom	angles [ ]	Atom	angles [ ]
N(2)-N(1)-C(6)	102.5(4)	N(1)-C(6)-C(11)	129.9(5)
N(1)-N(2)-N(3)	130.5(4)	N(1)-C(6)-C(7)	111.7(4)
N(1)-N(2)-N(4)	115.6(4)	C(11)-C(6)-C(7)	118.4(5)
N(3)-N(2)-N(4)	113.9(4)	C(8)-C(7)-N(4)	130.2(5)
N(2)-N(3)-C(2)	103.0(4)	C(8)-C(7)-C(6)	124.2(4)
C(1)-N(4)-N(2)	106.5(4)	N(4)-C(7)-C(6)	105.5(4)

C(1)-N(4)-C(7)	148.9(5)	C(7)-C(8)-C(9)	116.0(5)
N(2)-N(4)-C(7)	104.6(4)	C(7)-C(8)-H(8)	122.0
C(3)-N(5)-H(5A)	108.7	C(9)-C(8)-H(8)	122.0
C(3)-N(5)-H(5B)	109.9	C(8)-C(9)-C(10)	124.2(5)
H(5A)-N(5)-H(5B)	109.5	C(8)-C(9)-N(10)	114.4(5)
C(1)-N(6)-C(5)	109.6(4)	C(10)-C(9)-N(10)	121.4(4)
O(2)-N(7)-O(1)	122.2(5)	N(8)-C(10)-C(9)	122.9(5)
O(2)-N(7)-C(5)	120.2(4)	N(8)-C(10)-C(11)	120.6(5)
O(1)-N(7)-C(5)	117.6(5)	C(9)-C(10)-C(11)	116.5(4)
C(10)-N(8)-H(8A)	107.7	C(6)-C(11)-N(9)	118.7(5)
C(10)-N(8)-H(8B)	110.2	C(6)-C(11)-C(10)	120.3(5)
H(8A)-N(8)-H(8B)	109.5	N(9)-C(11)-C(10)	120.9(4)
O(3)-N(9)-O(4)	121.0(5)	C(12)-N(11)-C(13)	121.3(5)
O(3)-N(9)-C(11)	118.3(5)	C(12)-N(11)-C(14)	121.4(6)
O(4)-N(9)-C(11)	120.7(5)	C(13)-N(11)-C(14)	117.4(6)
O(5)-N(10)-O(6)	120.8(5)	O(7)-C(12)-N(11)	126.4(6)
O(5)-N(10)-C(9)	120.2(5)	O(7)-C(12)-H(12)	116.8
O(6)-N(10)-C(9)	119.0(5)	N(11)-C(12)-H(12)	116.8
N(6)-C(1)-N(4)	127.0(4)	N(11)-C(13)-H(13A)	109.5
N(6)-C(1)-C(2)	128.7(5)	N(11)-C(13)-H(13B)	109.5
N(4)-C(1)-C(2)	104.2(5)	H(13A)-C(13)-H(13B)	109.5
N(3)-C(2)-C(3)	129.1(5)	N(11)-C(13)-H(13C)	109.5
N(3)-C(2)-C(1)	112.4(4)	H(13A)-C(13)-H(13C)	109.5
C(3)-C(2)-C(1)	118.4(5)	H(13B)-C(13)-H(13C)	109.5
N(5)-C(3)-C(2)	121.8(5)	N(11)-C(14)-H(14A)	109.5
N(5)-C(3)-C(4)	124.1(5)	N(11)-C(14)-H(14B)	109.5
C(2)-C(3)-C(4)	114.1(5)	H(14A)-C(14)-H(14B)	109.5
C(5)-C(4)-C(3)	120.2(5)	N(11)-C(14)-H(14C)	109.5
C(5)-C(4)-H(4)	119.9	H(14A)-C(14)-H(14C)	109.5
C(3)-C(4)-H(4)	119.9	H(14B)-C(14)-H(14C)	109.5
N(6)-C(5)-C(4)	128.9(5)	C(4)-C(5)-N(7)	117.6(5)
N(6)-C(5)-N(7)	113.5(5)		

Table S14. Torsion angles [ ] for compound 8

C(5)-N(1)-N(2)-N(4)	-174.92(16)	N(7)-C(1)-C(6)-C(5)	-175.76(17)
C(7)-N(1)-N(2)-N(4)	-1.7(2)	C(4)-C(5)-C(6)-N(3)	-177.49(19)
C(5)-N(1)-N(2)-N(3)	1.4(2)	N(1)-C(5)-C(6)-N(3)	0.0(2)
C(7)-N(1)-N(2)-N(3)	174.60(16)	C(4)-C(5)-C(6)-C(1)	-1.3(3)

N(4)-N(2)-N(3)-C(6)	174.2(2)	N(1)-C(5)-C(6)-C(1)	176.18(17)
N(1)-N(2)-N(3)-C(6)	-1.3(2)	C(11)-N(5)-C(7)-N(1)	178.04(19)
N(3)-N(2)-N(4)-C(8)	-174.37(19)	C(11)-N(5)-C(7)-C(8)	-0.9(3)
N(1)-N(2)-N(4)-C(8)	1.2(2)	N(2)-N(1)-C(7)-N(5)	-177.81(19)
O(2)-N(7)-C(1)-C(2)	-33.2(3)	C(5)-N(1)-C(7)-N(5)	-9.7(4)
O(1)-N(7)-C(1)-C(2)	148.1(2)	N(2)-N(1)-C(7)-C(8)	1.3(2)
O(2)-N(7)-C(1)-C(6)	143.53(19)	C(5)-N(1)-C(7)-C(8)	169.5(3)
O(1)-N(7)-C(1)-C(6)	-35.1(3)	N(2)-N(4)-C(8)-C(7)	-0.2(2)
C(6)-C(1)-C(2)-C(3)	0.4(3)	N(2)-N(4)-C(8)-C(9)	177.3(2)
N(7)-C(1)-C(2)-C(3)	177.16(18)	N(5)-C(7)-C(8)-N(4)	178.4(2)
C(6)-C(1)-C(2)-Cl(1)	-179.14(15)	N(1)-C(7)-C(8)-N(4)	-0.7(2)
N(7)-C(1)-C(2)-Cl(1)	-2.4(3)	N(5)-C(7)-C(8)-C(9)	0.6(3)
C(1)-C(2)-C(3)-C(4)	-2.1(3)	N(1)-C(7)-C(8)-C(9)	-178.53(18)
Cl(1)-C(2)-C(3)-C(4)	177.51(16)	N(4)-C(8)-C(9)-N(6)	0.4(4)
C(1)-C(2)-C(3)-N(8)	-178.91(18)	C(7)-C(8)-C(9)-N(6)	177.8(2)
Cl(1)-C(2)-C(3)-N(8)	0.7(3)	N(4)-C(8)-C(9)-C(10)	-177.2(2)
O(3)-N(8)-C(3)-C(4)	104.7(2)	C(7)-C(8)-C(9)-C(10)	0.2(3)
O(4)-N(8)-C(3)-C(4)	-73.8(3)	N(6)-C(9)-C(10)-C(11)	-178.1(2)
O(3)-N(8)-C(3)-C(2)	-78.2(3)	C(8)-C(9)-C(10)-C(11)	-0.5(3)
O(4)-N(8)-C(3)-C(2)	103.3(3)	C(7)-N(5)-C(11)-C(10)	0.5(3)
C(2)-C(3)-C(4)-C(5)	1.9(3)	C(7)-N(5)-C(11)-N(9)	180.00(17)
N(8)-C(3)-C(4)-C(5)	178.78(18)	C(9)-C(10)-C(11)-N(5)	0.1(4)
C(3)-C(4)-C(5)-N(1)	-176.9(2)	C(9)-C(10)-C(11)-N(9)	-179.32(18)
C(3)-C(4)-C(5)-C(6)	-0.2(3)	O(5)-N(9)-C(11)-N(5)	0.6(3)
N(2)-N(1)-C(5)-C(4)	176.5(2)	O(6)-N(9)-C(11)-N(5)	178.3(2)
C(7)-N(1)-C(5)-C(4)	8.4(5)	O(5)-N(9)-C(11)-C(10)	-179.8(2)
N(2)-N(1)-C(5)-C(6)	-0.7(2)	O(6)-N(9)-C(11)-C(10)	-2.2(3)
C(7)-N(1)-C(5)-C(6)	-168.9(3)	C(14)-O(8)-C(12)-O(7)	2.0(4)
N(2)-N(3)-C(6)-C(1)	-174.8(2)	C(14)-O(8)-C(12)-C(13)	-175.5(2)
N(2)-N(3)-C(6)-C(5)	0.8(2)	C(12)-O(8)-C(14)-C(15)	174.7(2)
C(2)-C(1)-C(6)-N(3)	176.6(2)	N(7)-C(1)-C(6)-C(5)	-175.76(17)
N(7)-C(1)-C(6)-N(3)	-0.3(3)	C(4)-C(5)-C(6)-N(3)	-177.49(19)

Table S15 Hydrogen bond lengths /Å and angles / °of Compound **2** and Compound **8**·**DMF**.

compound	bond	d/ D-H…A	<D-H…A
2	N5-H5A…N3	2.7238	100.678
	N5-H5A…O3	2.6832	90.871
	N5-H5B…O3	2.4659	106.348
	N5-H5A…O1	2.1436	168.279
	N5-H5B…N1	2.3709	167.251
8·**DMF**	N5-H5A…N1	3.1583	142.485
	N5-H5A…N2	3.1733	123.405
	N5-H5A…O7	2.6198	112.059
	N5-H5A…N3	2.8360	92.383
	N5-H5B…N3	2.7771	102.913
	N5-H5B…O7	2.2225	148.456
	N8-H8A…O5	2.0320	127.076
	N8-H8B…O2	3.1248	70.850
	N8-H8A…O2	2.2789	135.761
	N8-H8A…N10	2.5302	108.988
	N8-H8A…O4	3.2870	153.310
	N8-H8B…O4	1.9216	128.553
	N8-H8B…N9	2.5066	105.353

3. NMR spectra

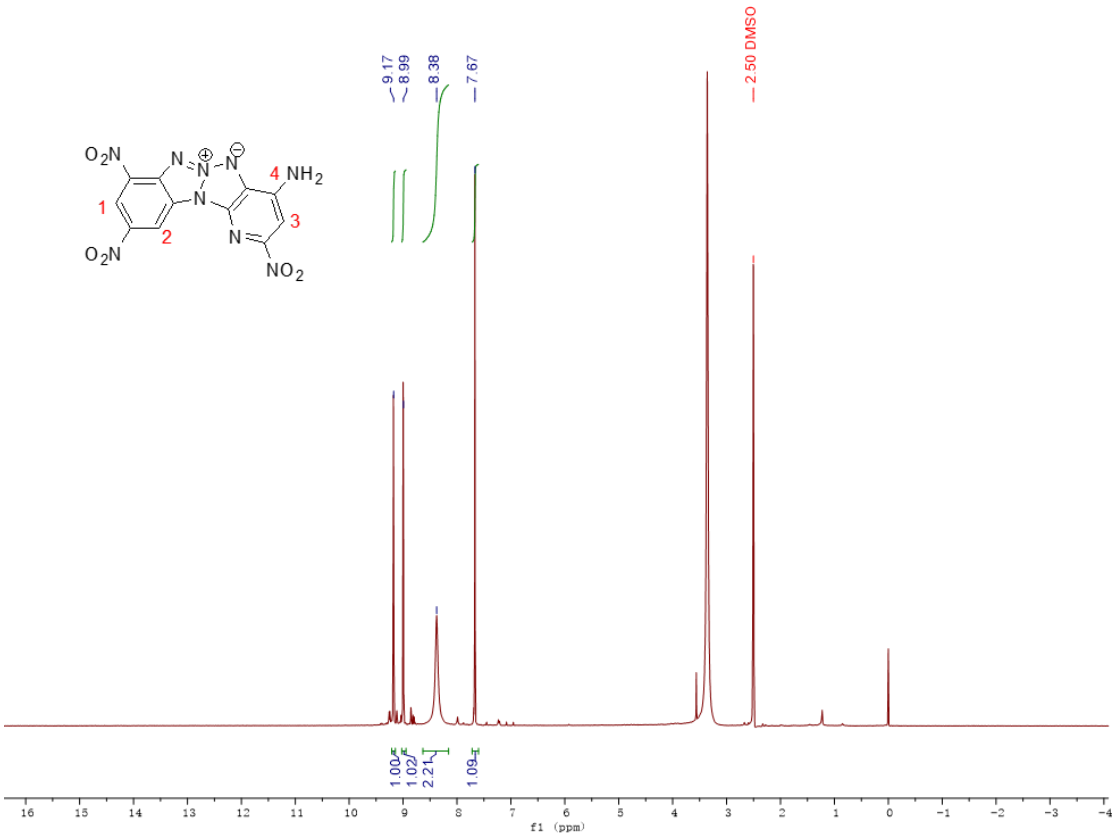


Figure S1. 1H NMR of energetic compound 2

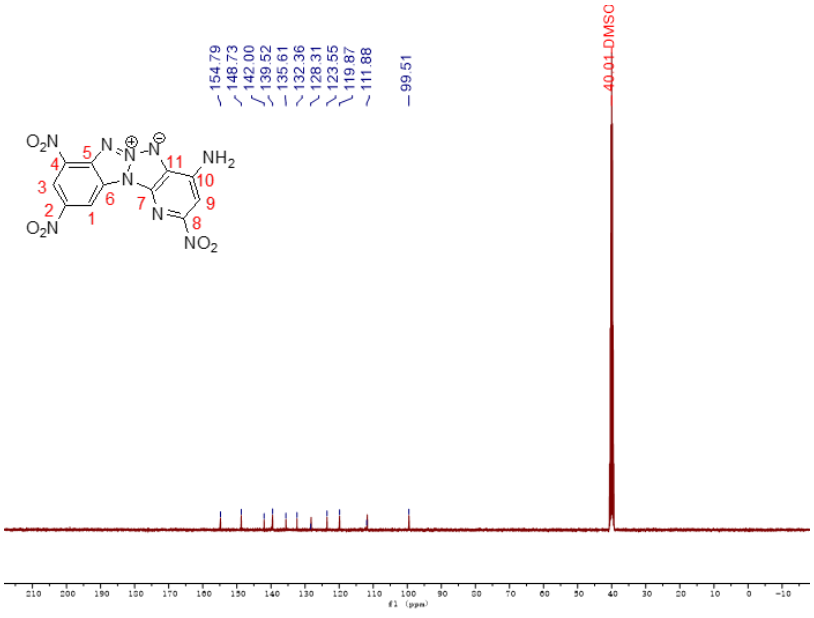


Figure S2. ^{13}C NMR of energetic compound **2**

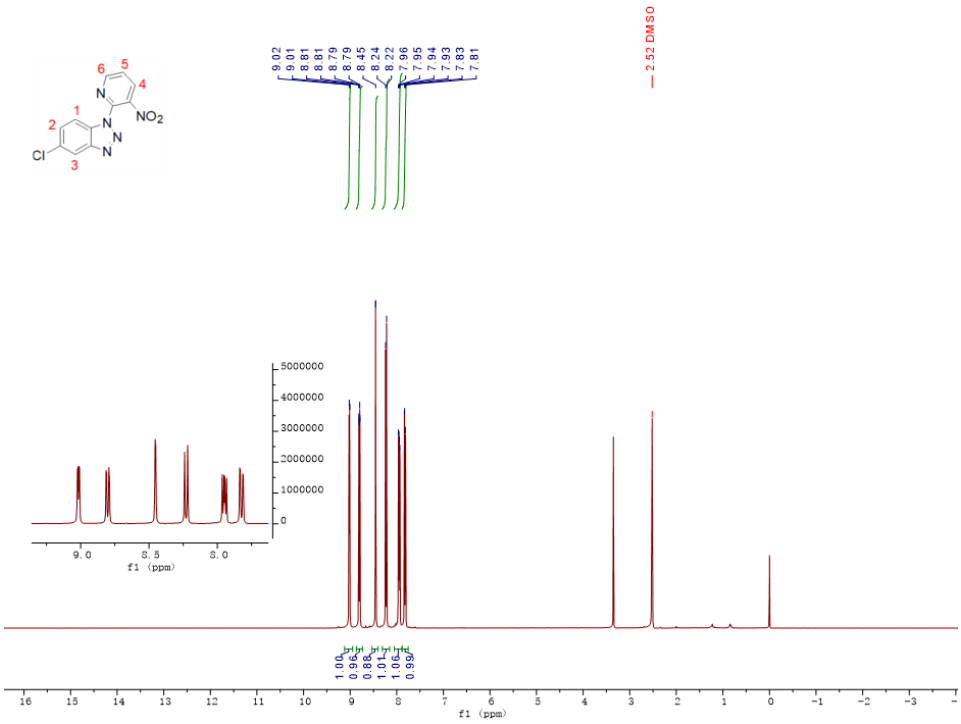


Figure S3. ^{1}H NMR of energetic compound **5**

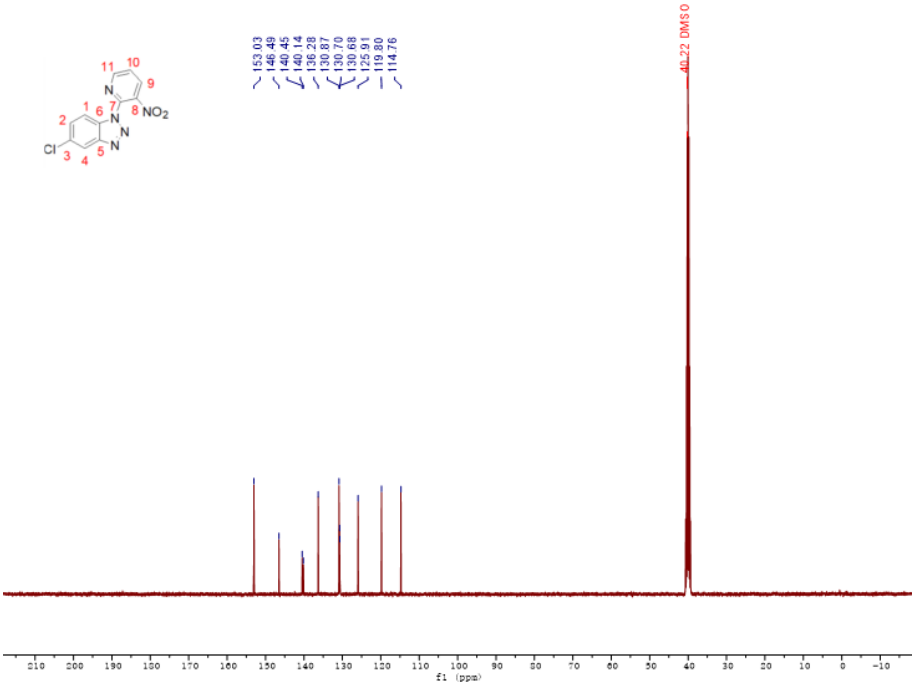


Figure S4. ^{13}C NMR of energetic compound **5**

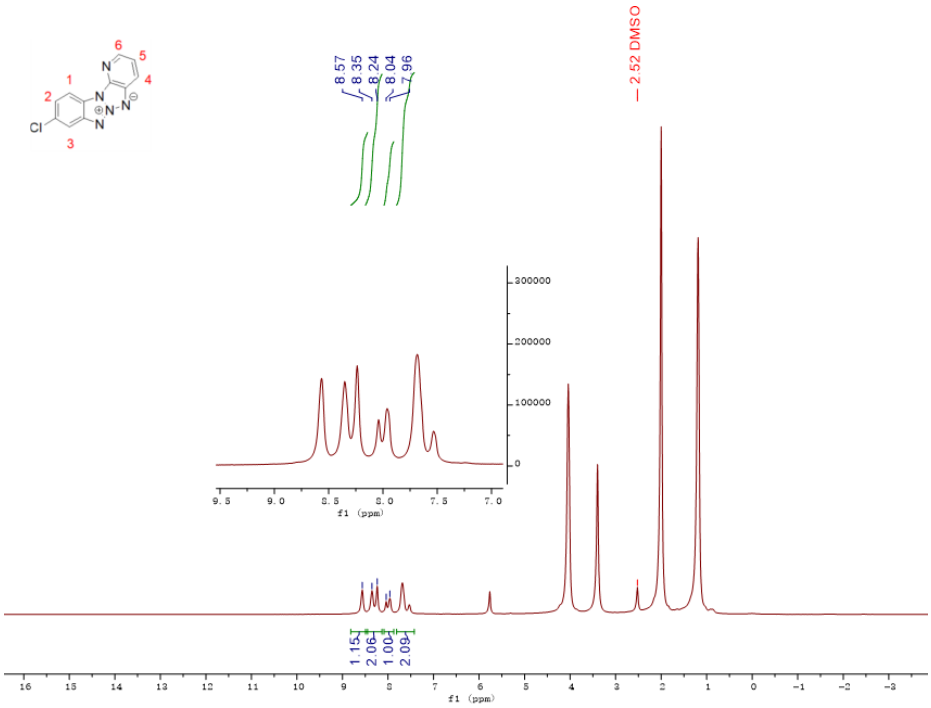


Figure S5. ^{1}H NMR of energetic compound **6**

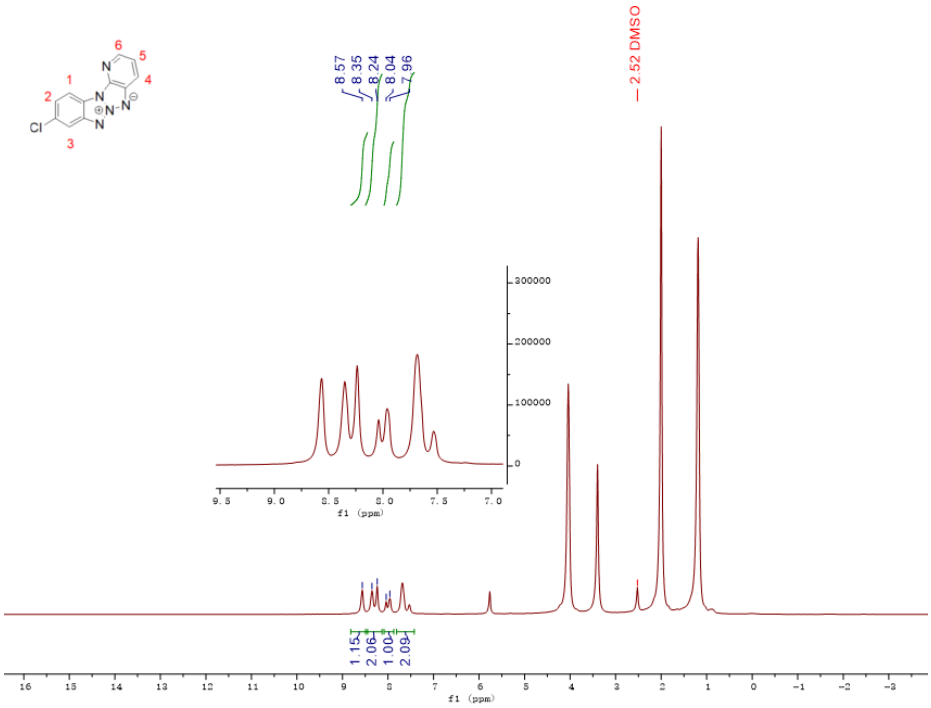


Figure S6. ^{13}C NMR of energetic compound **6**

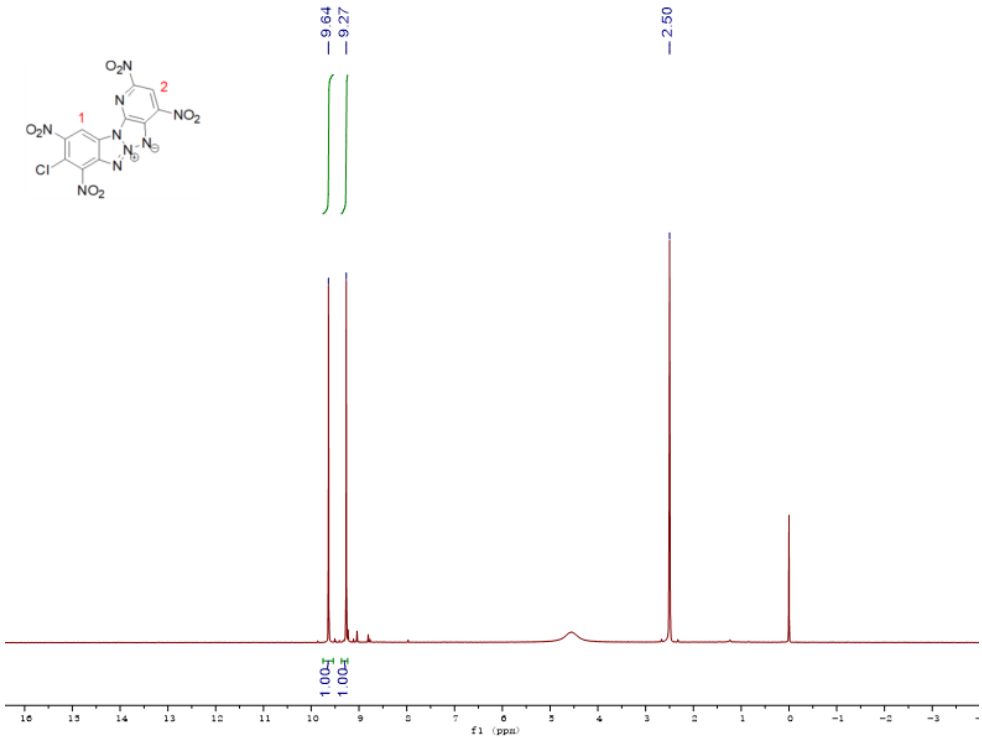


Figure S7. ^{1}H NMR of energetic compound **7**

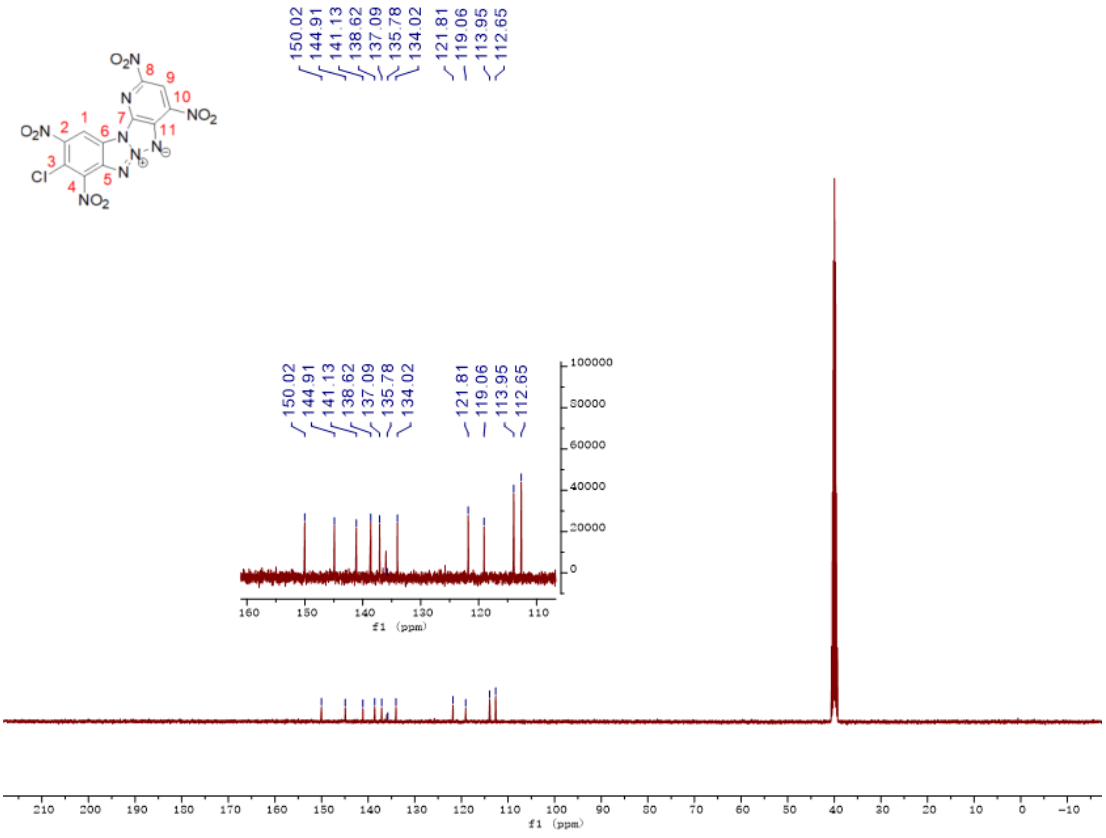


Figure S8. ^{13}C NMR of energetic compound **7**

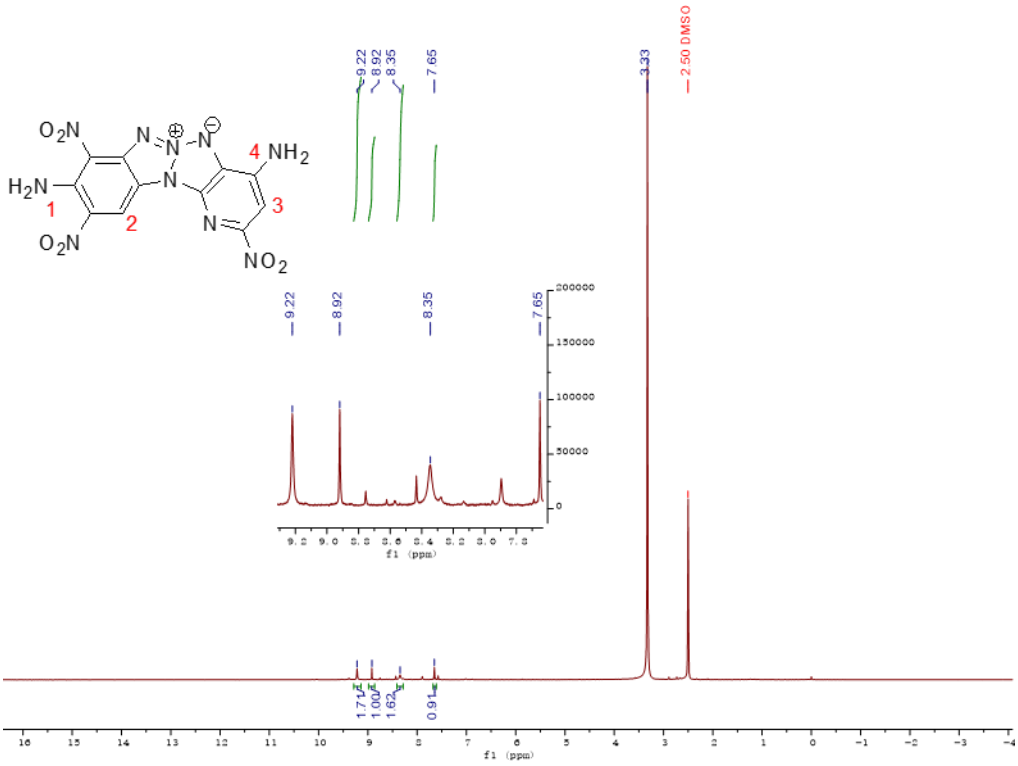


Figure S9. ^{1}H NMR of energetic compound **8 (weak solubility in DMSO)**

4. FT-IR spectra

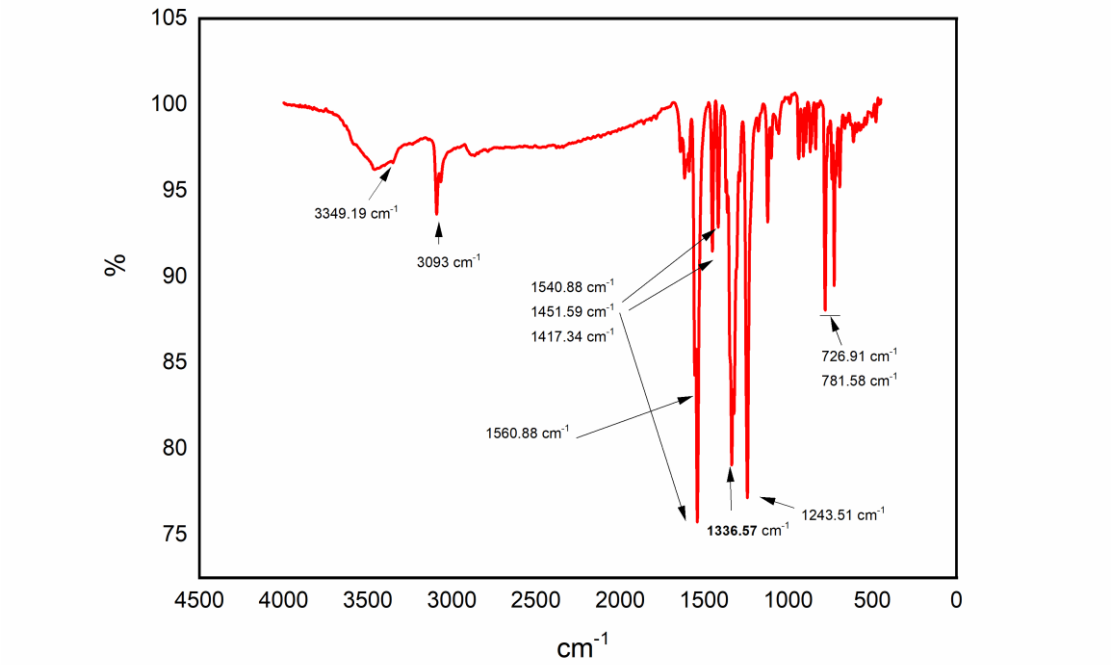


Figure S10. IR spectra of compound **2**

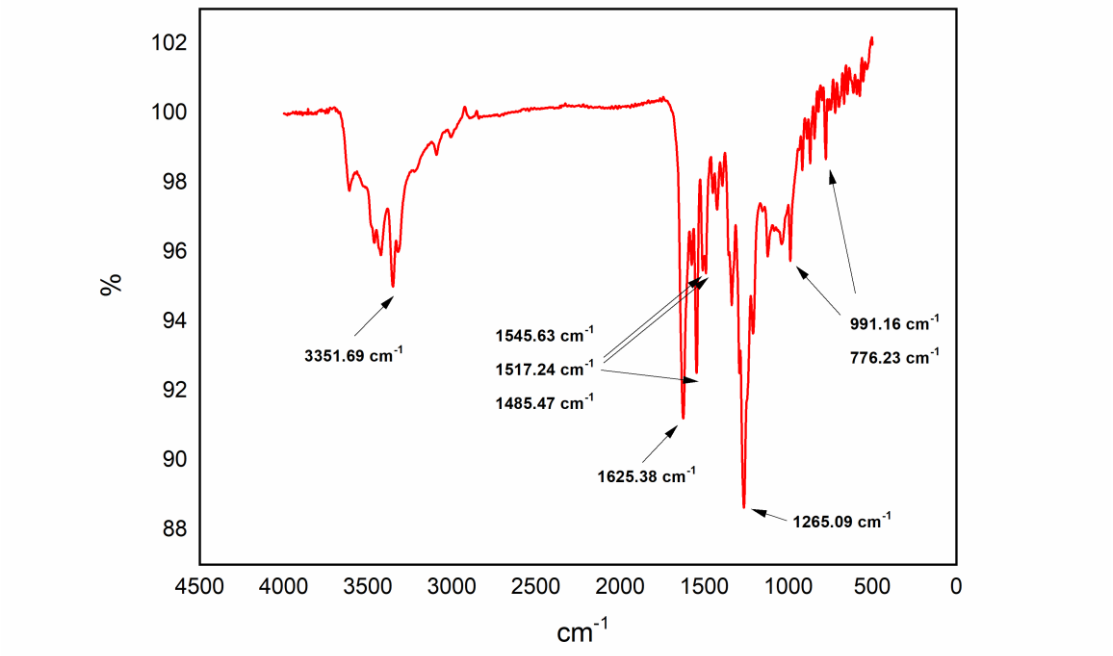


Figure S11. IR spectra of compound **8**

5. DSC-TG curves and thermal dynamic parameters

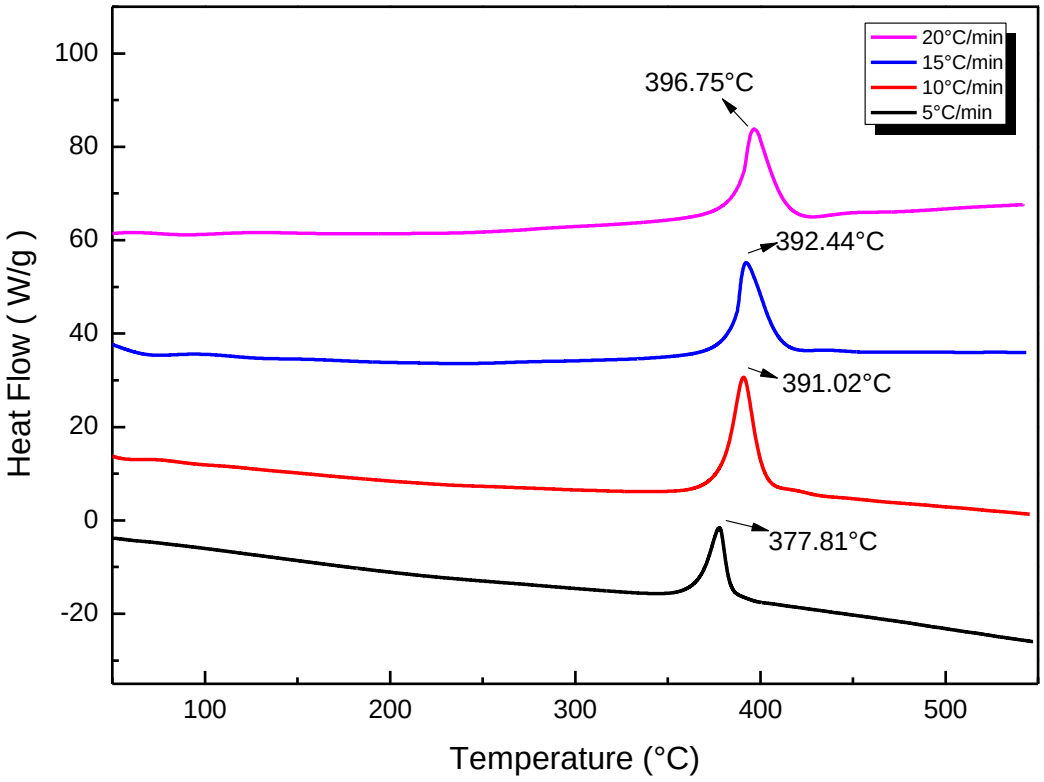


Figure S12. DSC curves of BPTAP

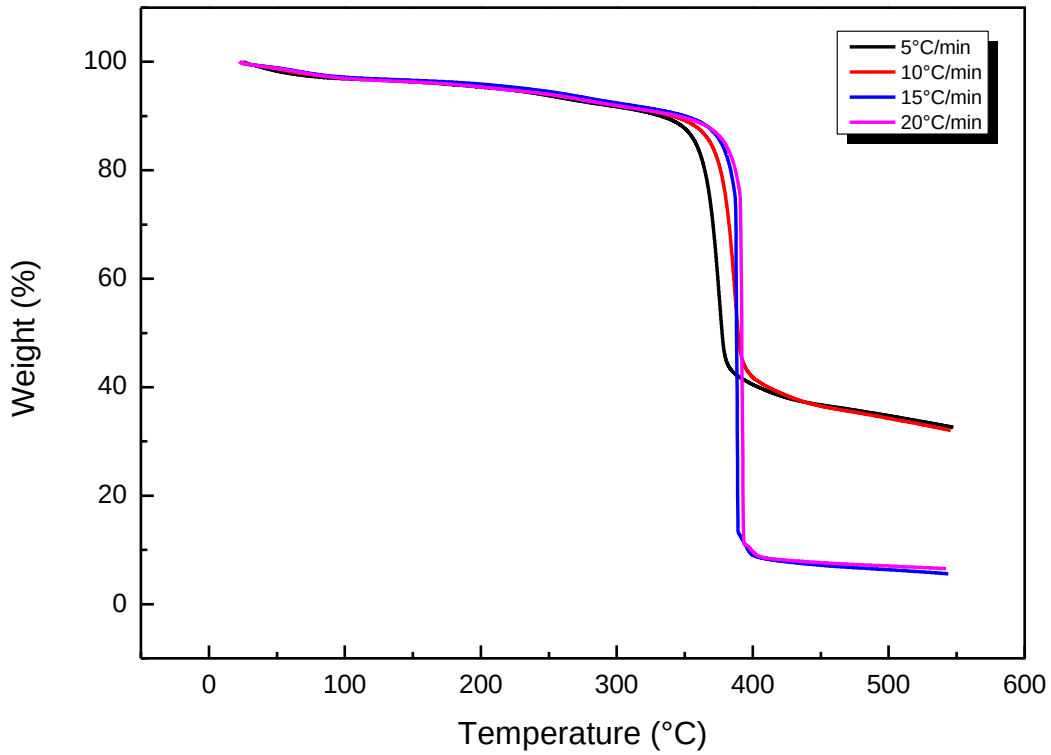


Figure S13. DSC curves of BPTAP

Table S16 Kinetic parameters of **BPTAP** obtained by **Kissinger** and **Ozawa method**

β/K·min^{-1}	T_P/K	Kissinger method			Ozawa method	
		E_K/kJ·mol^{-1}	lnA	r	E_o/kJ·mol^{-1}	r
5	650.96	247.52	37.74	0.9684	245.79	0.9709
10	664.17					
15	665.59					
20	669.9					

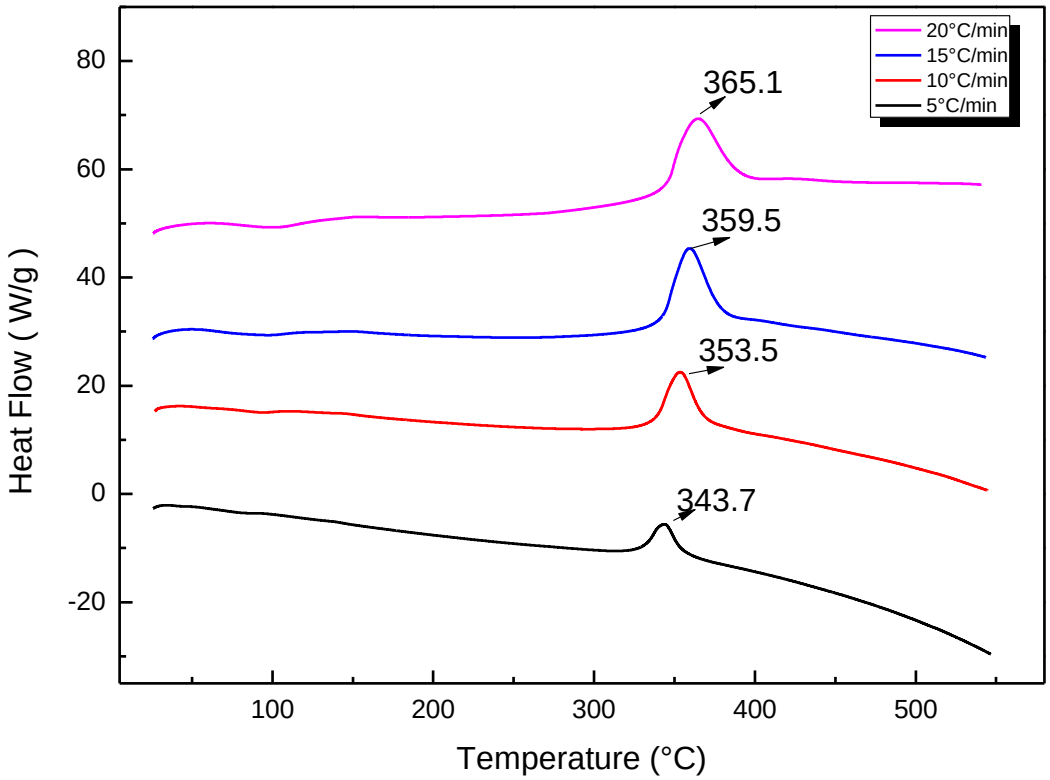


Figure S14. DSC curves of compound 2

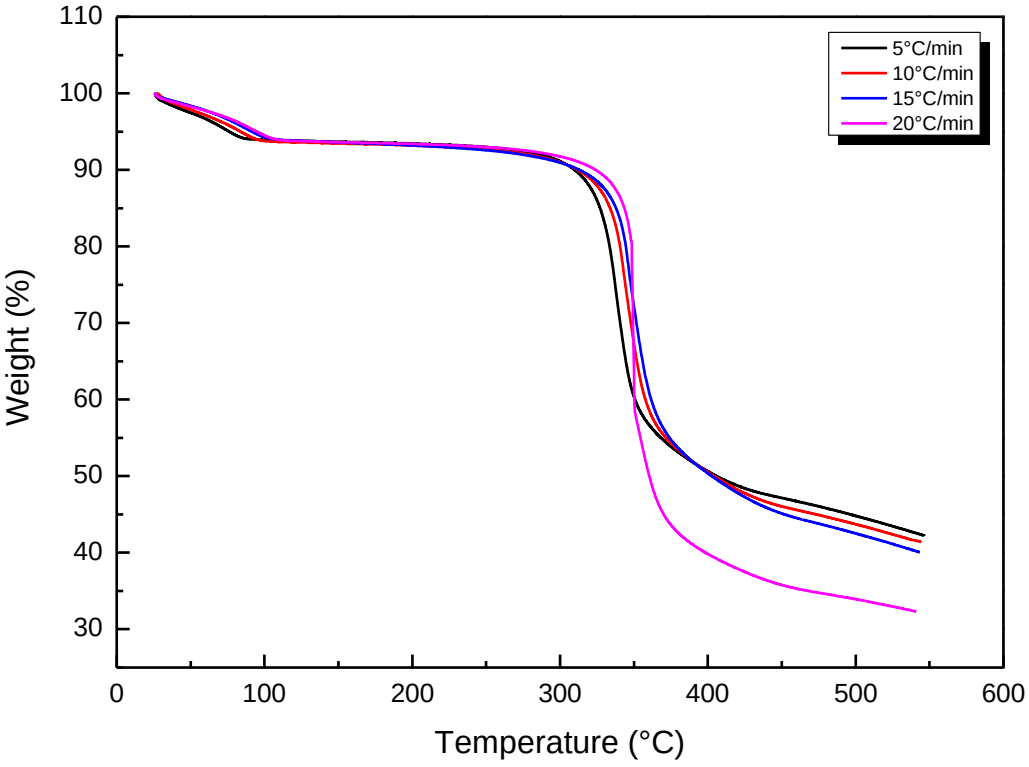


Figure S15. TG curves of compound **2**

Table S17 Kinetic parameters of **compound 2** obtained by **Kissinger** and **Ozawa method**

β/K·min^{-1}	T_P/K	Kissinger method			Ozawa method	
		E_K/kJ·mol^{-1}	lnA	r	E_o/kJ·mol^{-1}	r
5	616.85	204.022	21.126	0.9998	214.45	0.9955
10	626.65					
15	632.65					
20	638.25					

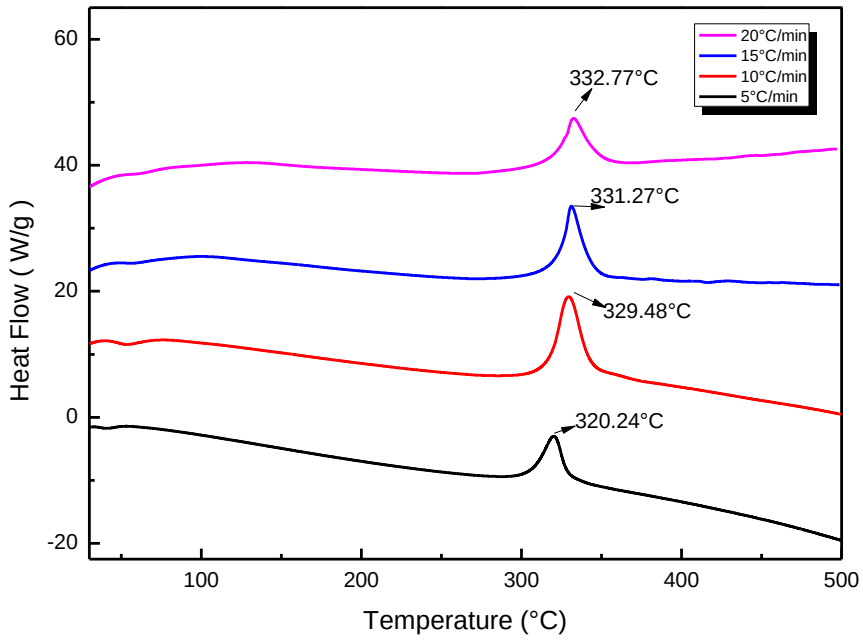


Figure S16. DSC curves of compound **8**

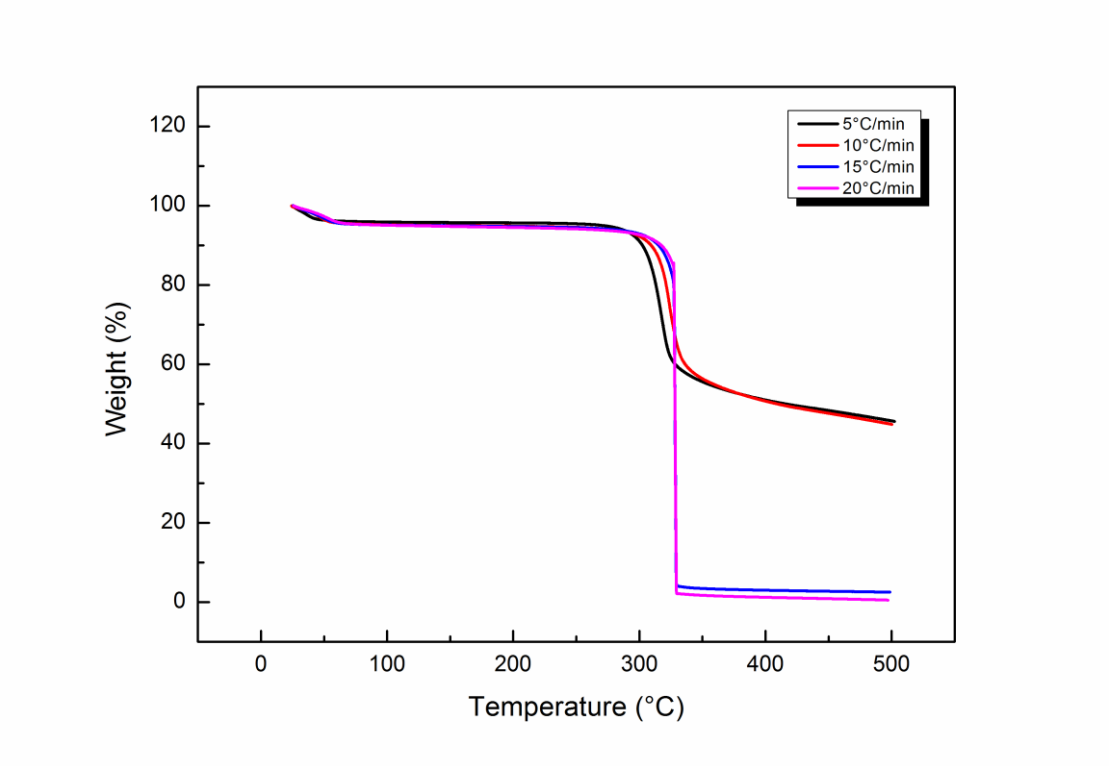


Figure S17. TG curves of compound **8**

Table S18 Kinetic parameters obtained by **Kissinger** and **Ozawa method**

β/K·min^{-1}	T_P/K	Kissinger method			Ozawa method	
		E_K/kJ·mol^{-1}	lnA	r	E_o/kJ·mol^{-1}	r
5	593.39	298.42	45.687	0.96534	293.256	0.96742
10	602.63					
15	604.42					
20	605.92					

References

[1] Huynh, M.H.V.; Hiskey, M.A.; Chavez, D. E.; Gilardi, R. D. Tetraazapentalene chemistry: unexpected intramolecular electron rearrangement induced by highly reactive ψ-dinitroso substituents. *Angew. Chem. Int. Ed.* **2005**, *44*, 7089-7094.