Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

Synthesis and Properties of Insensitive [1,2,4]Triazolo[4,3-b][1,2,4,5]tetrazine Explosives

Guilong Wang,[a] Tian Lu [a] Guijuan Fan,[b] Hongquan Yin[a] and Fu-Xue Chen[a]*

[a] School of Chemistry and Chemical Engineering, Beijing Institute of Technology, 5 South Zhongguancun street, Beijing 100081, China E-mail: fuxue.chen@bit.edu.cn.

[b] Institute of Chemical Materials, CAEP, Mianyang 621050, China.

Contents

1. Experimental Section

General Information ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz (Buruker Avance 400) nuclear magnetic resonance spectrometers operating at 400 and 100 MHz, respectively. ^{15}N NMR spectra were measured on a 700 MHz (Buruker Avance 700) nuclear magnetic resonance spectrometers operating at 70 MHz. FT-IR spectra were taken using KBr pellets on a Bruker ALPHA FT-IR-Spektrometer. DSC (Shimadzu TA-60ws) was employed to measure the melt points and decomposition temperatures at a scan rate of 5 °C min^{-1} in argon atmosphere. High resolution mass spectrometry was recorded on Bruker Apex IV FTMS.

Procedure for Synthesis:

Caution! Although no dangerous situation was encountered in the synthesis of these energetic materials, it is recommended to carry out these procedures on a small scale and always use proper protective equipment.

6-(3,5-Dimethyl-1H-pyrazol-1-yl)-[1,2,4]triazolo[4,3-b]-1,2,4,5-tetrazine (**2a**) [s2] and **3-chloro-6-(3,5-dimethyl-1H-pyrazol-1-yl)-[1,2,4]triazolo[4,3-b]-1,2,4,5-tetrazine** (**2b**). A dropping funnel was charged with a solution of $NaNO_2$ (5.6 g, 81.2 mmol) in water (20 mL) which was slowly added dropwise to an ice-bath cooled and vigorously stirred solution of **1** (2.0 g, 8.6 mmol) in 6 M HCl (20 mL). After addition, the suspension was heated to 50 °C for 2 h. After normal aqueous workup, the residue was applied onto a silica gel column with ethyl acetate (EA): petroleum ether (PE) = 1:3, yielding **2b** and **2a** in 1.44 g (66.4 %) and 226 mg (12.1%), respectively.

2a, ^{1}H NMR (400 MHz, DMSO-*d6*): δ = 10.01 (s, 1H), 6.38 (s, 1H), 2.60 (s, 3H), 2.83 (s, 3H). **2b**, ^{1}H NMR (400 MHz, DMSO-*d6*): δ = 6.43 (s, 1H), 2.62 (s, 3H), 2.31 (s, 3H); IR (KBr): ν 3420, 2920, 1531, 1393, 1279, 1105, 1042, 970, 829, 746, 667, 665, 457 cm^{-1}; HRMS: calc. for $C_8H_8ClN_8$ [*M*+H]$^{+}$, 251.0055 found: 251.0053.

6-(3,5-Dimethyl-1H-pyrazol-1-yl)-3-nitro-[1,2,4]triazolo[4,3-b]-1,2,4,5-tetrazine (**2c**). A dropping funnel was charged with a solution of $NaNO_2$ (2.8 g, 40.6 mmol) in water (20 mL) which was added dropwise to an ice-cooled and vigorously stirred solution of **1** (1.0 g, 4.3 mmol) in 65% HNO_3 (20 mL). After addition, the suspension was heated to 50 °C for 2 h. After normal aqueous workup, the residue was applied onto a silica gel column with EA:PE = 1:3, yielding **2c** in 200 mg (17.7 %) and **2a** 88.8 mg (9.5%).

2c, ^{1}H NMR (400 MHz, DMSO-*d6*): δ = 6.43 (s, 1H), 2.62 (s, 3H), 2.31 (s, 3H); IR (KBr): ν 3447, 3109, 3003, 2934, 2154, 1734, 1584, 1531, 1383, 1281, 1225, 1107, 1078, 1032, 968, 827, 785, 746, 667, 615, 565, 455 cm^{-1}.

***N*-(6-(3,5-Dimethyl-4-nitro-1H-pyrazol-1-yl)-[1,2,4]triazolo-[4,3-b]-1,2,4,5-tetrazin-3-yl)nitramide** (**2d'**). Conc. H_2SO_4 (5 mL) was solved in fuming HNO_3 (5 mL), followed by the addition of **2a** (1.0 g, 4.6 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 19 h. After normal aqueous workup, the residue was applied onto a silica gel column with EA:PE = 1:3, resulting in **2d'** 590 mg (48.8%) as a red solid. ^{1}H NMR (400 MHz, DMSO-*d6*): δ = 10.23 (s, 1H), 2.90 (s, 3H), 2.59 (s, 3H). IR (KBr): ν 3433, 3094, 1580, 1541, 1508, 1476, 1412, 1381, 1350, 1321, 1290, 1231, 1163, 1069, 1016, 945, 868, 851, 802, 764, 660, 611, 500, 442 cm^{-1}.

***N*-(6-(3,5-Dimethyl-4-nitro-1*H*-pyrazol-1-yl)-[1,2,4]triazolo[4,3-b]-1,2,4,5-tetrazin-3-yl)nitramide** (**2e**)**.** P_2O_5 (2.0 g, 14.1 mmol) was solved in fuming HNO_3 (10 mL), followed by the addition of **1** (1.0 g, 4.3 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 10

h. Then, it was poured into ice water. After normal aqueous workup, the residue was applied to a silica gel column with eluent EA:PE = 1:2, giving **2e** (800 mg, 57.6% yield) as a red solid. ^{1}H NMR (400 MHz, DMSO-*d6*) δ 10.02 (s, 1H), 3.32 (s, 3H), 2.90 (s, 3H); HRMS [*M*-H]$^-$ calc. for $C_8H_6N_{11}O_4$ 320.0610, found 320.0623; IR (KBr) ν 3094, 2918, 2849, 1742, 1580, 1558, 1508, 1412, 1383, 1358, 1269, 1236, 1065, 1016, 993, 849 cm^{-1}.

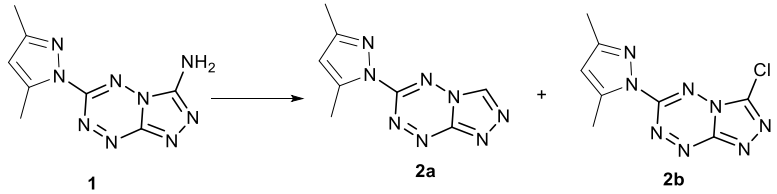
[1,2,4]Triazolo[4,3-b]-1,2,4,5-tetrazin-6-amine (3a). [s2] A 100 mL capacity pressure reactor equipped with a magnetic stirrer was charged with **2d'** (1.0 g, 3.8 mmol) and acetonitrile (20 mL). Ammonium hydroxide (25%, 2.0 mL) was introduced into the closed vessel. The reactor was heated to 100 °C for 4 h. When it was cooled to room temperature, the resulting mixture was concentrated under vacuum. The residue was applied onto a silica gel column with eluent EA:PE = 1:2, resulting in **3a** 489 mg (93.1%) as a yellow solid. mp: 224.8 °C; ^{1}H NMR (400 MHz, DMSO-*d6*): δ = 9.34 (s, 1H), 8.08 (s, 2H); ^{13}C NMR (100 MHz, DMSO-*d6*): δ = 156.66, 149.81, 136.03; IR (KBr): ν 3308, 3102, 1653, 1558, 1360, 1302, 1153, 1049, 972, 943, 864, 735, 681, 610, 511, 446 cm^{-1}.

3-Chloro-[1,2,4]triazolo[4,3-b]-1,2,4,5-tetrazin-6-amine (**3b**) Similar procedure of **3a**, **3b** was isolated in 629 mg (83.5%) as a yellow solid from **2b** (1.10 g, 4.4 mmol) with eluent EA: PE = 1:2.5. mp: 227.4 °C; ^{1}H NMR (400 MHz, DMSO-d6): δ = 8.35 (s, 1H); ^{13}C NMR (100 MHz, DMSO-*d6*): δ = 156.98, 150.40, 133.27. ^{15}N NMR (70 MHz, DMSO-*d6*): δ = 55.06, 37.85, –55.12, –63.07, –182.21, –301.24; IR (KBr): ν 3433, 3294, 3208, 3161, 1638, 1560, 1387, 1294, 1109, 1063, 735, 675, 529 cm^{-1}; GC-MS: calc. for $C_3H_2N_8O_2$, 171.0; found: 171.0.

3-Nitro-[1,2,4]triazolo[4,3-b]-1,2,4,5-tetrazin-6-amine (TTNA). Similar to **3a**, **TTNA** was obtained in 100 mg (71.7 %) as a yellow solid from **2c** (200 mg, 0.766 mmol) with eluent EA:PE = 1:2.5. ^{13}C NMR (100 MHz, CD_3OD): δ = 160.32, 159.27, 150.48. ^{15}N NMR (70 MHz, DMSO-*d6*): δ = 58.26, 44.94, –35.70, –46.22, –63.40, –177.01, –183.65, –296.59; IR (KBr): ν 3360, 1647, 1541, 1391, 1294, 1115, 1007, 824, 741, 669, 598 cm^{-1}; HRMS: calc. for $C_3H_1N_8O_2$ [*M*-H]$^-$. 181.0228 found: 181.0228.

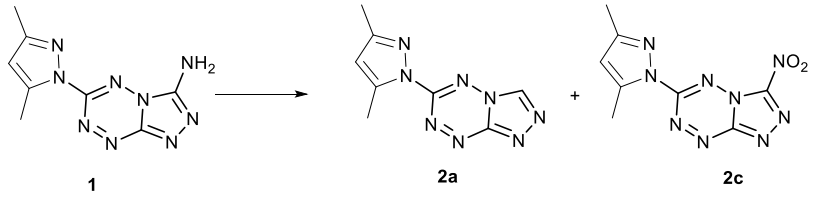
***N*-(6-Amino-[1,2,4]triazolo[4,3-b]-1,2,4,5-tetrazin-3-yl)nitramide** (**TTDAN**). Similar to **3a, TTDAN** was yielded in 570 mg (92.9%) as red solid from **2e** (1.0 g, 3.1 mmol) with eluent MeOH:CH_2Cl_2 = 1:5. ^{1}H NMR (400 MHz, DMSO-*d6*): δ = 7.76 (s, 2H); ^{13}C NMR (100 MHz, DMSO-*d6*): δ = 156.07, 149.24, 148.48; ^{15}N NMR (70 MHz, DMSO-*d6*): δ = 49.54, 18.58, –12.64, –56.70, –66.04, –152.79, –176.86, –195.33, –306.16; IR (KBr): ν 3566, 3308, 3144, 1636, 1607, 1558, 1516, 1468, 1395, 1333, 1053, 1015, 849, 760, 708, 669, 532, 501 cm^{-1}; HRMS: calc. for $C_3H_2N_9O_2$ [*M*-H]$^-$. 196.0337 found: 196.0341.

2. Other control experiments and trials

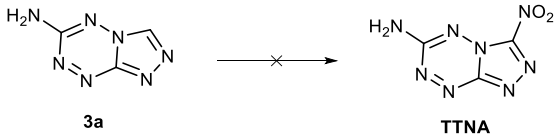


1 2a 2b

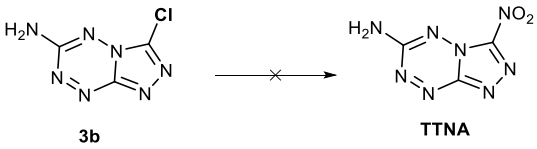
1) $NaNO_2$, 2M HCl, **2a** (49.2% yield), **2b** (29.7% yield).
2) $NaNO_2$, 4M HC, **2a** (39.8% yield), **2b** (42.2% yield).
3) $NaNO_2$, 6M HCl, **2a** (12.1% yield), **2b** (66.4% yield).



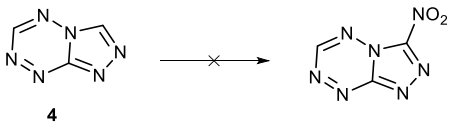
1) $NaNO_2$, 0.5M H_2SO_4, **2a** (0% yield), **2c** (0% yield).
2) $NaNO_2$, 1M H_2SO_4, **2a** (5.6% yield), **2c** (4.3% yield).
3) $NaNO_2$, 2M H_2SO_4, **2a** (13.2% yield), **2c** (10.3% yield).
4) $NaNO_2$, 4M H_2SO_4, **2a** (11.1% yield), 2c (12.3% yield).
5) $NaNO_2$, 6M H_2SO_4, **2a** (12.4% yield), **2c** (10.1% yield).
6) $NaNO_2$, 25%HNO_3, **2a** (13.7% yield), **2c** (10.9% yield).
7) $NaNO_2$, 65%HNO_3, **2a** (9.5% yield), **2c** (17.7% yield).



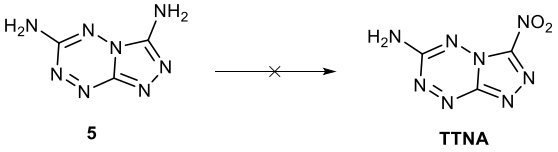
1) HNO_3, H_2SO_4, no conversion.



1) KNO_2, CuI, N,N,N',N'-Tetramethylethylenediamine, DMF, no conversion.
2) $AgNO_2$, THF, no conversion.



1) HNO_3, H_2SO_4, no conversion.



1) Na_2WO_4, 50% H_2O_2, conc.H_2SO_4, **TTNA** (0% yield).
2) 50% H_2O_2 TFA, DCM, no conversion.
3) Fuming HNO_3, P_2O_5, **TTNA** (0% yield).
4) $NaNO_2$, 2 M H_2SO_4, **TTNA** (0% yield).

Scheme S1 Control experiments and others reactions

3. X-ray Diffraction

Crystal data of **1** was collected on a Bruker APEX-II CCD diffractometer at 296 K

employing graphite-monochromated MoKa radiation (λ=0.71073 Å). The structure was solved by direct methods and refined by the least-squares method on F^2 using the SHELXTL-97 suite of programs.[S1] All non-hydrogen atoms were refined anisotropically. Details of the x-ray data collection and structure refinements are summarized in Table S1. Supplementary crystallographic data for this paper can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif with the CCDC number 1883370 and 1817250.

Table S1 Crystallographic data for **3b** and **4**.

	3b	**4**
Formula	C3H2ClN7	C3 H2 N6
Mw[g mol^{-1}]	171.57	122.11
T[K]	296(2) K	296(2)
Crystal size[mm^3]	0.150 x 0.130 x 0.100	0.150 x 0.120 x 0.100
Crystal system	Orthorhombic	Orthorhombic
Space group	*P n m a*	*P 21 21 21*
a[Å]	7.5145(11)	5.4334(7)
b[Å]	6.2774(9)	6.5582(9)
c[Å]	13.7315(19)	13.8317(19)
α[°]	90	90
β[°]	90	90
γ[°]	90	90
V[Å^3]	647.74(16)	492.87(11)
Z	4	4
ρ_{calc}[g cm^{-3}]	1.759	1.646
μ[mm^{-1}]	0.525	0.124
F[000]	344	248
ϑ range[°]	2.967 to 28.289	2.945-25.046
Reflections collected	7415 / 869	4153 / 872
Index ranges	-9<=h<=9, -8<=k<=8, -18<=l<=18	-6<=h<=6, -7<=k<=7, -16<=l<=16
R_{int}	0.0176	0.0195
Data/restraints/parameters	869 / 0 / 67	872 / 1 / 83
Final *R* index[$I > 2\sigma(I)$]	R1 = 0.0295, wR2 = 0.0897	R1 = 0.0886, wR2 =0.2403
Final *R* index[all data]	R1 = 0.0312, wR2 = 0.0919	R1 = 0.0916, wR2 = 0.2426
GOF on F^2	1.027	0.995
CCDC	1883370	1817250

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. $wR_2 = [(w(F_o^2 - F_c^2)^2) / w(F_o^2)^2]^{1/2}$.

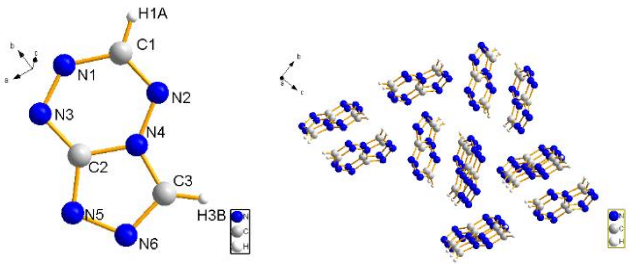


Figure S1. (left) Single-crystal X-ray structure of compound **4**. (right) Crystal packing diagram of compound **4**.

Suitable crystals for **4** was obtained by slowly evaporation of solutions of ethyl acetate/petroleum at room temperature and ambient pressure. The single crystal X-ray structures are shown in ***Figure S1***. The crystal forms in the $P2_12_12_1$ space group and the orthorhombic crystal system. The crystal density of **4** is 1.646 g cm^{-3} at 278 K. As expected, the 1,2,4-triazole ring and the 1,2,3,4-tetrazine ring are coplanar(N(2)-N(4)-C(2)-N(5) -179.1(7)°).

Table **S2**. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **3b**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cl(1)	2712(1)	2500	-2191(1)	46(1)
N(6)	2840(2)	2500	-240(1)	30(1)
N(5)	1052(2)	2500	-55(1)	34(1)
N(2)	5466(2)	2500	-939(1)	43(1)
N(4)	2059(2)	2500	1642(1)	42(1)
N(1)	5733(2)	2500	45(1)	45(1)
N(7)	-897(2)	2500	1234(1)	48(1)
N(3)	3707(2)	2500	1419(1)	43(1)
C(3)	758(2)	2500	892(1)	35(1)
C(1)	3721(2)	2500	-1100(1)	35(1)
C(2)	4129(2)	2500	451(1)	35(1)

Table **S3**. Bond lengths [A] and angles [deg] for **3b**.

Cl(1)-C(1)	1.6786(17)
N(6)-C(2)	1.3561(18)
N(6)-C(1)	1.354(2)
N(6)-N(5)	1.3674(17)
N(5)-C(3)	1.319(2)
N(2)-C(1)	1.330(2)
N(2)-N(1)	1.365(2)
N(4)-N(3)	1.276(2)
N(4)-C(3)	1.420(2)
N(1)-C(2)	1.328(2)
N(7)-C(3)	1.330(2)
N(7)-H(7A)	0.8600
N(7)-H(7B)	0.8600
N(3)-C(2)	1.367(2)
C(2)-N(6)-C(1)	105.13(13)
C(2)-N(6)-N(5)	124.89(13)
C(1)-N(6)-N(5)	129.98(13)
C(3)-N(5)-N(6)	110.34(13)

C(1)-N(2)-N(1)	108.03(14)
N(3)-N(4)-C(3)	119.64(14)
C(2)-N(1)-N(2)	106.39(14)
C(3)-N(7)-H(7A)	120.0
C(3)-N(7)-H(7B)	120.0
H(7A)-N(7)-H(7B)	120.0
N(4)-N(3)-C(2)	117.28(14)
N(5)-C(3)-N(7)	120.35(15)
N(5)-C(3)-N(4)	126.85(15)
N(7)-C(3)-N(4)	112.80(14)
N(2)-C(1)-N(6)	109.68(14)
N(2)-C(1)-Cl(1)	126.44(13)
N(6)-C(1)-Cl(1)	123.88(13)
N(1)-C(2)-N(6)	110.77(15)
N(1)-C(2)-N(3)	128.23(15)
N(6)-C(2)-N(3)	121.00(15)

Symmetry transformations used to generate equivalent atoms:

Table **S4**. Anisotropic displacement parameters (A^2 x 10^3) for **3b**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Cl(1)	52(1)	61(1)	26(1)	0	1(1)	0
N(6)	29(1)	36(1)	26(1)	0	-2(1)	0
N(5)	29(1)	47(1)	27(1)	0	0(1)	0
N(2)	36(1)	50(1)	44(1)	0	6(1)	0
N(4)	50(1)	52(1)	25(1)	0	-2(1)	0
N(1)	34(1)	55(1)	46(1)	0	-3(1)	0
N(7)	41(1)	70(1)	33(1)	0	9(1)	0
N(3)	46(1)	53(1)	31(1)	0	-11(1)	0
C(3)	38(1)	39(1)	28(1)	0	1(1)	0
C(1)	34(1)	40(1)	31(1)	0	4(1)	0
C(2)	33(1)	42(1)	32(1)	0	-7(1)	0

Table **S5**. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **3b**.

	x	y	z	U(eq)
H(7A)	-1783	2500	838	58
H(7B)	-1082	2500	1852	58

Table **S6**. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **4**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	1046(17)	10859(12)	9361(6)	58(2)
N(2)	-1652(13)	8127(11)	9388(5)	42(2)
N(3)	2702(13)	10117(11)	8780(5)	41(2)
N(4)	0(14)	7239(12)	8785(5)	48(2)
N(5)	3296(18)	6917(13)	7886(6)	62(2)
N(6)	1901(16)	5233(11)	7827(5)	52(2)
C(1)	-1101(14)	9957(12)	9670(5)	34(2)
C(2)	2097(12)	8210(10)	8488(4)	24(1)
C(3)	-84(16)	5415(11)	8376(5)	33(2)

Table **S7**. Bond lengths [A] and angles [deg] for **4**.

N(1)-N(3)	1.300(11)
N(1)-C(1)	1.376(12)
N(2)-C(1)	1.297(10)
N(2)-N(4)	1.357(10)
N(3)-C(2)	1.355(10)
N(4)-C(3)	1.324(10)
N(4)-C(2)	1.369(10)
N(5)-C(2)	1.356(10)
N(5)-N(6)	1.342(12)

N(6)-C(3)	1.324(12)
C(1)-H(1A)	0.9300
C(3)-H(3B)	0.9300

N(3)-N(1)-C(1)	128.1(8)
C(1)-N(2)-N(4)	115.4(7)
N(1)-N(3)-C(2)	111.2(7)
C(3)-N(4)-N(2)	128.9(7)
C(3)-N(4)-C(2)	108.7(7)
N(2)-N(4)-C(2)	122.4(7)
C(2)-N(5)-N(6)	106.3(8)
C(3)-N(6)-N(5)	110.6(7)
N(2)-C(1)-N(1)	120.0(7)
N(2)-C(1)-H(1A)	120.0
N(1)-C(1)-H(1A)	120.0
N(3)-C(2)-N(5)	130.1(7)
N(3)-C(2)-N(4)	122.8(7)
N(5)-C(2)-N(4)	107.0(7)
N(6)-C(3)-N(4)	107.4(7)
N(6)-C(3)-H(3B)	126.3
N(4)-C(3)-H(3B)	126.3

Symmetry transformations used to generate equivalent atoms:

Table **S8**. Anisotropic displacement parameters (A^2 x 10^3) for **4**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
N(1)	70(5)	47(5)	56(4)	-5(4)	-4(4)	7(4)
N(2)	45(4)	44(4)	36(3)	-1(3)	6(3)	1(3)
N(3)	47(4)	33(3)	42(3)	1(3)	-1(3)	1(3)
N(4)	46(4)	51(5)	46(4)	10(3)	-8(4)	-5(4)
N(5)	75(6)	64(5)	48(4)	-7(4)	-4(4)	15(5)
N(6)	68(5)	36(4)	51(4)	-12(3)	-6(4)	2(4)
C(1)	38(4)	28(4)	35(3)	-2(3)	6(3)	7(3)
C(2)	28(3)	21(3)	22(3)	0(3)	-1(3)	-3(3)
C(3)	39(4)	22(4)	37(4)	-4(3)	-4(3)	-2(3)

Table **S9**. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **4**.

	x	y	z	U(eq)
H(1A)	-2157	10660	10081	40
H(3B)	-1311	4442	8458	39

Table **S10**. Torsion angles [deg] for **4**.

C(1)-N(1)-N(3)-C(2)	-0.6(12)
C(1)-N(2)-N(4)-C(3)	-179.1(7)
C(1)-N(2)-N(4)-C(2)	-0.4(10)
C(2)-N(5)-N(6)-C(3)	-0.9(9)
N(4)-N(2)-C(1)-N(1)	-0.4(11)
N(3)-N(1)-C(1)-N(2)	1.0(13)
N(1)-N(3)-C(2)-N(5)	179.6(8)
N(1)-N(3)-C(2)-N(4)	-0.2(10)
N(6)-N(5)-C(2)-N(3)	-179.2(7)
N(6)-N(5)-C(2)-N(4)	0.6(8)
C(3)-N(4)-C(2)-N(3)	179.7(7)
N(2)-N(4)-C(2)-N(3)	0.8(11)
C(3)-N(4)-C(2)-N(5)	-0.2(8)
N(2)-N(4)-C(2)-N(5)	-179.1(7)
N(5)-N(6)-C(3)-N(4)	0.8(9)
N(2)-N(4)-C(3)-N(6)	178.4(7)
C(2)-N(4)-C(3)-N(6)	-0.4(8)

Symmetry transformations used to generate equivalent atoms:

Table **S11**. Hydrogen bonds for **4** [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

4. Computation details

Computations were performed by using the Gaussian09 (Revision B.01) suite of programs. The geometric optimization of molecules and frequency analysis were accomplished by using B3LYP with the 6-31+G** basis set.

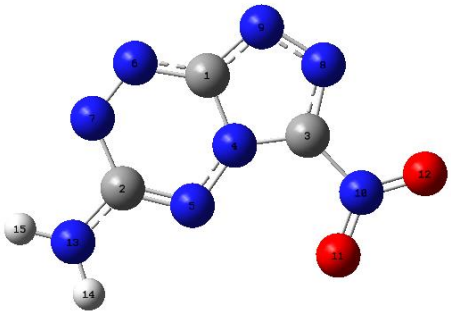


Figure S2. The optimized structure of **TTNA** at B3LYP/6-31+G** level.

Table S12. Cartesian coordinates of the optimized structure **TTNA**.

	X	Y	Z
C_1	-0.5362463	1.3661841	-0.0000075
C_2	-2.1010154	-0.7111967	-0.0000248
C_3	1.3119545	0.2583627	0.0000183
N_4	-0.0353665	0.0753662	-0.0000062
N_5	-0.8143429	-1.0289341	-0.0000085
N_6	-1.8695325	1.5954162	-0.0000196
N_7	-2.6561670	0.5788729	-0.0000268
N_8	1.6026685	1.5620466	0.0000165
N_9	0.4635272	2.2590948	0.0000053
N_{10}	2.3030458	-0.7946138	0.0000261
O_{11}	1.8754143	-1.9507533	-0.0000704
O_{12}	3.4784235	-0.4498042	0.0000962
N_{13}	-3.0165348	-1.6980910	-0.0000101
H_{14}	-2.7248227	-2.6631221	0.0000243
H_{15}	-3.9951212	-3.9951212	0.0000164

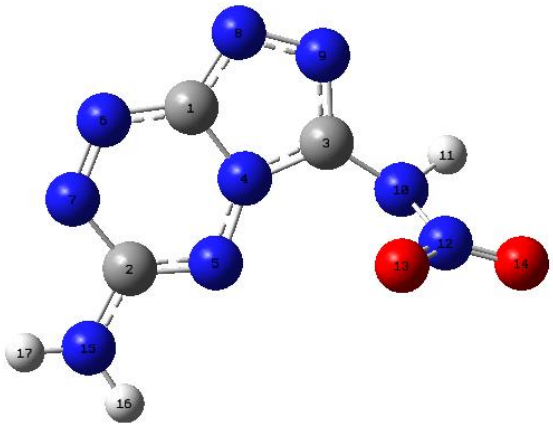
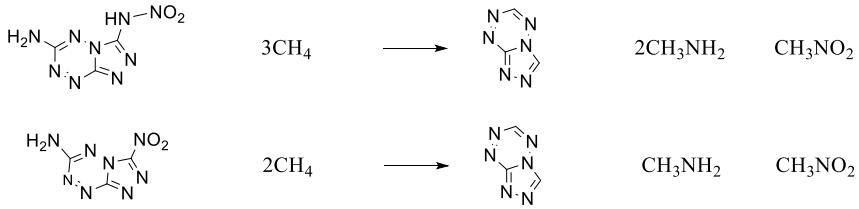


Figure S3. The optimized structure of **TTDAN** at B3LYP/6-31+G** level.

Table S13. Cartesian coordinates of the optimized structure **TTDAN**.

	X	Y	Z
C_1	-1.1583629	1.3396050	0.1275614
C_2	-2.0841269	-1.0847725	-0.1244842
C_3	0.8824660	0.8104300	-0.3587898
N_4	-0.3523778	0.2733229	-0.2281939
N_5	-0.7904175	-0.9973832	-0.3786502
N_6	-2.4760048	1.1519693	0.3746239
N_7	-2.9454993	-0.0393489	0.2584591
N_8	-0.4412000	2.4668078	0.1764160
N_9	0.8244374	2.1273122	-0.1184212
N_{10}	2.0093203	0.1067356	-0.7642077
H_{11}	2.7015302	0.6270256	-1.2950512
N_{12}	2.6731186	-0.6987467	0.2068178
O_{13}	2.0181689	-1.0394365	1.1779285
O_{14}	3.8213313	-1.0043496	-0.0766871
N_{15}	-2.7055196	-2.2774088	-0.2458149
H_{16}	-2.1631882	-3.1126215	-0.4023932
H_{17}	-3.6652023	-2.3485123	0.0545877

The heats of formation of the [1,2,4]triazolo[4,3-*b*][1,2,4,5]tetrazine derivatives were computed by using the Gaussian09 (Revision B.01) suite of programs based on isodesmic reactions(Scheme S2) at the MP2 level of theory.



Scheme S2 Isodesmic reactions for [1,2,4]Triazolo[4,3-b][1,2,4,5]tetrazine derivatives

Table S14. Calculated (B3LYP/6-31+G**//MP2/6-311++G**) total energy (E_0), Zero-Point Energy (ZPE), values of thermal correction (H_T), and heats of formation (HOF) of **TTDAN** and **TTNA**.

Name	E_0 (a.u.)	ZPE (a.u.)	H_T (a.u.)	HOF (kJ·mol^{-1})
TTDAN	-757.6795337	0.104436	0.116348	634.3
TTNA	-702.4348669	0.086908	0.097864	656.8
[1,2,4]triazolo[4,3-b][1,2,4,5]tetrazine	-443.027497	0.068714	0.07522	667.5[a]
CH_3NO_2	-244.5543604	0.049856	0.055129	-80.8[b]
CH_3NH_2	-95.6318757	0.064027	0.068396	-22.5[b]
CH_4	-40.3984876	0.044793	0.048605	-74.6[b]
NH_3NO_2	-260.554147	0.038261	0.042605	-3.9[b]

[a] T. Wei, W. Zhu, J. Zhang, H. Xiao, *J. Hazardous Mat.,* **2010**, *179*, 581–590; [b] D. R. Lide, Handbook of Chemistry and Physics (Section 5), 84th ed.; CRC Press: Boca Raton, FL, 2003−2004.

5. Spectroscopy

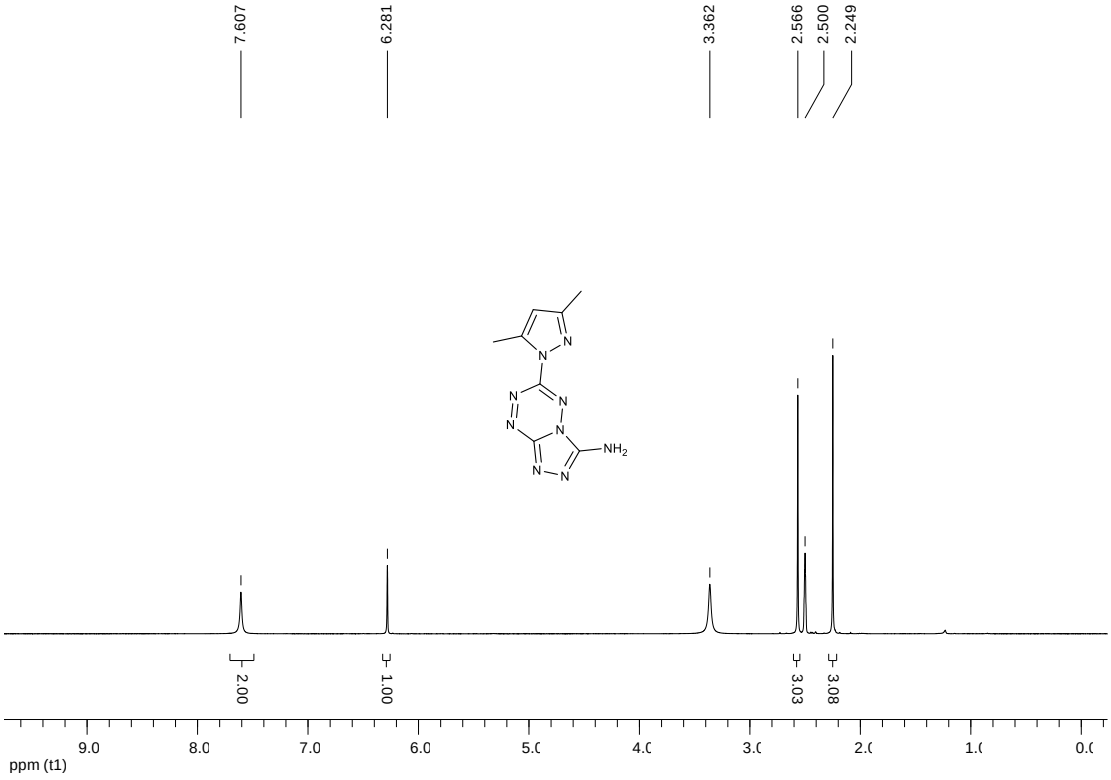


Figure S4 ^{1}H NMR spectra of **1**. [S2]

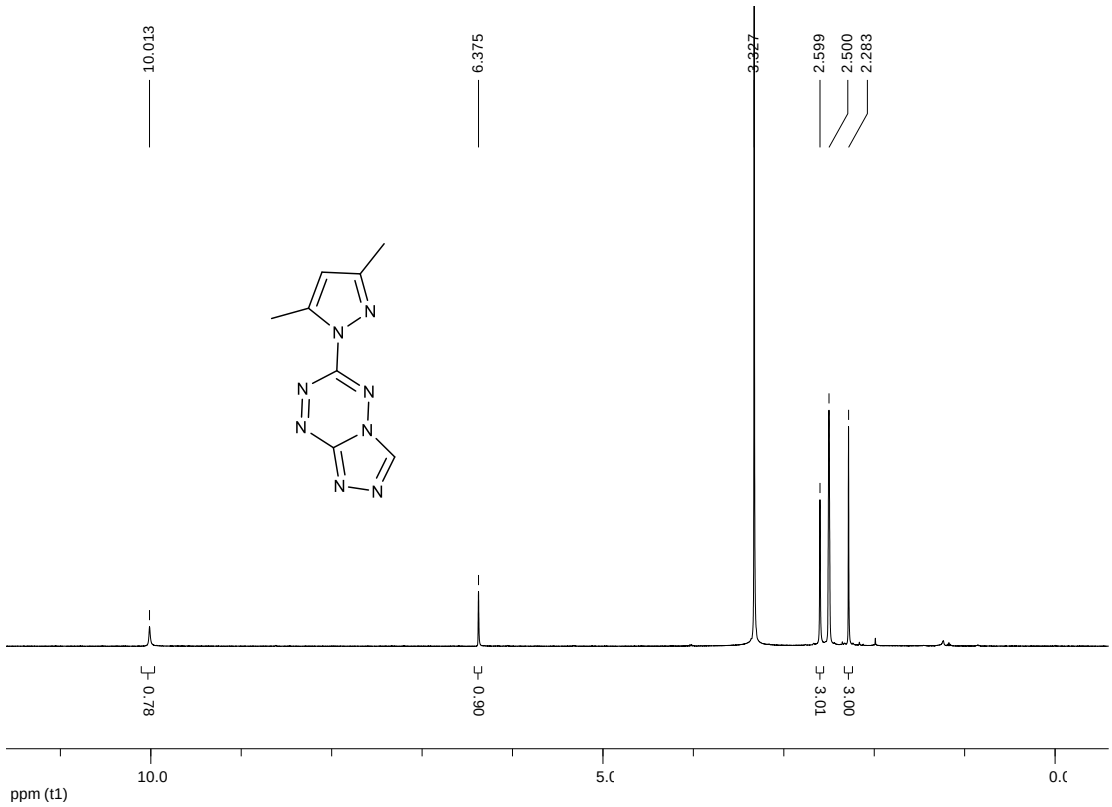


Figure S5 ^{1}H NMR spectra of **2a**. [S2]

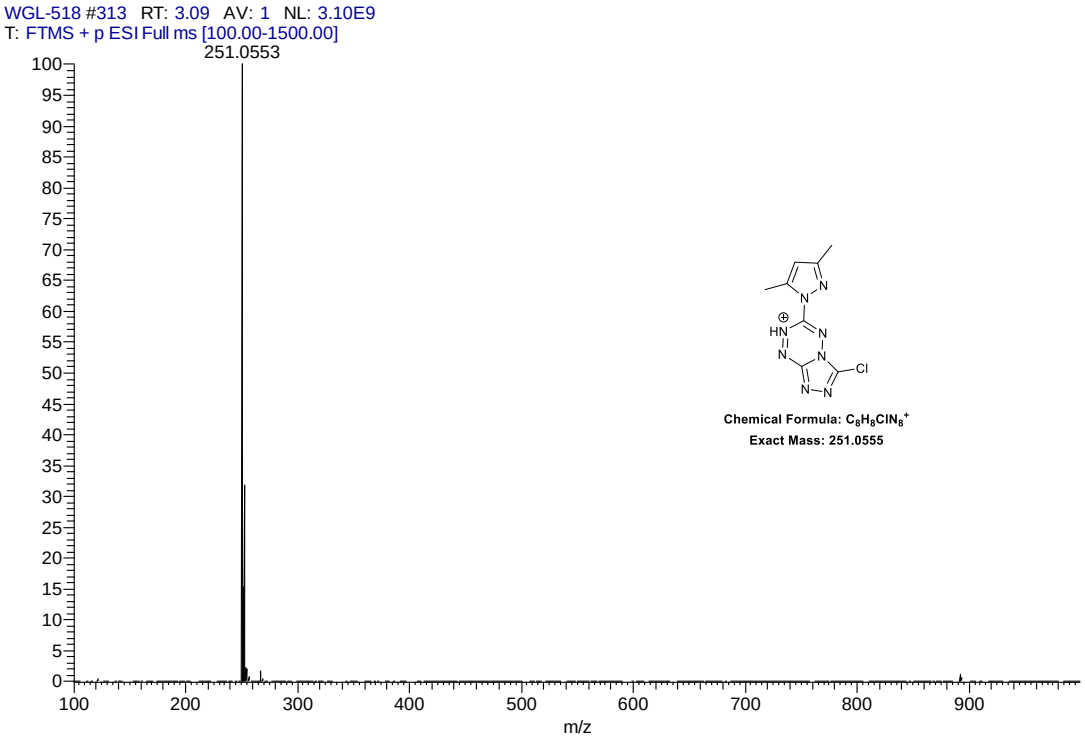


Figure S6 ESI-MS of **2b**.

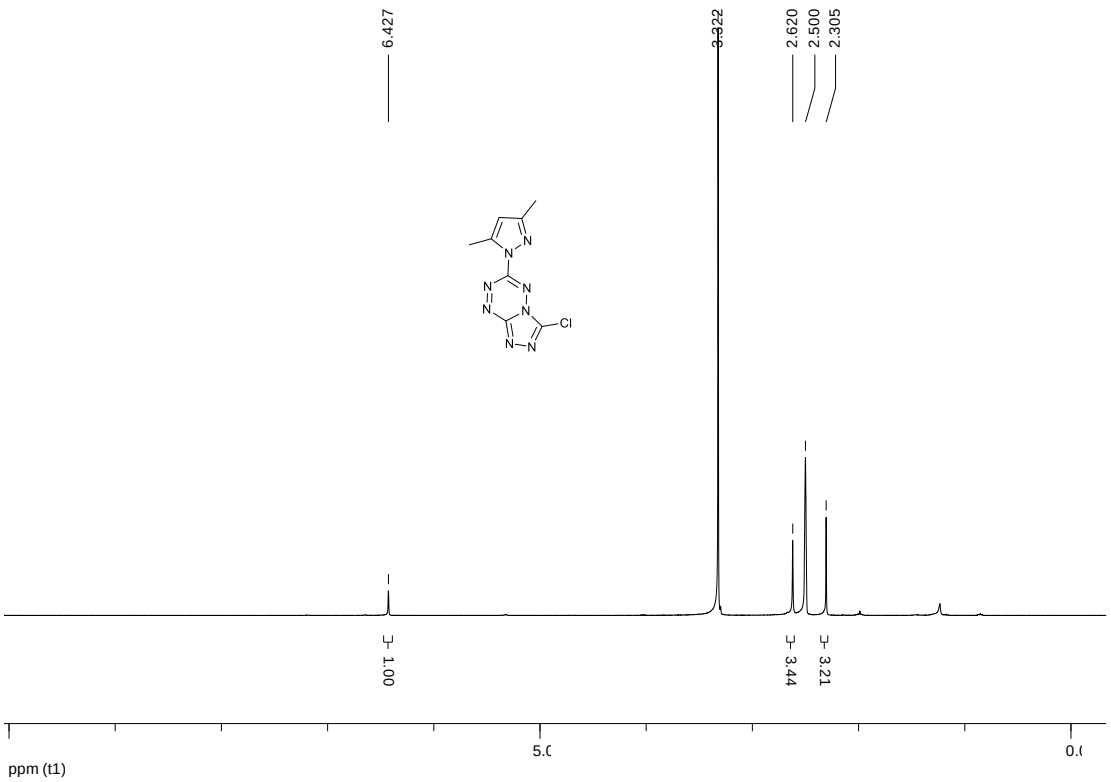


Figure S7 ^{1}H NMR spectra of **2b**.

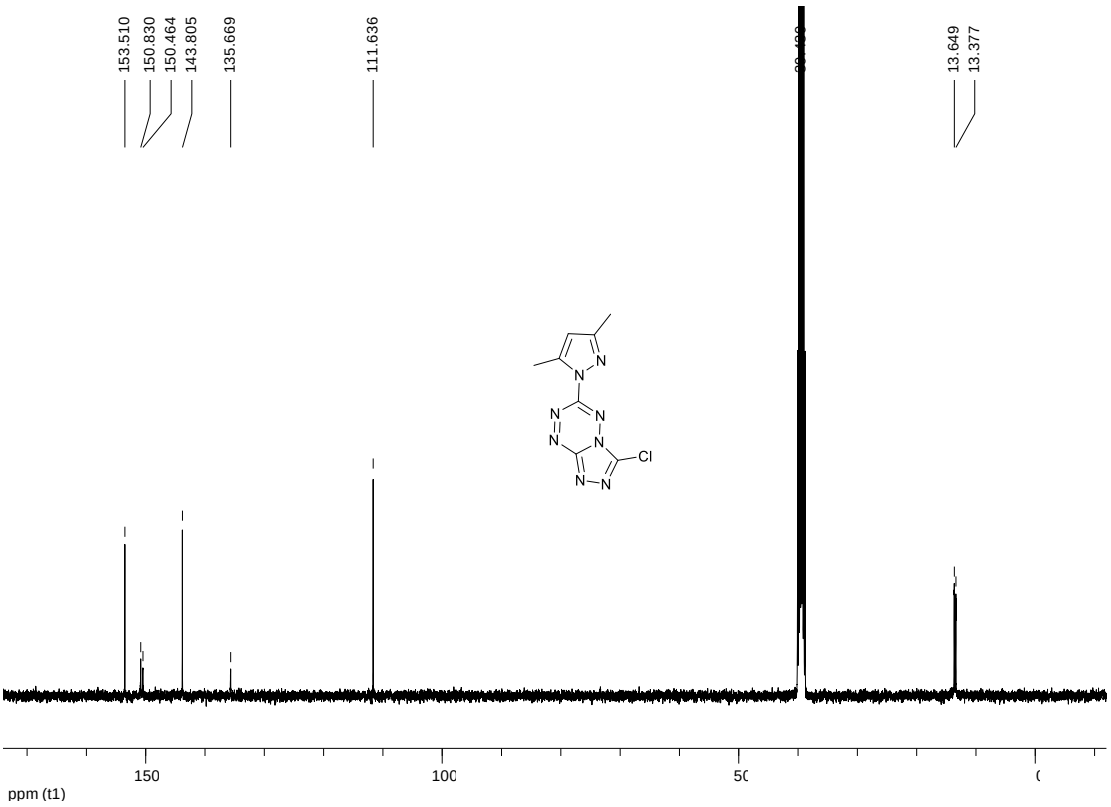


Figure S8 ^{13}C NMR of **2b**.

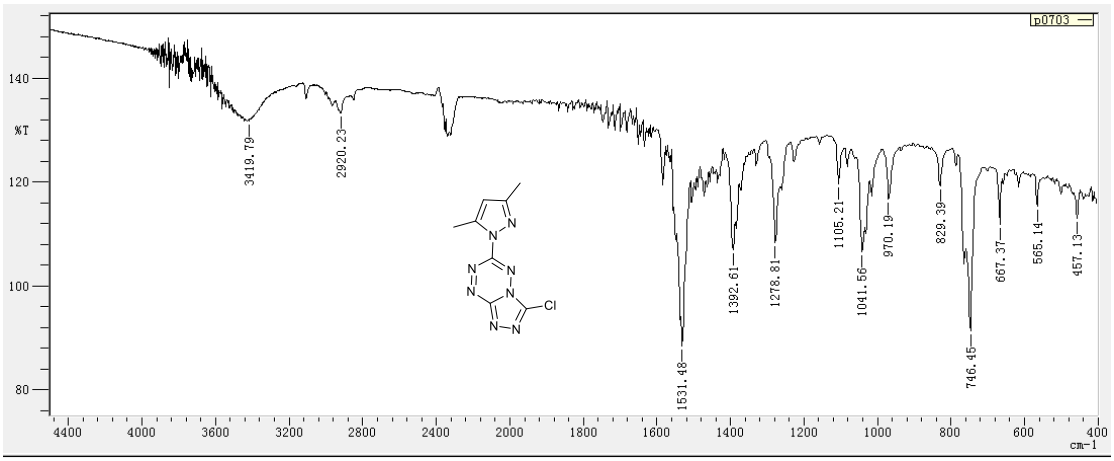


Figure S9 IR of **2b**

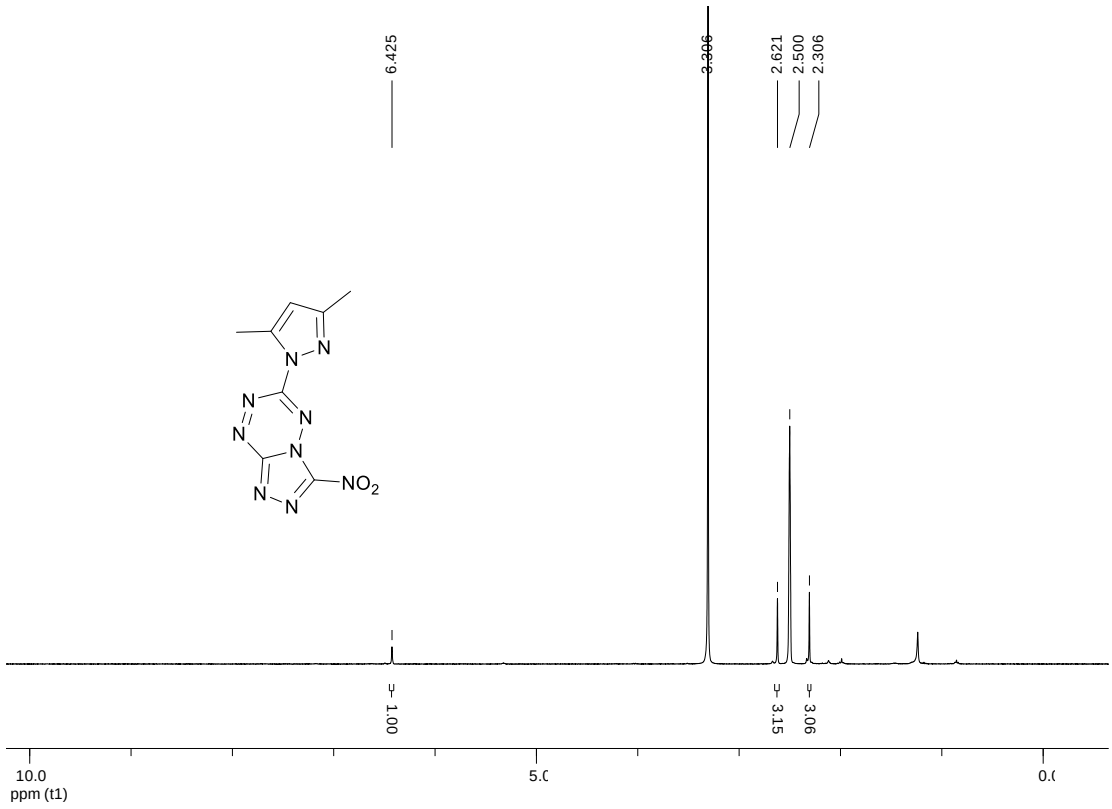


Figure S10 ^{1}H NMR of **2c**.

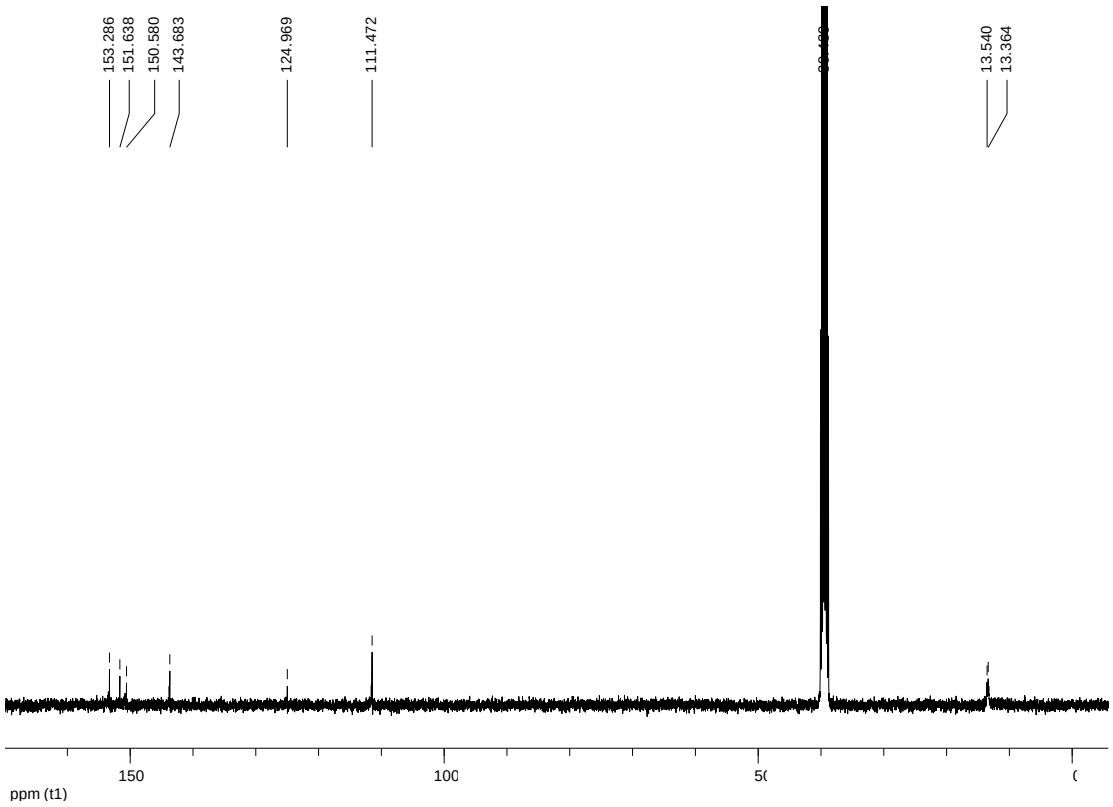


Figure S11 ^{13}C NMR of **2c.**

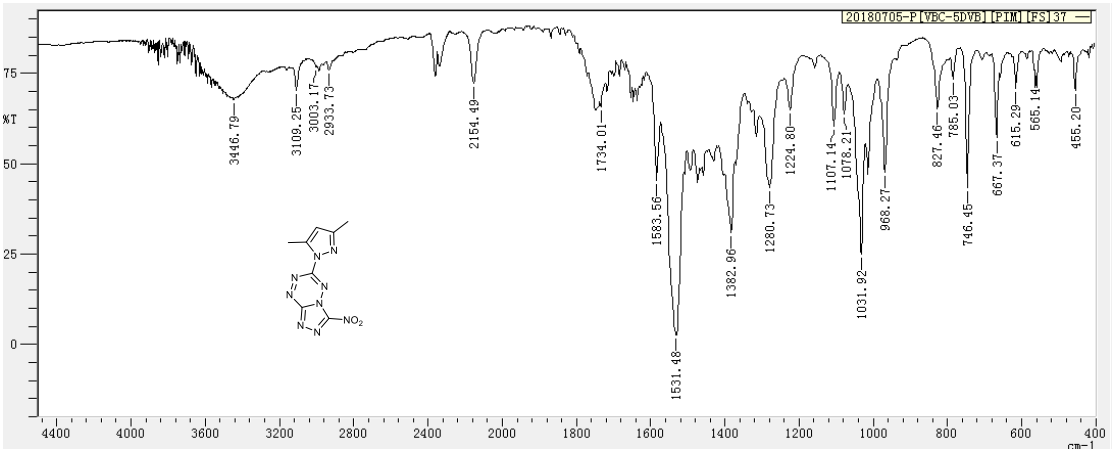


Figure S12 IR of **2c**.

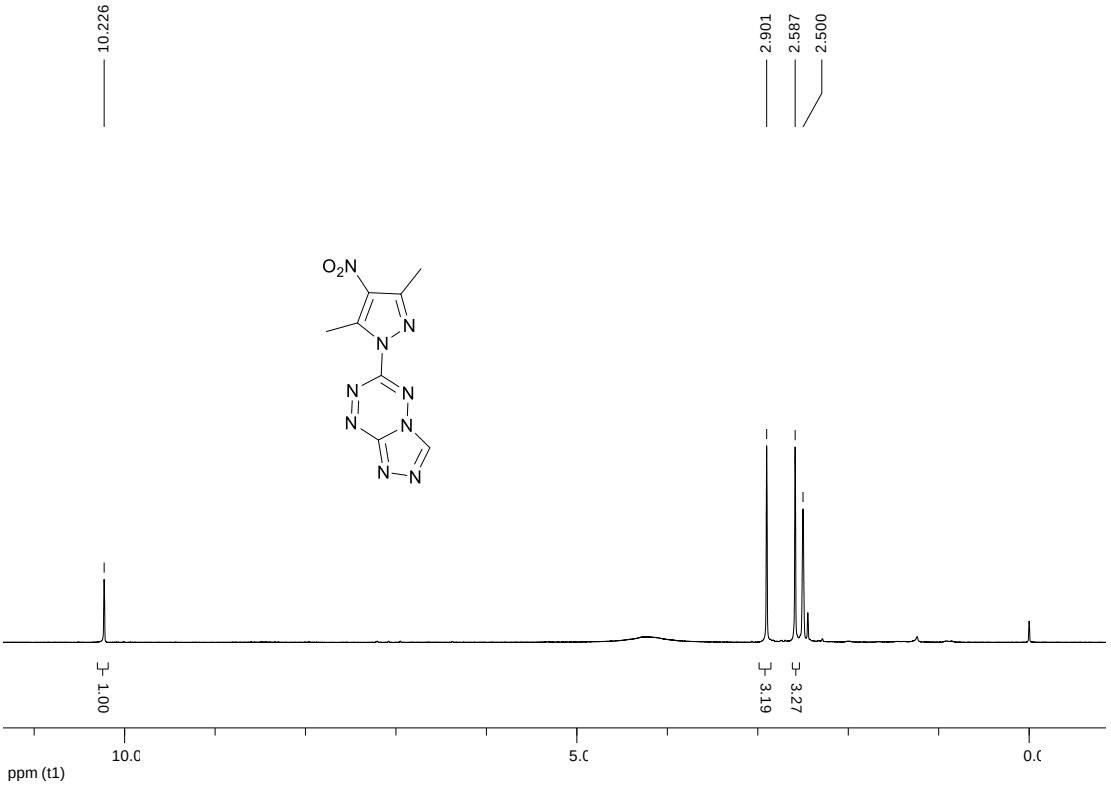


Figure S13 ^{1}H NMR of **2d**.

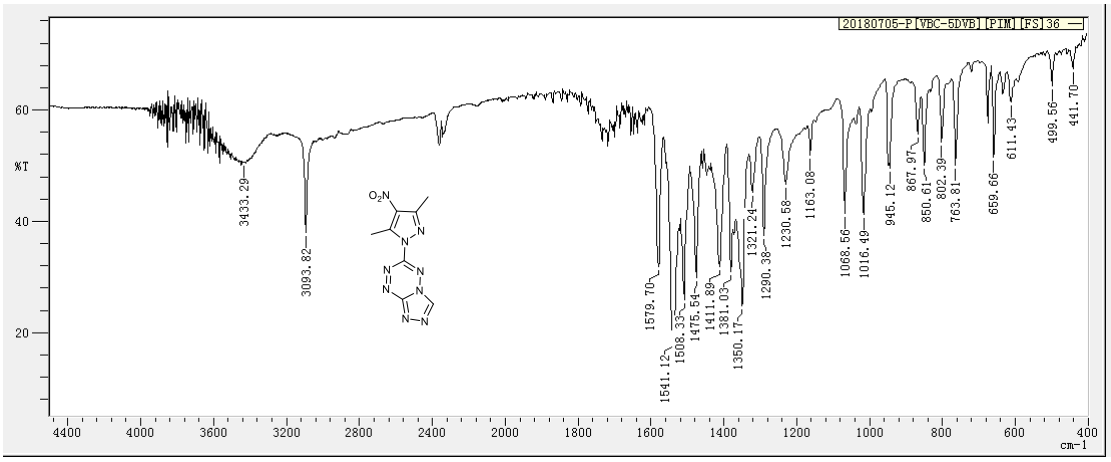


Figure S14 IR of **2d**.

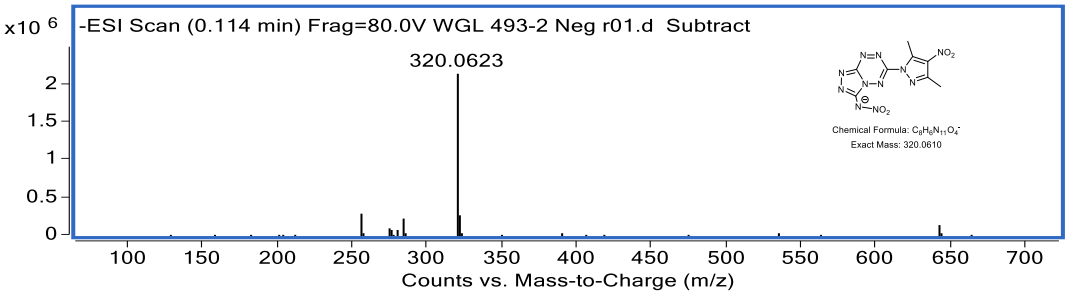


Figure S15 ESI-MS of **2e**.

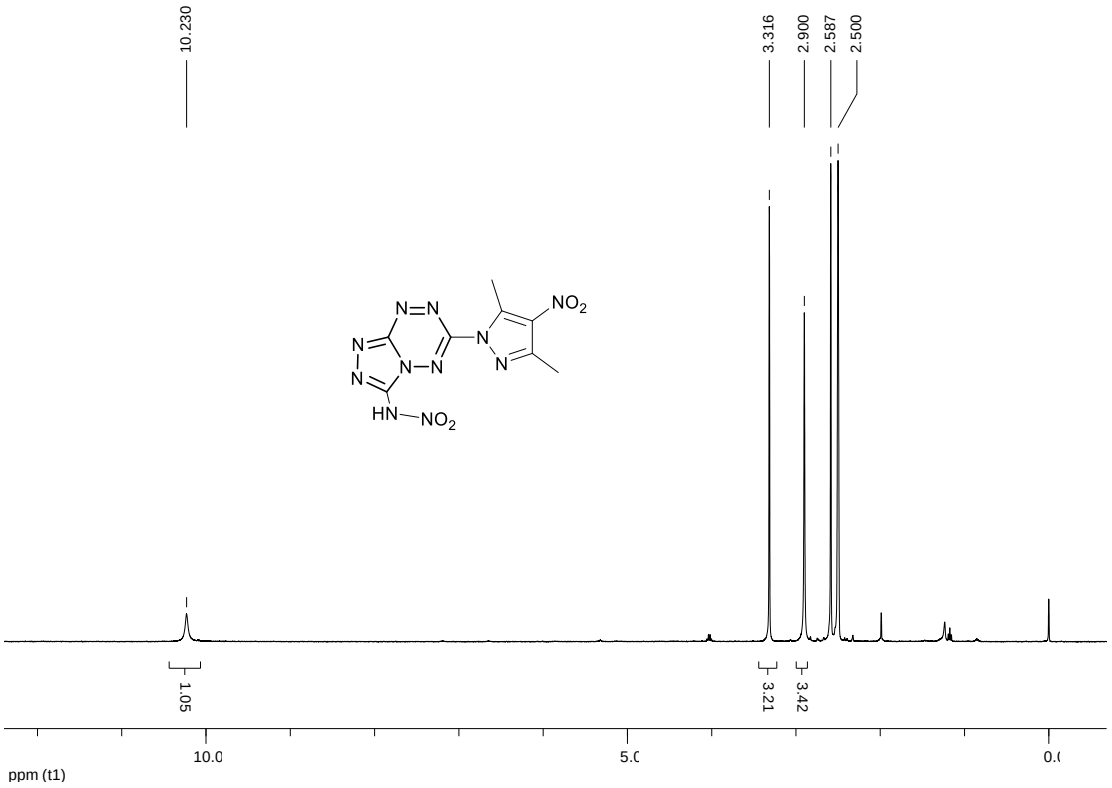


Figure S16 ^{1}H NMR of **2e**.

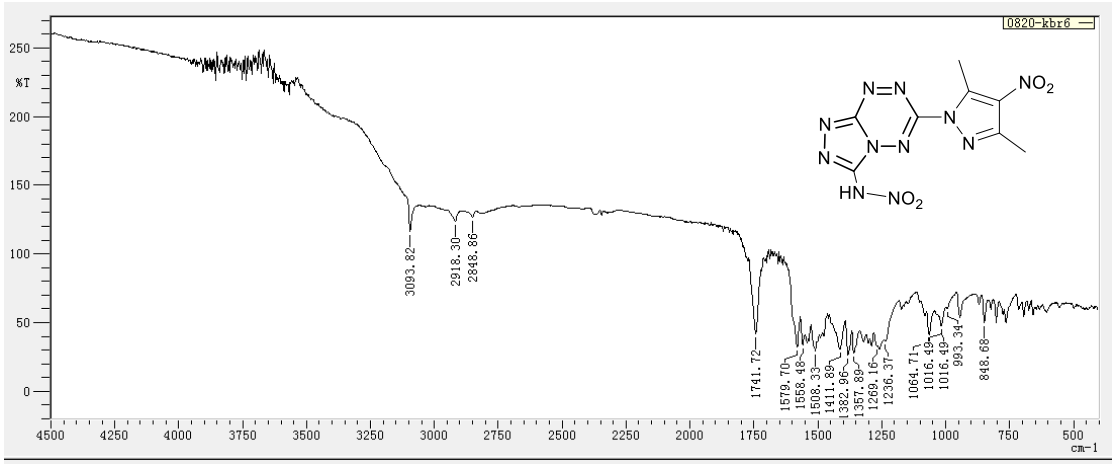


Figure S17 IR of **2e**.

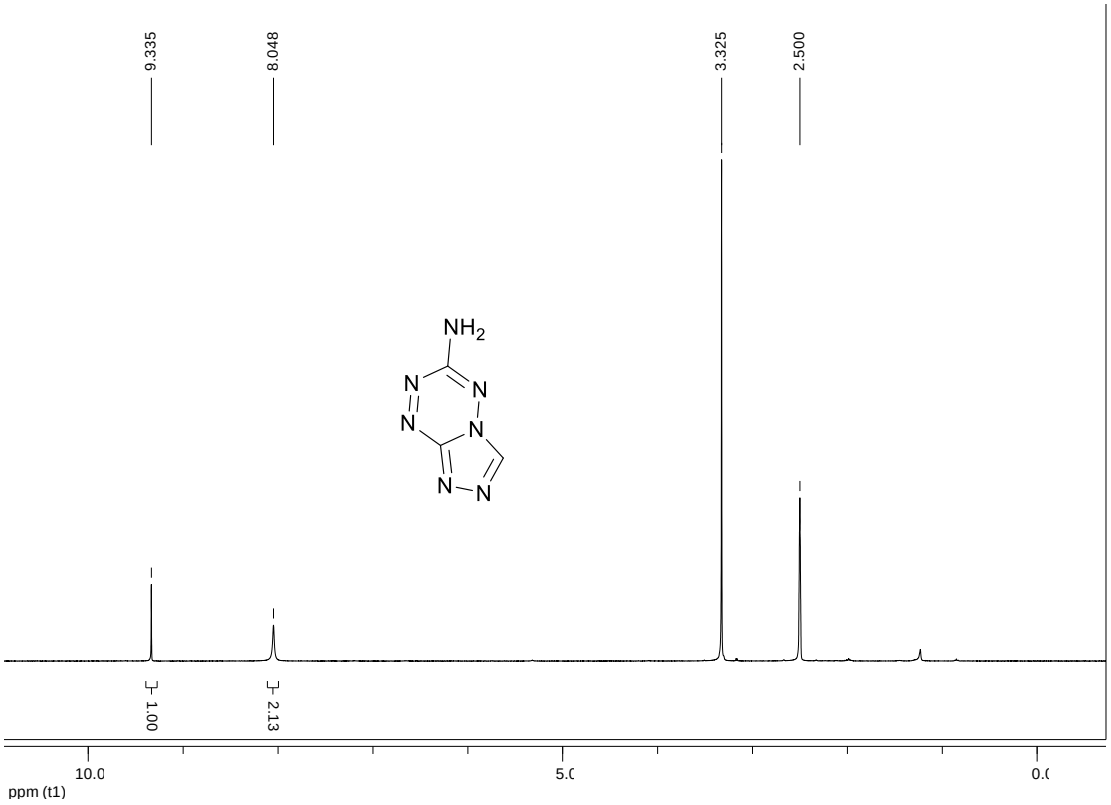


Figure S18 ^{1}H NMR of **3a.** [S2]

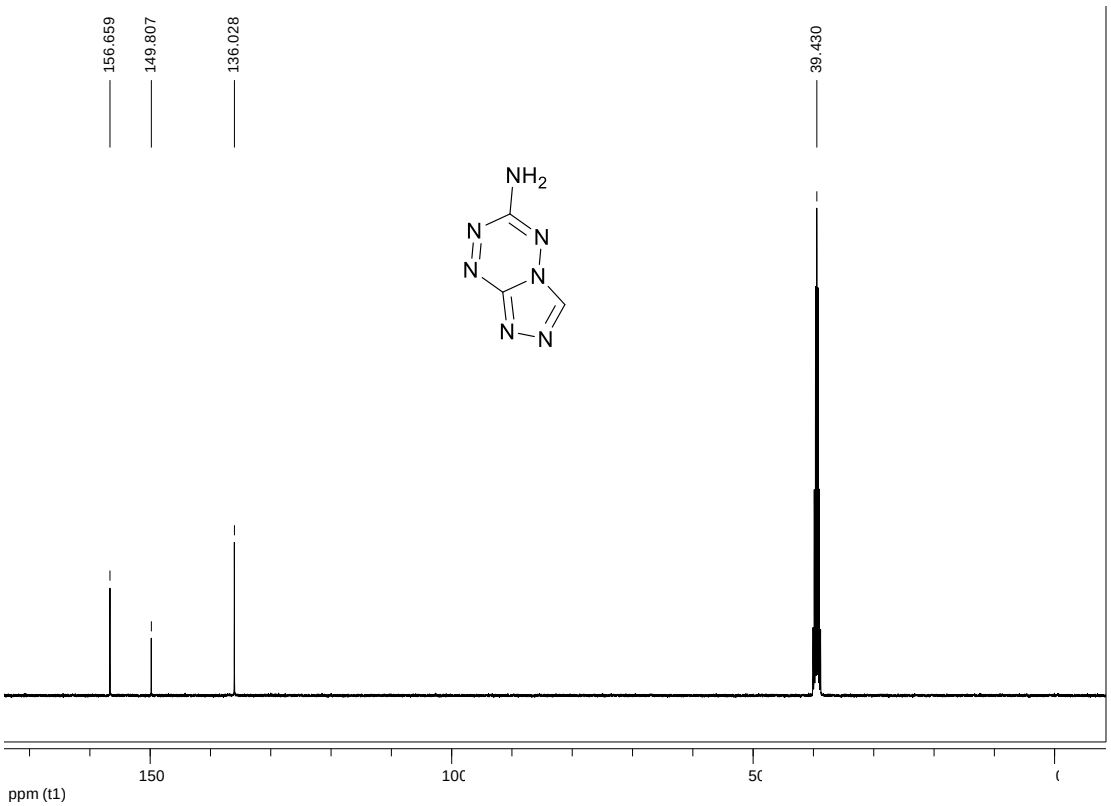


Figure S19 ^{13}C NMR of **3a**. [S2]

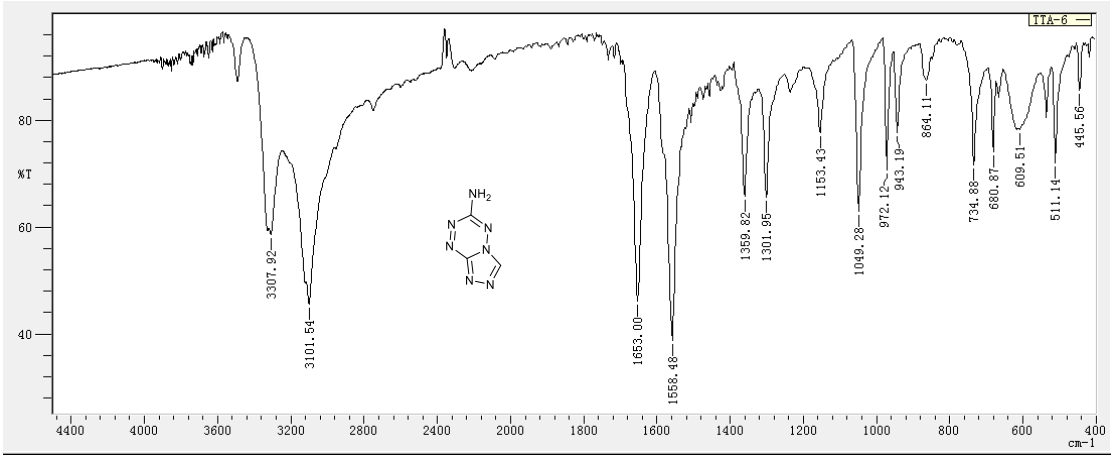


Figure S20 IR of **3a**. [S2]

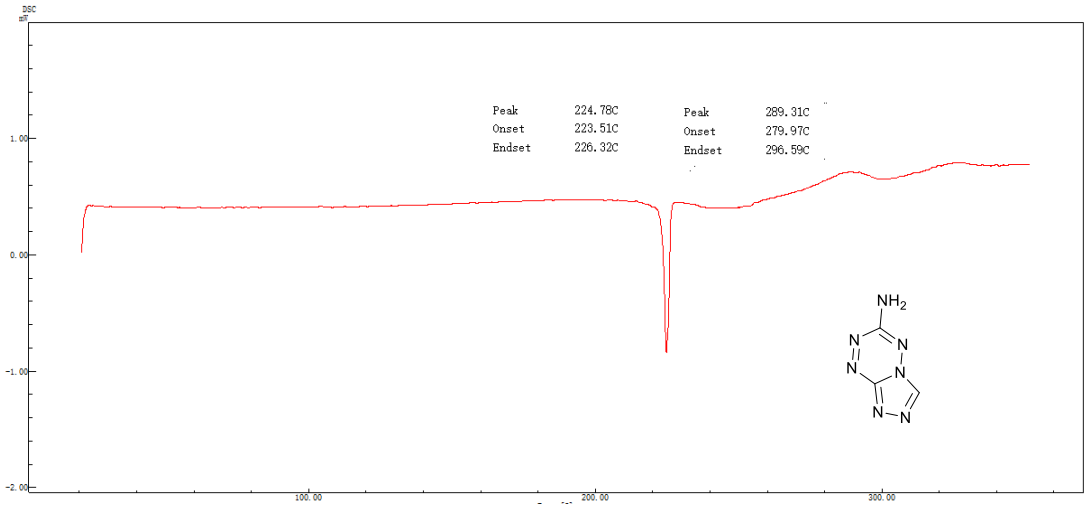


Figure S21 DSC curve of **3a** (5 ºC/min). [S2]

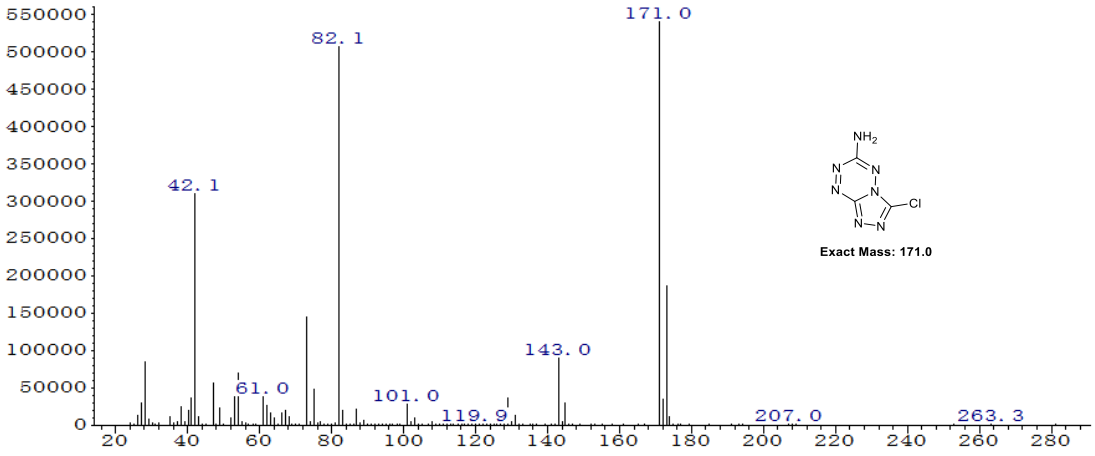


Figure S22 GC-MS of **3b**.

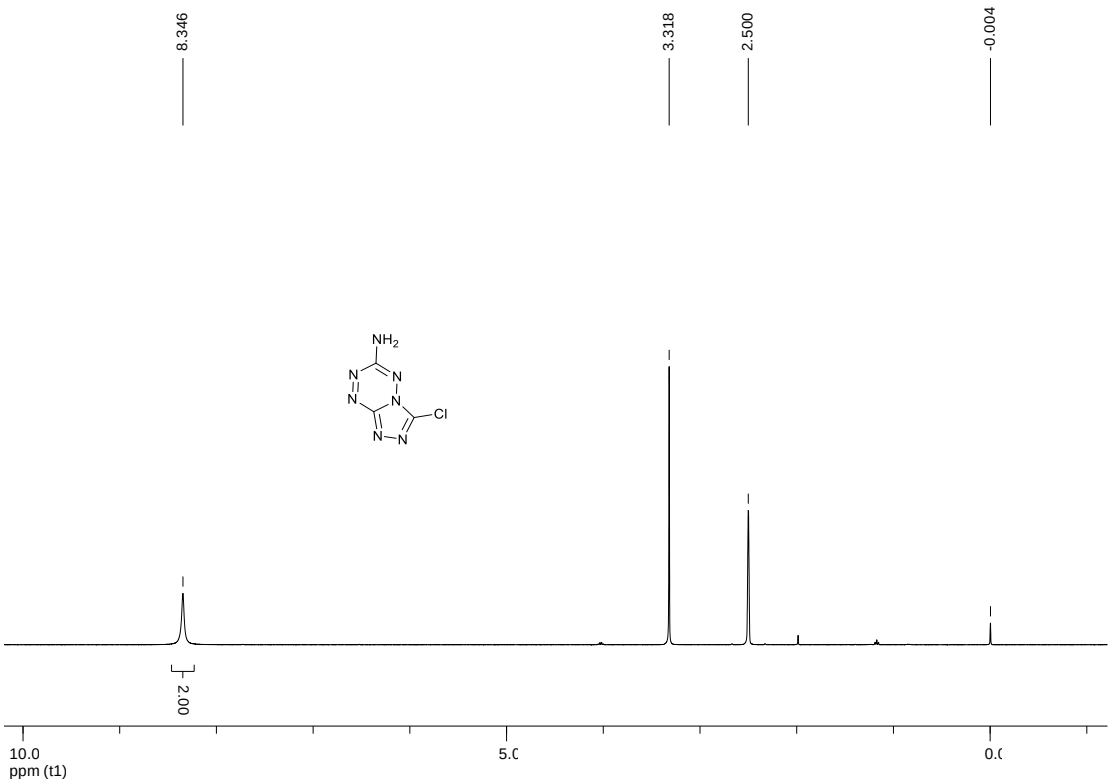


Figure S23 ^{1}H NMR spectra of **3b**.

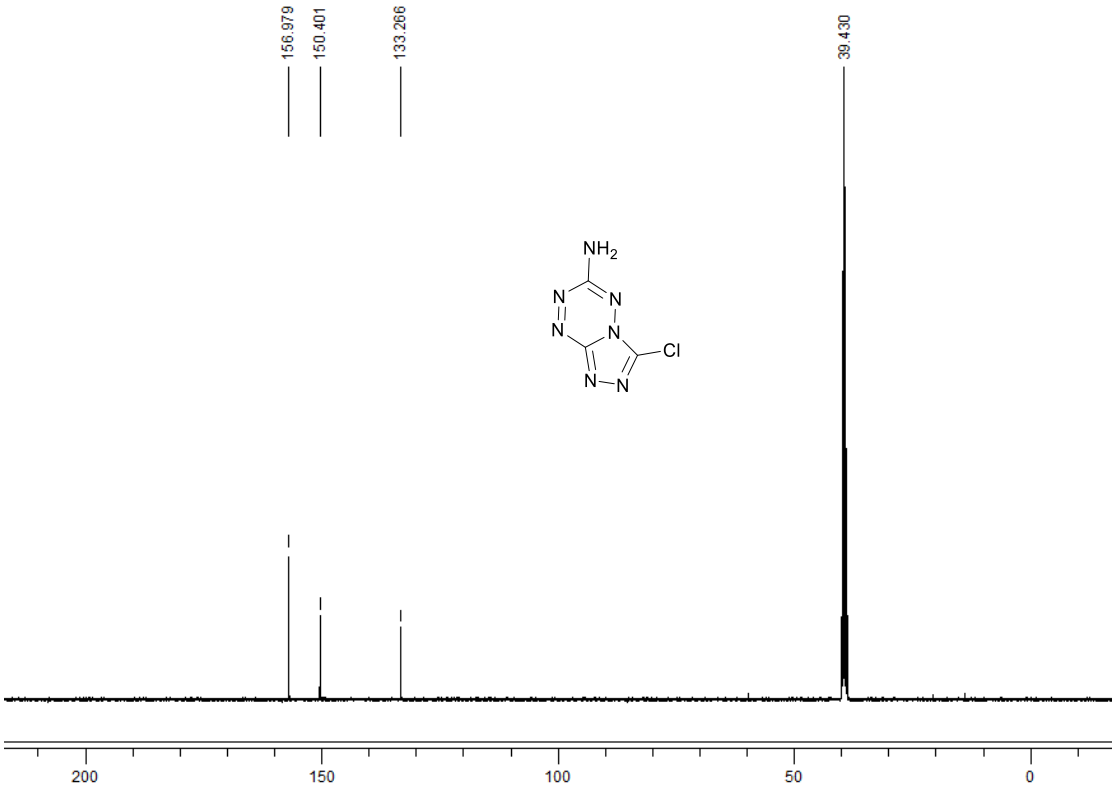


Figure S24 ^{13}C NMR of **3b**.

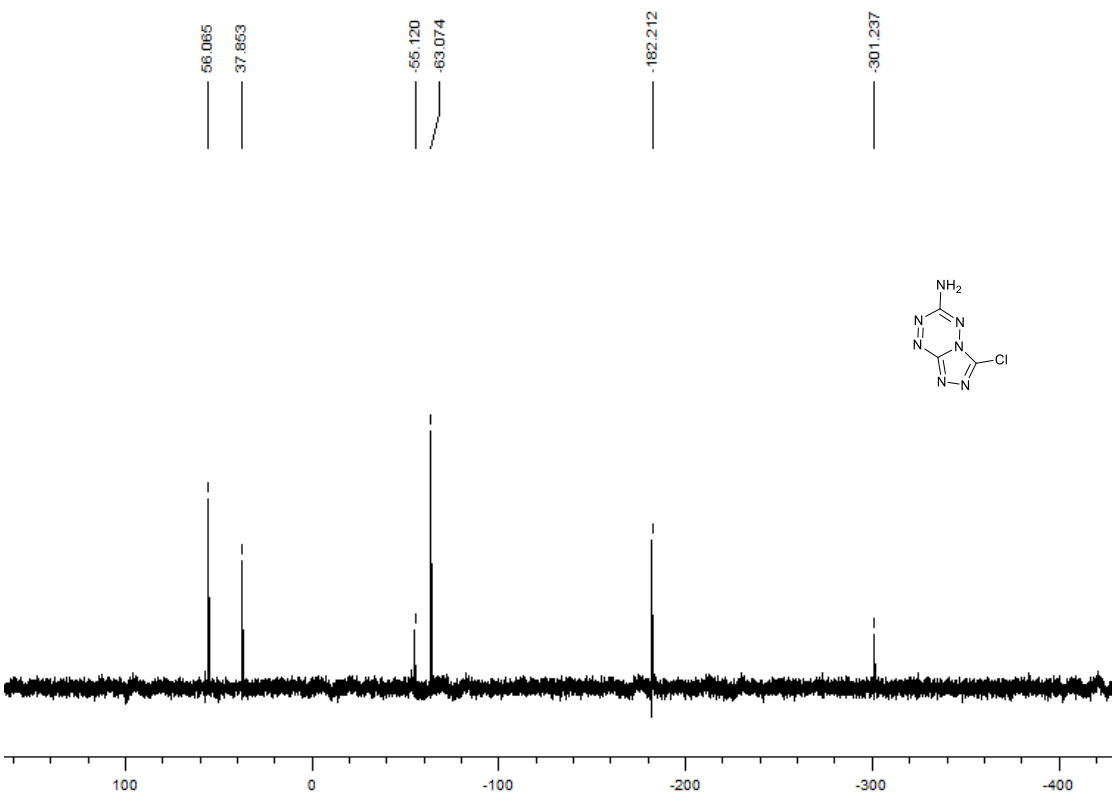


Figure S25 ^{15}N NMR of **3b**.

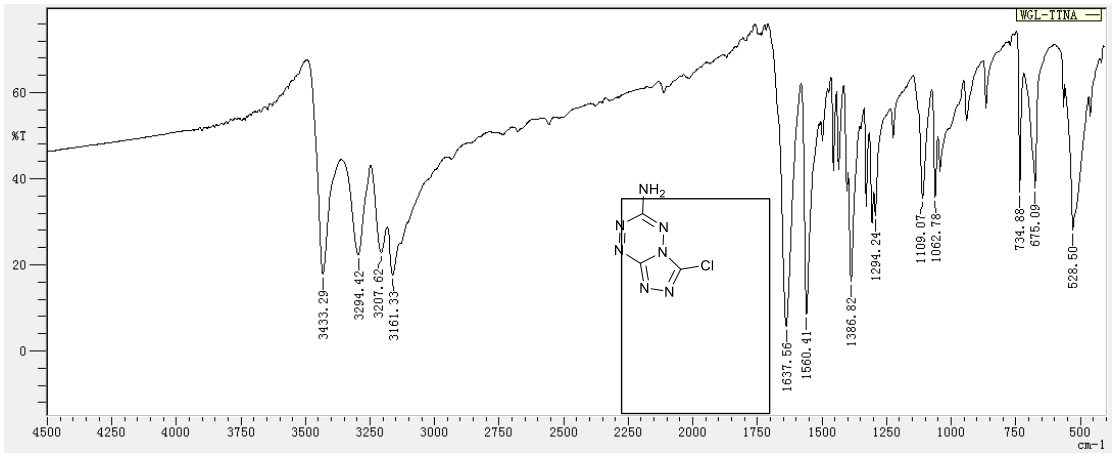


Figure S26 IR of **3b**.

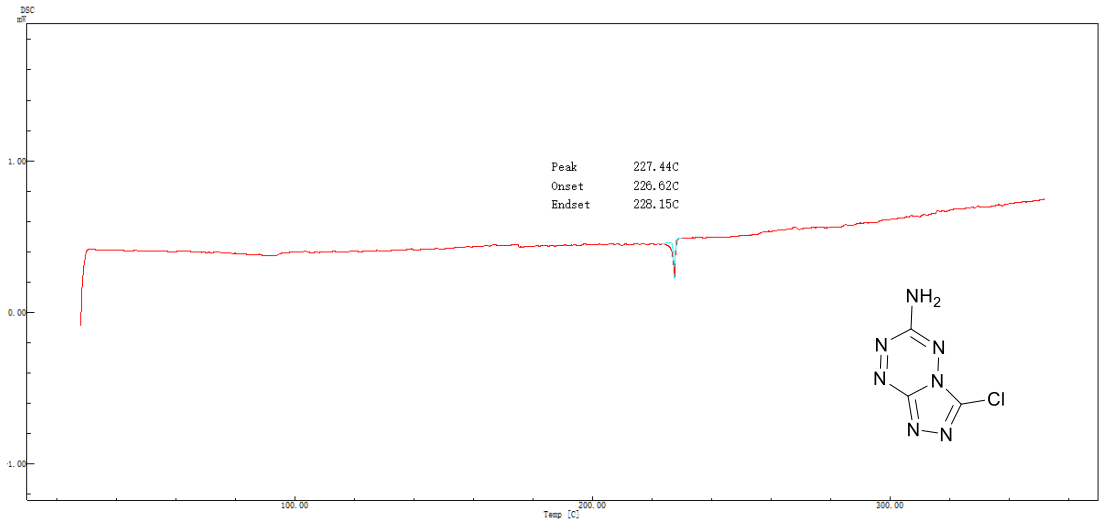


Figure S27 DSC curve of **3b** (5 ºC/min).

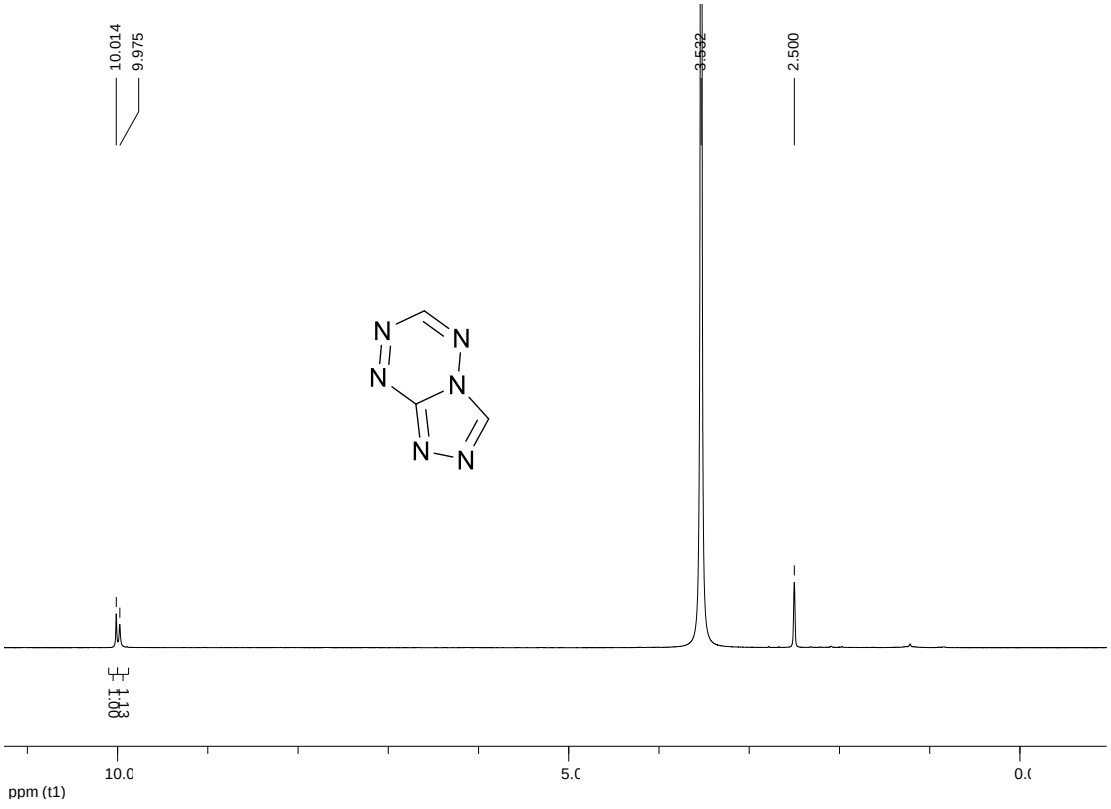


Figure S28 ^{1}H NMR of **4**. [S2]

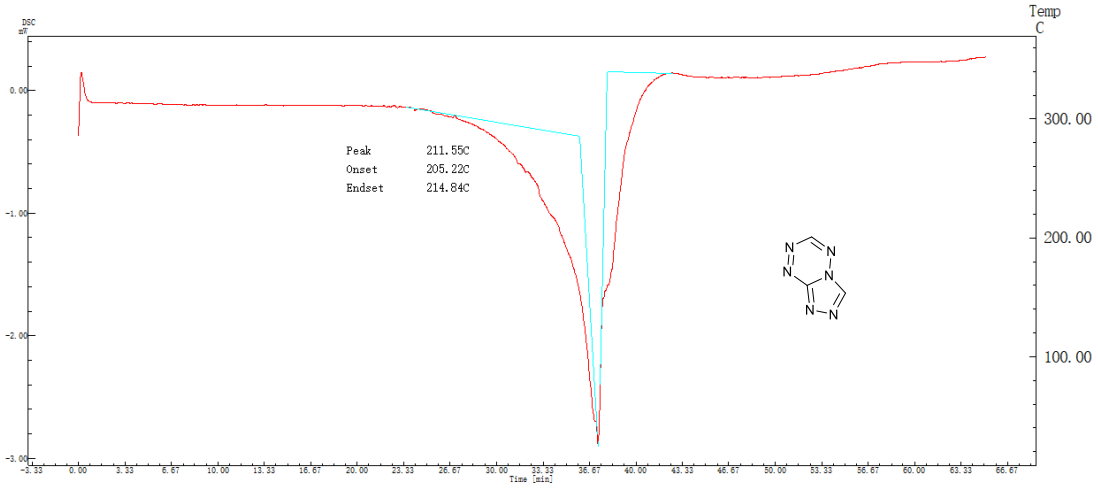


Figure S29 DSC curve of **4** (5 ºC/min). [S2]

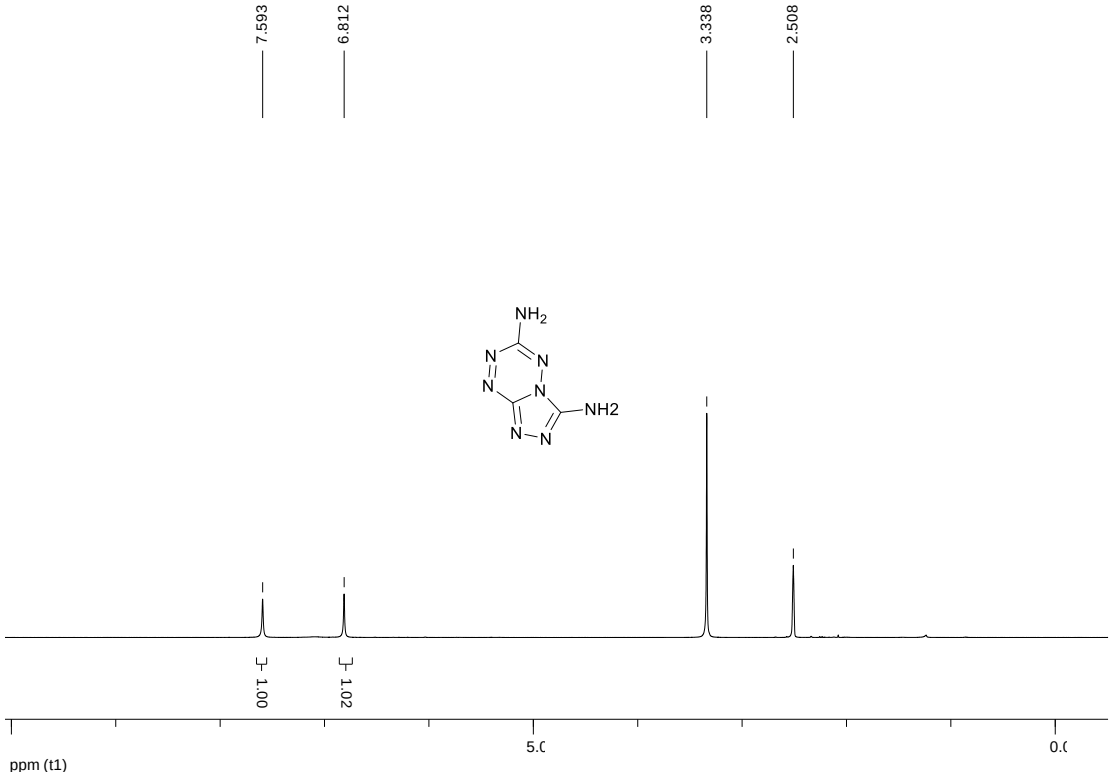


Figure S30 ^{1}H NMR of **5.** [S2]

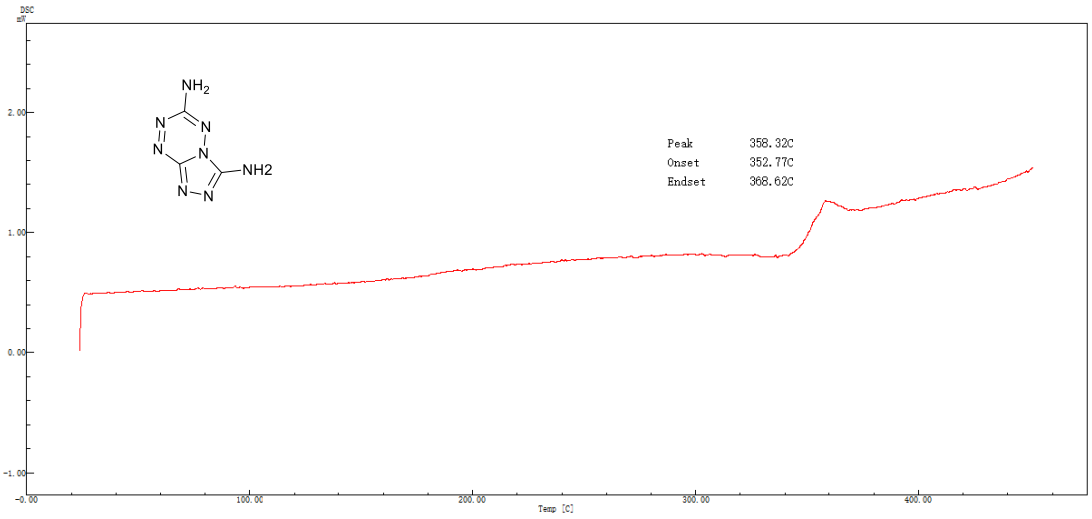


Figure S31 DSC curve of **5** (5 ºC/min). [S2]

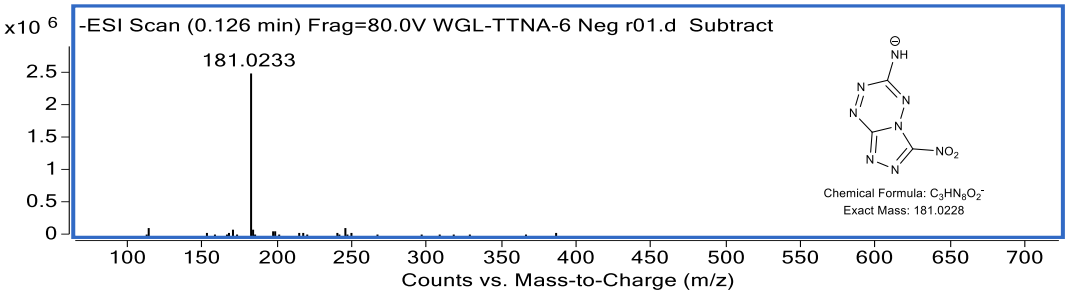


Figure S32 ESI-MS of **TTNA**.

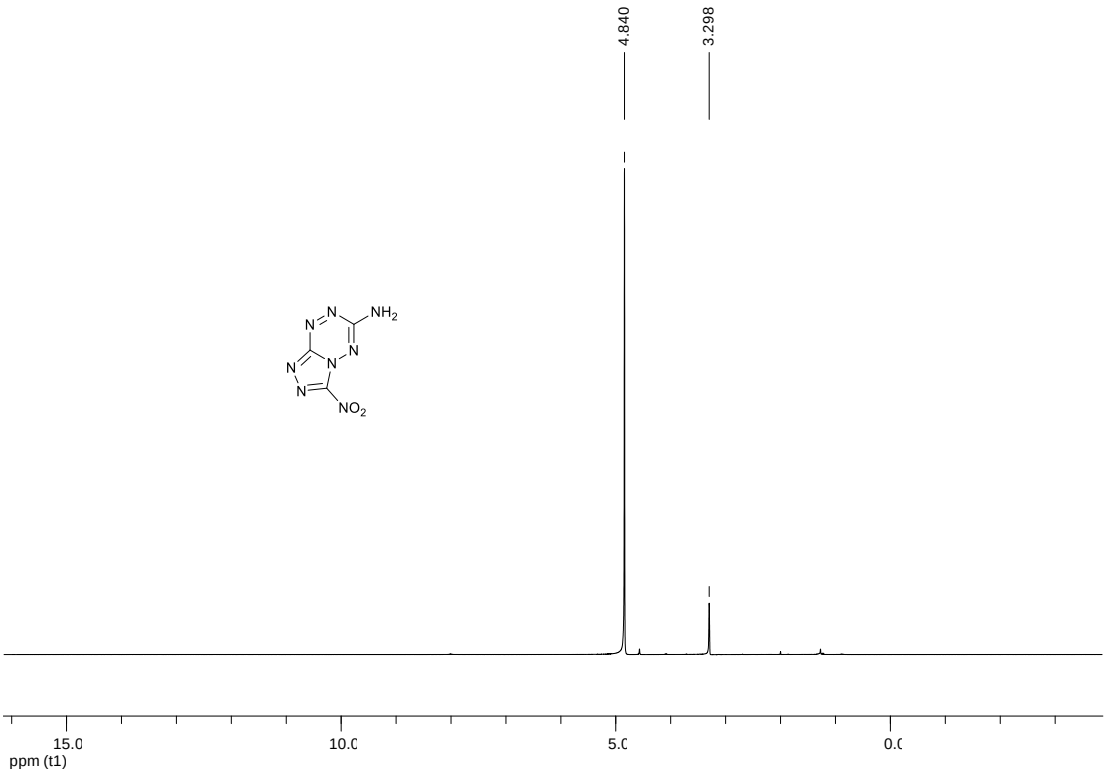


Figure S33 ^{1}H NMR of **TTNA**.

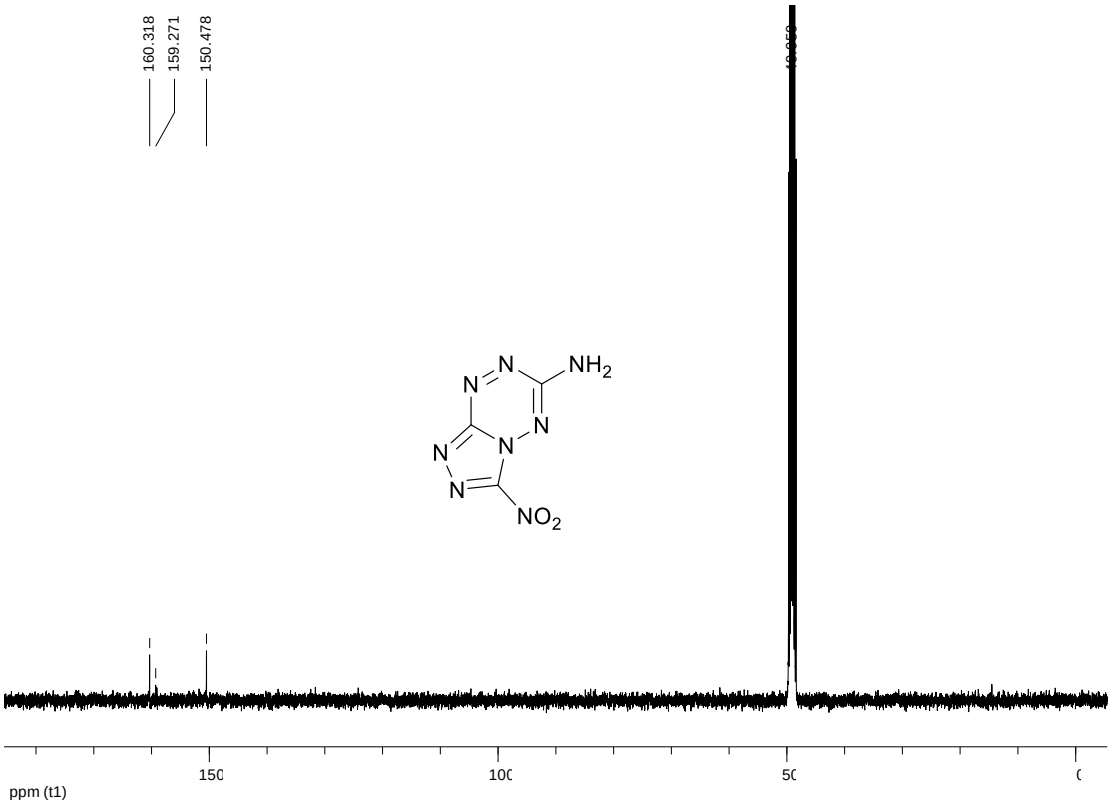


Figure S34 ^{13}C NMR of **TTNA**.

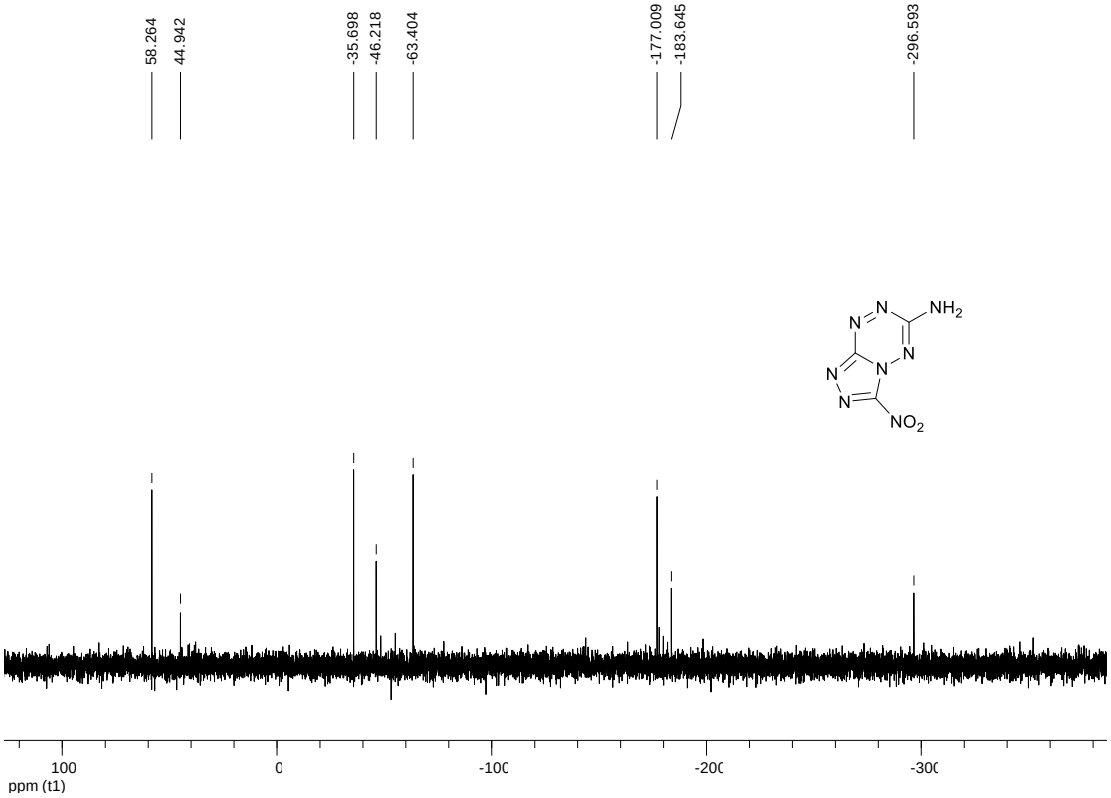


Figure S35 ^{15}N NMR of **TTNA**.

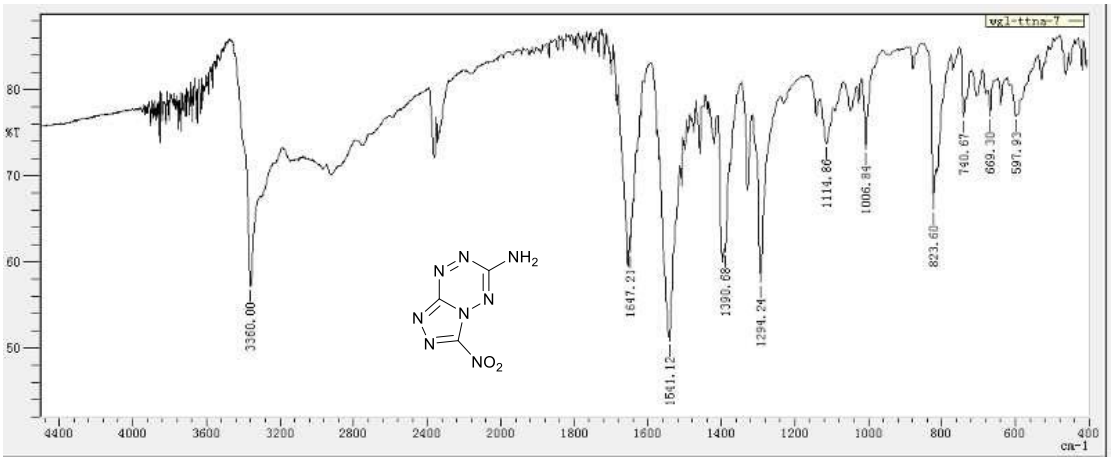


Figure S36 IR of **TTNA**.

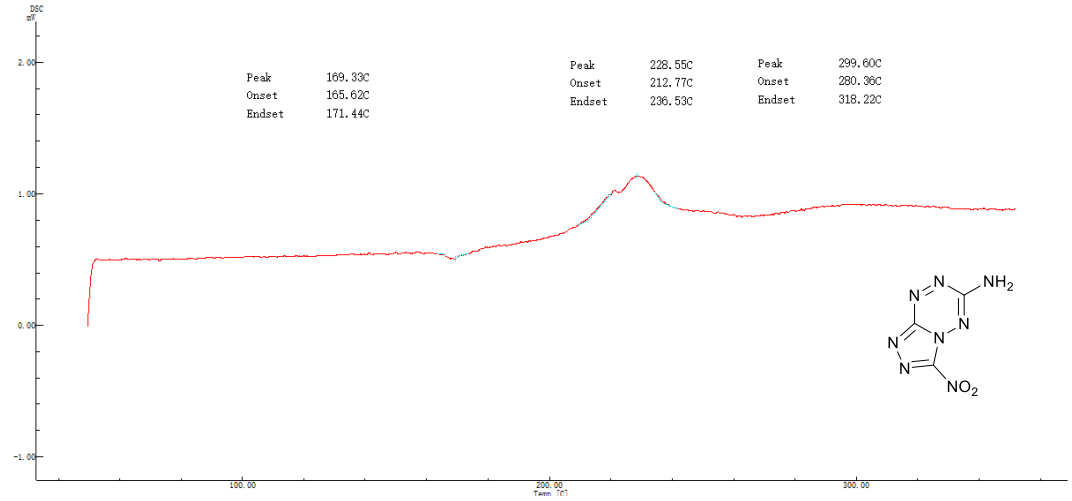


Figure S37 DSC curve of **TTNA** (5 ºC/min).

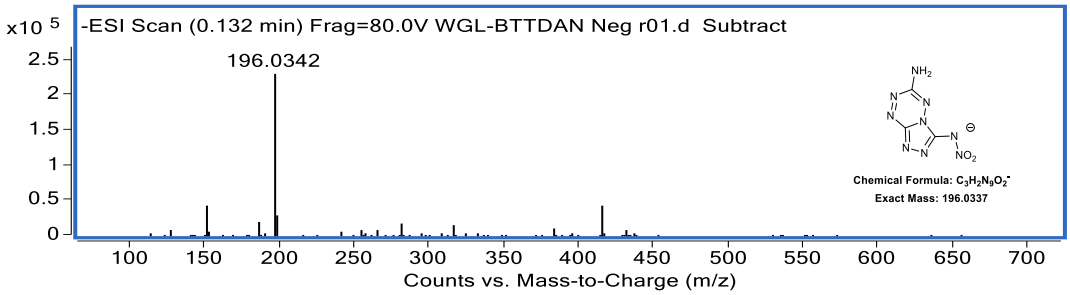


Figure S38 ESI-MS of **TTDAN**.

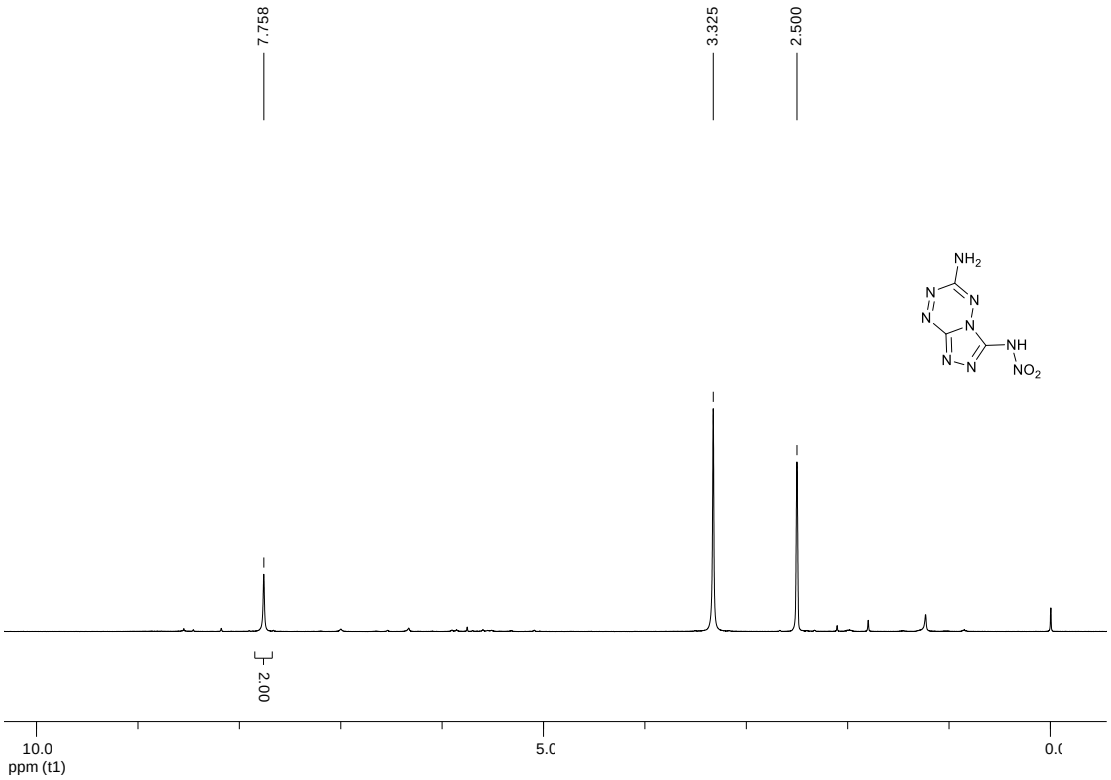


Figure S39 ^{1}H NMR of **TTDAN**.

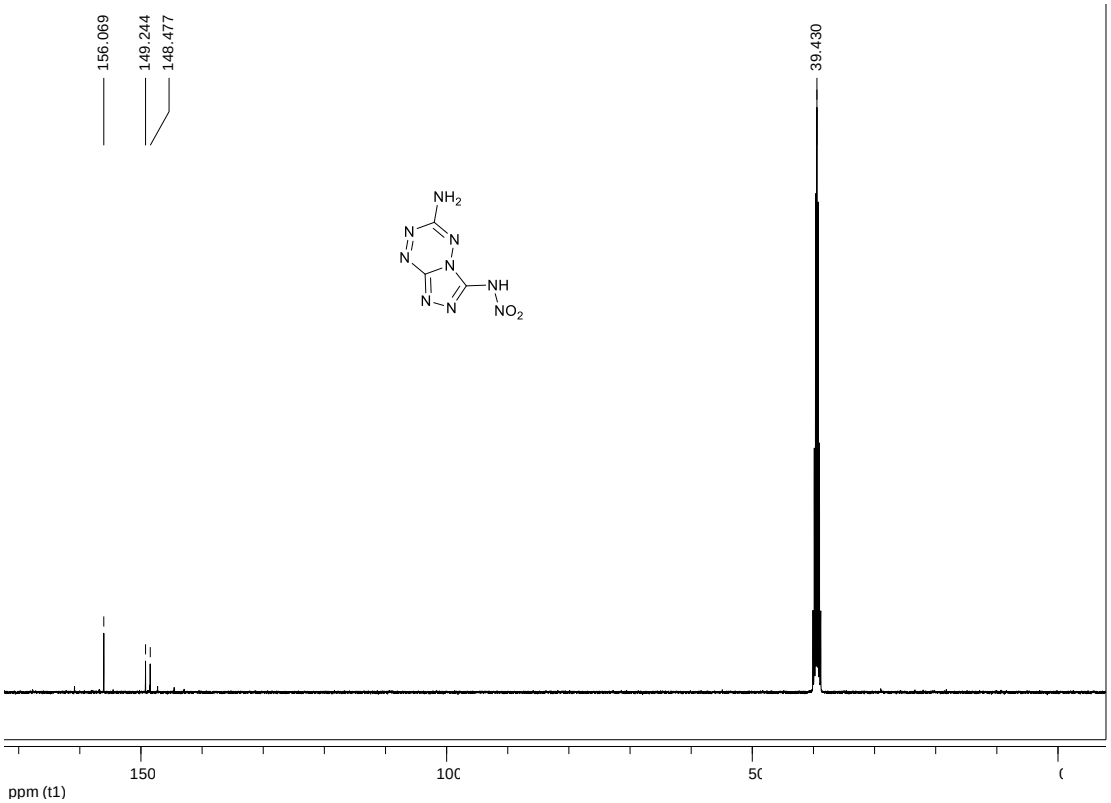


Figure S40 ^{13}C NMR of **TTDAN**.

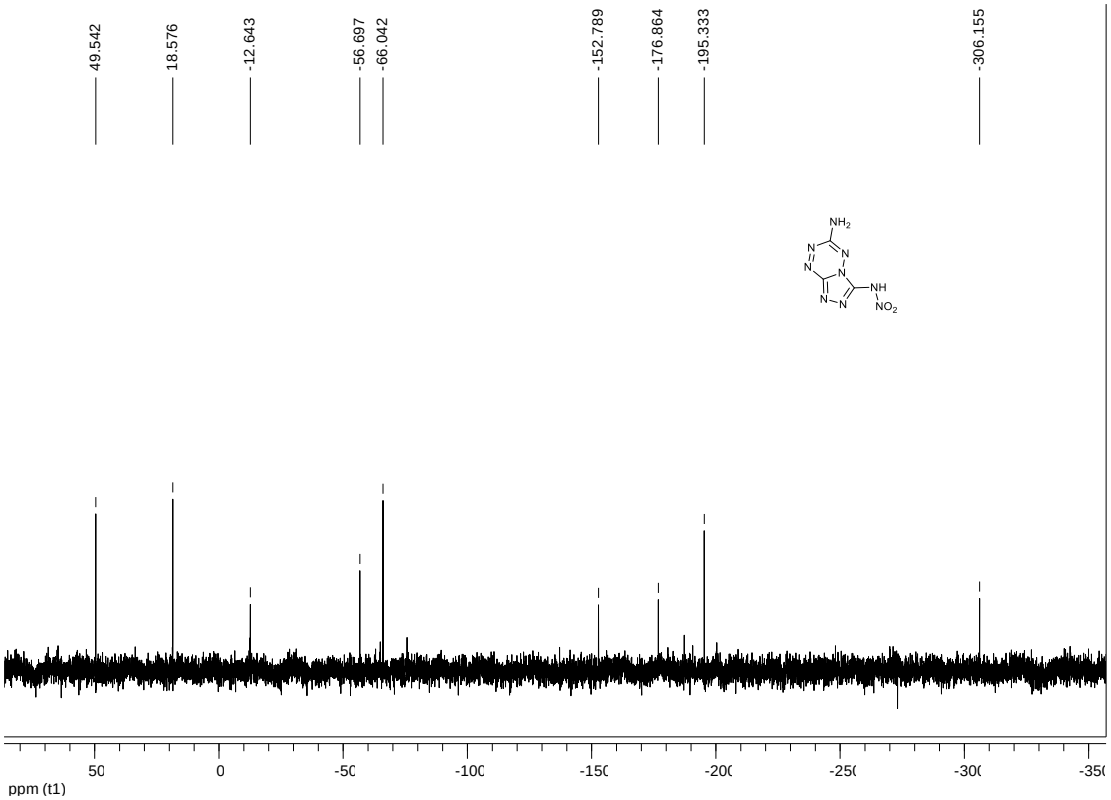


Figure S41 ^{15}N NMR of **TTDAN**.

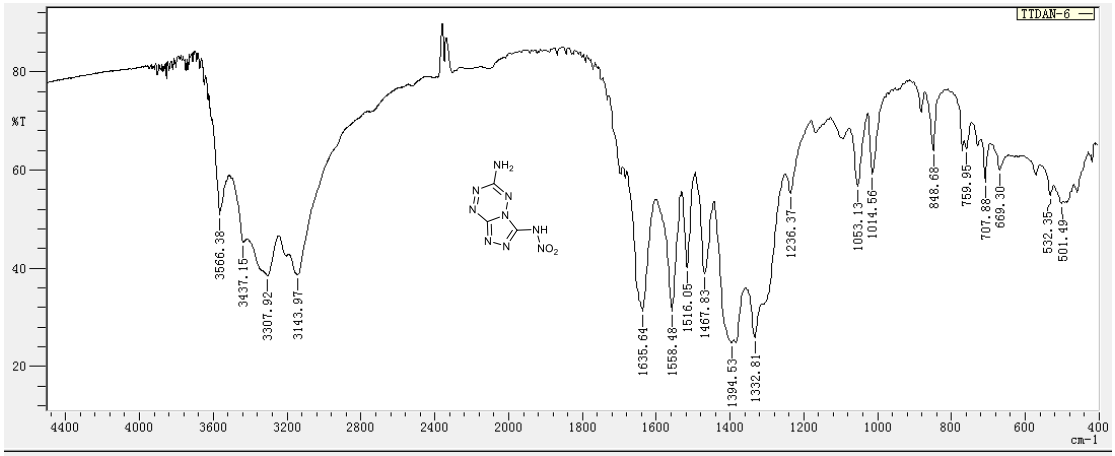


Figure S42 IR of **TTDAN**

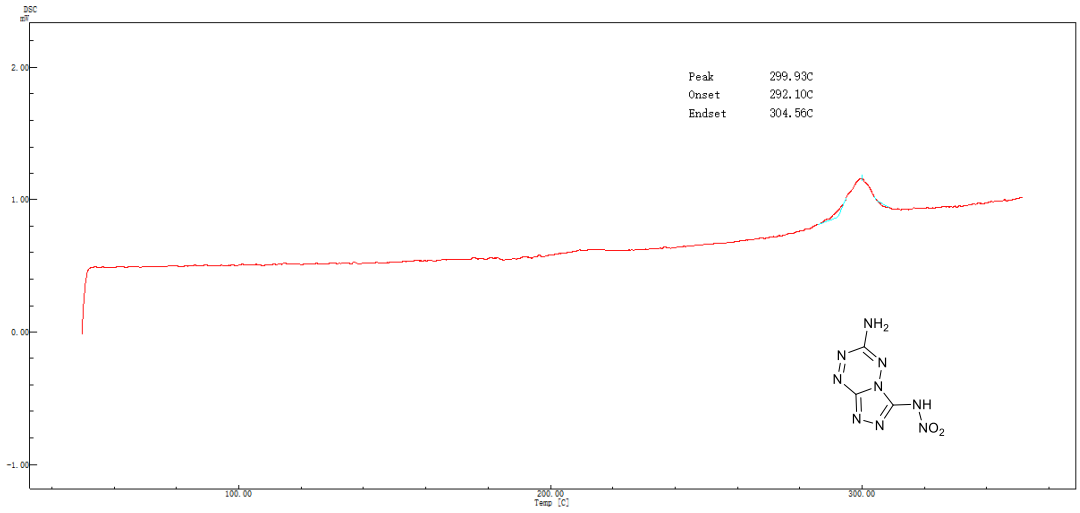


Figure S43 DSC curve of **TTDAN** (5 ºC/min).

6. References

[S1] G. M. Sheldrick, SHELXTL-97, Structure Determination Software Suite, Bruker AXS, Madison, **2008**.

[S2] D. E. Chavez, M. A. Hiskey, *J. Heterocylic Chem.*, **1998**, *35*, 1329–1332.