Supporting Information (SI)

Multi-energetic groups synergies driven design and synthesis of [1,2,4] triazolo [5,1-c] [1,2,4] triazine fused energetic compounds

Yubing Liu[ab], Jie Li[ab] Xun Zhang [ab], Chunlin He *[abcd] and Siping Pang *[a]

[a]*School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, China.*
[b]*Experimental Center of Advanced Materials, School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, China.*
[c]*Yangtze Delta Region Academy of Beijing Institute of Technology, Jiaxing 314019, China.*
[d]*Chongqing Innovation Center, Beijing Institute of Technology, Chongqing 401120, China.*
*Email: chunlinhe@bit.edu.cn, pangsp@bit.edu.cn

Table of Contents

1. Experimental Sections

1.1 Safety Precaution

In this work, all new compounds are potential energetic materials that tend to explode under certain external stimuli. Therefore, the whole experimental process should be carried out by using proper safety equipment, such as safety shields, eye protection, and leather gloves.

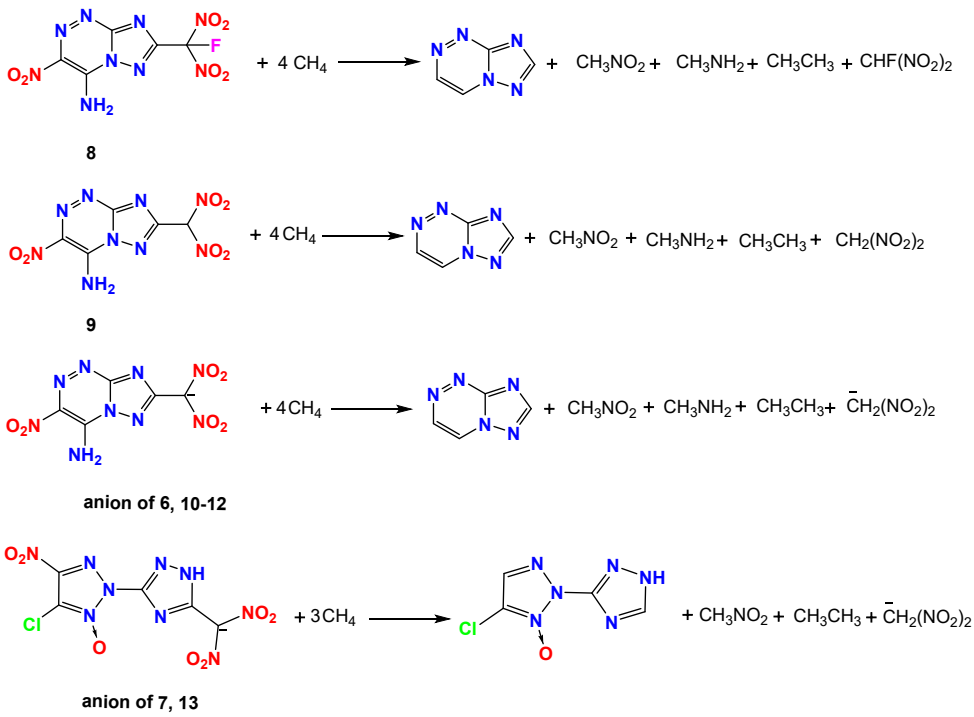
1.2 General methods

^{1}H NMR, ^{13}C NMR and ^{15}N NMR spectra were recorded at 25 °C on a Bruker 400 MHz, 100 MHz and 40 MHz, respectively, and TMS as internal standard. Chemical shifts were reported in parts per million (ppm). The onset decomposition temperature was measured using a TA Instruments DSC25 differential scanning calorimeter at a heating rate of 5 °C min^{-1} under dry nitrogen atmosphere. Infrared spectra (IR) were obtained on a PerkinElmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Elemental analyses of C/H/N were investigated on a Vario EL III Analyzer. Impact and friction sensitivities were tested by a BAM fallhammer and friction tester. Densities were determined at room temperature by employing a Micromeritics AccuPyc 1340 gas pycnometer. X-ray diffractions of all single crystals were carried out on a Bruker D8 VENTURE diffractometer using Mo-Kα radiation (λ = 0.71073 Å).

2. Theoretical calculation

The calculation 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 geometric optimization and frequency analyses of the structures were calculated using B3LYP/6-311++G** level, and the single energy points were calculated at the M062X/de2tzvpp level. The heats of formation for complex structures were obtained by atomization using G2 ab initio method.[1] The enthalpy of sublimation was calculated by using Trouton's rule.[2] Solid state heats of formation of the resulting compounds were calculated with equation (1) in which $T_{m/d}$ is the melting temperature or decomposition temperature.

$$\Delta H_{f(solid)} = \Delta H_{f(g)} - \Delta H_{sub} = \Delta H_{f(g)} - 188[J\ mol^{-1}\ K^{-1}] * T_{m/d} \qquad (1)$$



Scheme S1. Isodesmic reactions.

3. X-ray Crystallographic Datas

Table S1. Crystal data, data collection, and refinement for **2**, **3** and **4**

	2·MeOH·CD_3CN	**3**·3 DMF	**4**
CCDC No.	2151871	215273	2151872
Empirical Formula	$C_{13}H_{13}Cl_2N_{17}O_7$	$C_{14}H_{24}N_{10}O_7$	$C_5H_2ClN_9O_6$
Formula Weight	590.30	444.43	319.61
Temperature (K)	140.0	150.0	150.0
Crystal System	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$Pca2_1$
a (Å)	17.345(3)	12.259(6)	37.714(5)
b (Å)	5.5381(9)	6.700(3	6.7183(12)
c (Å)	25.004(4)	26.067(11)	13.638(2)
α (°)	90	90	90
β (°)	105.662(5)	98.140(14)	90
γ (°)	90	90	90
Volume ($Å^3$)	2312.6(6)	2119.5(16)	3455.5(9)
Z	4	4	12
Density ($g·cm^{-3}$)	1.695	1.393	1.843

μ (mm^{-1})	0.359	0.113	0.385
F (000)	1200.0	936.0	1920.0
Crystal size/mm^3	0.11 × 0.06 × 0.03	0.15× 0.08 × 0.03	0.18×0.16×0.14
Index ranges	-19 ≤ h ≤ 21, -6 ≤ k ≤ 6, -29 ≤ l ≤ 30	-14≤ h ≤ 14 -7≤ k ≤ 8 -31 l ≤ 31	-46 ≤ h ≤ 42 -6 ≤ k ≤ 8 -12 ≤ l ≤ 17
2Θrange for data collection (°)	4.878 to 51.54	6.182 to 50.496	4.32 to 52.764
Reflections collected	11145	13290	15732
Independent reflections	4383 [R_{int} = 0.1202, R_{sigma} = 0.1678]	3721 [R_{int} = 0.1123, R_{sigma} = 0.1102]	6057 [R_{int} = 0.0991, R_{sigma} = 0.1190]
Data/restraints/parameters	4383/0/359	3721/0/287	6057/27/569
Goodness-of-fit on F^2	1.024	1.050	1.084
Final R indexes [I>=2σ(I)]	R_1 =0.0768, wR_2 = 0.1319	R_1 = 0.0936, wR_2 = 0.2394	R_1 = 0.0784, wR_2 = 0.1788
Final R indexes [all data]	R_1=0.1786, wR_2 = 0.1758	R_1= 0.0936, wR_2 = 0.2800	R_1= 0.1497, wR_2 = 0.2217
Largest diff. peak/hole(e·$Å^{-3}$)	0.45/-0.55	0.39/-0.44	0.76/-0.56

Table S2. Crystal data, data collection, and refinement for **6** and **10**

	6·1.5 H_2O	**10**·H_2O
CCDC No.	2151873	2151874
Empirical Formula	$C_{10}H_{10}K_2N_{18}O_{15}$	$C_5H_8N_{10}O_7$
Formula Weight	700.56	320.21
Temperature (K)	170.0	150.0
Crystal System	monoclinic	triclinic
Space group	C2/c	P–1
a (Å)	43.231(8)	10.2673(4)
b (Å)	9.0006(15)	10.8434(5)
c (Å)	12.327(2)	11.9935(5)
α (°)	90	80.6090(10)
β (°)	102.157(5)	70.4600(10)
γ (°)	90	80.229(2)

Volume (Å^3)	4689.0(14)	1231.95(9)
Z	8	4
Density (g·cm^{-3})	1.985	1.726
μ (mm^{-1})	0.522	0.158
F (000)	2832.0	656.0
Crystal size/mm^3	0.08 × 0.05 × 0.04	0.15 × 0.08 × 0.05
Index ranges	-50 ≤ h ≤ 51 -10 ≤ k ≤ 10 -14 ≤ l ≤ 14	-12 ≤ h ≤ 12 -13 ≤ k ≤ 13 -14 ≤ l ≤ 15
2Θ range for data collection (°)	4.628 to 50.752	3.836 to 52.892
Reflections collected	18926	14147
Independent reflections	4254[R_{int} = 0.1119, R_{sigma} = 0.1119]	5000[R_{int} = 0.0566, R_{sigma} = 0.0636]
Data/restraints/parameters	4254/2/412	5000/4/461
Goodness-of-fit on F^2	1.033	1.073
Final R indexes [I>=2σ(I)]	R_1= 0.0593, wR_2 = 0.1144	R_1= 0.0433, wR_2 = 0.0933
Final R indexes [all data]	R_1 =0.1279, wR_2 = 0.1456	R_1 = 0.0735, wR_2 = 0.1077
Largest diff. peak/hole (e·Å^{-3})	0.41/-0.39	0.31/-0.35

Table S2. Crystal data, data collection, and refinement for **7** and **13**

	7·0.5 H_2O	**13**·0.5 H_2O
CCDC No.	2151868	2151869
Empirical Formula	$C_2H_2ClKN_9O_{7.5}$	$C_{10}H_{18}C_{l2}N_{22}O_{15}$
Formula Weight	382.71	757.36
Temperature (K)	170	170
Crystal System	monoclinic	monoclinic
Space group	C2/c	C2/c
a (Å)	21.576(4)	33.372(4)
b (Å)	7.2159(11)	6.9585(7)
c (Å)	15.648(2)	25.558(3)
α (°)	90	90
β (°)	94.847(5)	111.533(4)
γ (°)	90	90
Volume (Å^3)	2427.5(7)	5520.8(11)
Z	8	8
Density (g·cm^{-3})	2.094	1.822

μ (mm^{-1})	0.727	0.348
F (000)	1528.0	3088.0
Crystal size/mm^3	0.12 × 0.08 × 0.04	0.15 × 0.08 × 0.04
Index ranges	26 ≤ h ≤ 26 -9 ≤ k ≤ 9 -19 ≤ l ≤ 15	-41 ≤ h ≤ 39 -8 ≤ k ≤ 8 -32 ≤ l ≤ 30
2Θrange for data collection (°)	3.788 to 52.9	5.024 to 52.872
Reflections collected	8788	22759
Independent reflections	2486 [R_{int} = 0.0718, R_{sigma} = 0.0673]	5612 [R_{int} = 0.0949, R_{sigma} = 0.0869]
Data/restraints/parameters	2486/2/221	5612/28/442
Goodness-of-fit on F^2	1.043	1.012
Final R indexes [I>=2σ(I)]	R_1= 0.0482, wR_2 = 0.0971	R_1 = 0.0538, wR_2 = 0.0922
Final R indexes [all data]	R_1= 0.0843, wR_2 = 0.1129	R_1 = 0.1171, wR_2 = 0.1157
Largest diff. peak/hole (e·$Å^{-3}$)	0.35/-0.44	0.33/-0.41

Table S3 Bond Length in Å for **6**·1.5 H_2O

Atom1	**Atom2**	Length/ Å
C1	C2	1.423(7)
C1	N1	1.353(6)
C1	N2	1.440(7)
C2	N3	1.370(6)
C2	N5	1.359(7)
C3	N3	1.312(7)
C3	N4	1.371(6)
C3	N8	1.352(6)
C4	C5	1.417(6)
C4	N4	1.354(7)
C4	N6	1.306(6)
C5	N7	1.327(6)
C5	N9	1.448(7)
C6	C7	1.428(6)
C6	N11	1.432(7)
C6	N13	1.334(6)
C7	N10	1.295(6)
C7	N14	1.366(6)
C8	N12	1.357(6)
C8	N14	1.370(6)
C8	N16	1.308(6)
C9	C10	1.448(7)

C9	N15	1.346(6)
C9	N16	1.367(6)
C10	N17	1.361(6)
C10	N18	1.427(7)
K1	O2	2.760(4)
K1	O3	2.739(5)
K1	O11	3.223(3)
K1	O12	2.733(3)
K2	O3	2.709(4)
K2	O12	2.748(4)
K2	O13	2.845(4)
N1	O1	1.272(6)
N1	O2	1.254(6)
N2	O4	1.242(7)
N2	O5	1.227(6)
N4	N5	1.367(5)
N6	H6A	0.88
N6	H6B	0.879
N7	N8	1.316(6)
N9	O7	1.225(6)
N9	O8	1.224(6)
N10	H10A	0.88
N10	H10B	0.878
N11	O9	1.223(5)
N11	O10	1.223(5)
N12	N13	1.308(6)
N14	N15	1.362(5)
N17	O11	1.254(5)
N17	O12	1.261(5)
N18	O13	1.248(5)
N18	O14	1.238(5)
O3	H3A	0.87(4)
O3	H3B	0.86(4)
O15	H15A	0.871
O15	H15B	0.689
O6	H6C	0.871
O6	H6D	0.756
N10	H10B	0.878
N11	O9	1.223(5)

Table S4 Bond Length in Å for **7**·0.5 H_2O

Atom1	Atom2	Length/ Å
C1	C2	1.374(5)
C1	Cl1	1.667(4)

C1	N1	1.350(4)
C2	N3	1.318(4)
C2	N4	1.448(5)
C3	N2	1.416(4)
C3	N5	1.346(4)
C3	N6	1.307(4)
C4	C5	1.444(5)
C4	N5	1.342(4)
C4	N7	1.349(4)
C5	N8	1.377(4)
C5	N9	1.420(5)
K1	N3	2.932(3)
K1	N5	2.914(3)
K1	O4	2.856
K1	O5	2.745(3)
N1	N2	1.375(4)
N1	O3	1.252(4)
N2	N3	1.330(4)
N4	O1	1.208(4)
N4	O2	1.216(4)
N6	N7	1.363(4)
N7	H7	0.88
N8	O7	1.236(4)
N8	O8	1.274(4)
N9	O5	1.236(4)
N9	O6	1.229(4)
O4	H4	0.822

Table S5 Hydrogen Bond information for **10**·H_2O

D	H	A	d(D-H)/ Å	d(H-A)/ Å	d(D-A)/ Å	D-H-A/ deg
O1	H1A	O12	0.83	2.14	2.954(2)	166
O1	H1B	O3	0.89	2.15	2.995(2)	157
O2	H2A	N16	0.84	2.02	2.867(3)	178
O2	H2B	N3	0.88	2.00	2.874(2)	169
N8	H8A	N4	0.88	2.48	2.804(2)	102
N8	H8A	O3	0.88	2.12	2.909(2)	148
N8	H8A	O5	0.88	2.28	3.002(2)	139
N8	H8B	O8	0.88	2.12	2.695(2)	122
N8	H8B	O11	0.88	2.17	2.963(2)	149
N13	H13A	N15	0.88	2.46	2.792(3)	103
N13	H13A	O10	0.88	2.21	2.944(2)	140
N13	H13A	O12	0.88	2.19	2.940(2)	144
N13	H13B	O6	0.88	2.13	2.948(2)	154
N13	H13B	O14	0.88	2.15	2.707(2)	121

N19	H19A	O1	1.00	1.92	2.905(3)	167
N19	H19B	O2	0.91	1.85	2.746(3)	167
N19	H19C	O9	0.96	2.54	3.128(3)	120
N19	H19C	O10	0.96	2.16	3.116(3)	173
N19	H19D	O3	0.89	2.26	3.041(3)	146
N20	H20A	O4	0.89	2.41	2.756(3)	103
N20	H20A	N6	0.89	2.50	3.214(3)	138
N20	H20A	N7	0.89	2.00	2.875(3)	168
N20	H20B	O1	0.90	1.95	2.835(2)	168
N20	H20C	N12	0.88	2.44	2.974(3)	120
N20	H20C	O6	0.88	2.32	3.045(2)	141
N20	H20D	O13	0.86	2.38	2.917(3)	121
N20	H20D	O9	0.86	2.22	2.797(2)	125

Table S6 Hydrogen Bond information for **13**·0.5 H_2O

D	H	A	d(D-H)/ Å	d(H-A)/ Å	d(D-A)/ Å	D-H-A/ deg
O15	H15A	O4	0.87	2.45	3.063(4)	128
O15	H15B	O10	0.87	2.39	3.054(4)	133
O15	H15B	O11	0.87	2.24	3.097(4)	171
N19	H19A	O15	0.93	1.9	2.826(5)	177
N19	H19B	O3	0.93	2.29	3.113(5)	147
N19	H19C	O4	0.93	2.28	2.965(5)	131
N19	H19D	O5	0.93	2.25	2.929(4)	129
N19	H19D	N3	0.93	2.28	3.095(4)	146
N20	H20A	O9	0.91	2.53	2.924(4)	106
N20	H20A	N5	0.91	1.96	2.838(4)	161
N20	H20B	O2	0.92	2.1	2.938(4)	151
N20	H20B	O9	0.92	2.52	3.022(4)	115
N20	H20C	O10	0.92	2.56	3.065(4)	115
N20	H20C	O2	0.92	2.06	2.904(4)	152
N20	H20D	O5	0.92	2.35	3.122(4)	142
N20	H20D	N3	0.92	2.57	3.240(4)	130
N21	H21A	N13	0.93	1.9	2.829(4)	173
N21	H21B	N14	0.92	2.06	2.924(4)	154
N21	H21C	O11	0.92	2.55	3.253(4)	134
N21	H21C	O1	0.92	2.43	2.805(4)	105
N21	H21D	O12	0.93	2.42	2.917(4)	114
N21	H21D	N12	0.93	2.37	3.208(4)	151
N22	H22A	N12	0.92	2.06	2.948(4)	162
N22	H22B	O8	0.93	2.08	2.959(4)	158
N22	H22C	N4	0.93	1.99	2.869(4)	159
N22	H22D	O1	0.93	2.2	2.946(4)	137
N22	H22D	O2	0.93	2.11	2.960(4)	152

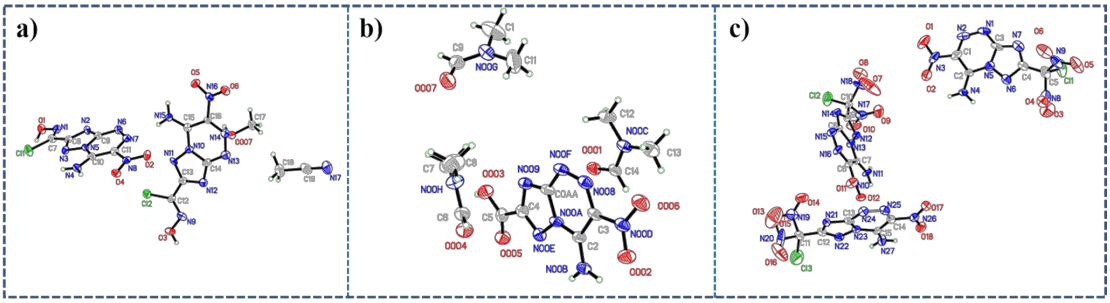
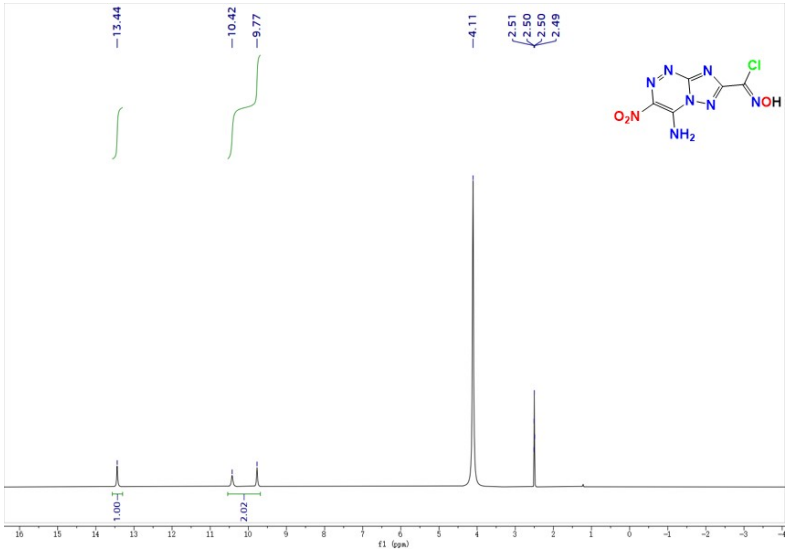
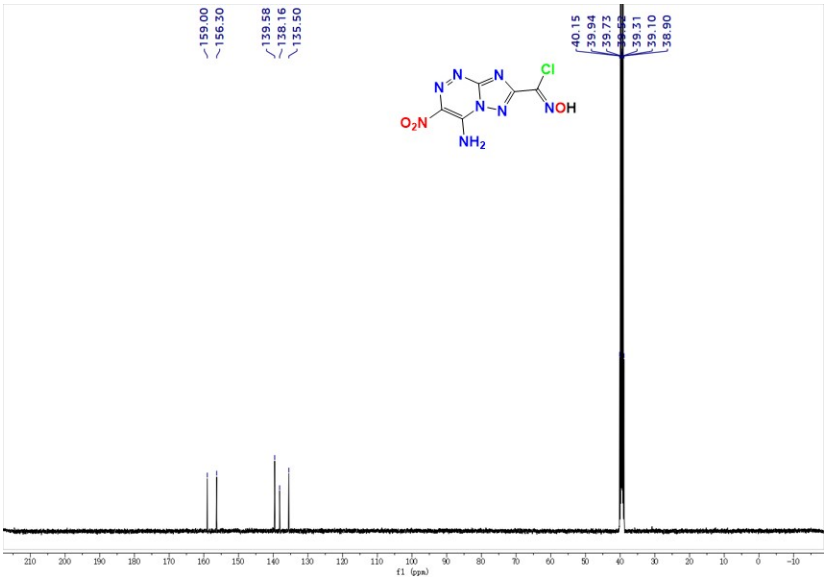


Fig. S1. Crystal structures of a) **2**·CH_3CN·CH_3OH, b) **3**·3 DMF and c) **4** at the 50% probability level.

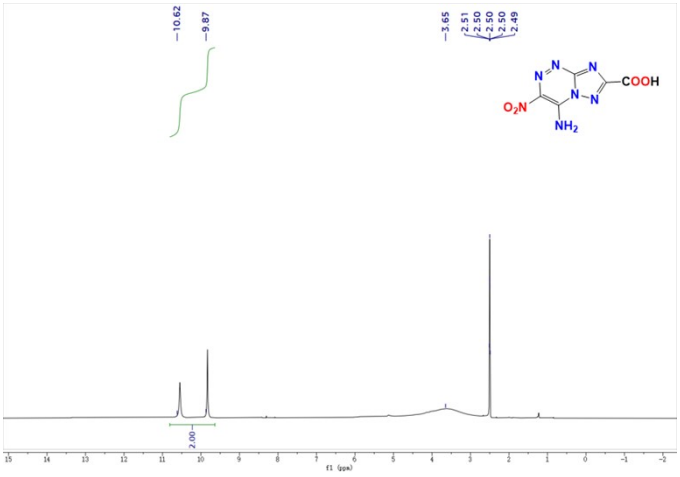
4. Spectrums for all new compounds



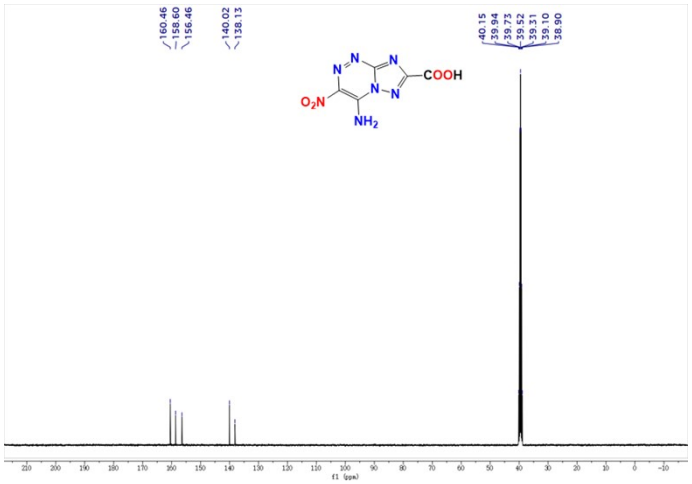
^{1}H NMR spectrum of **2** in d_6-DMSO.



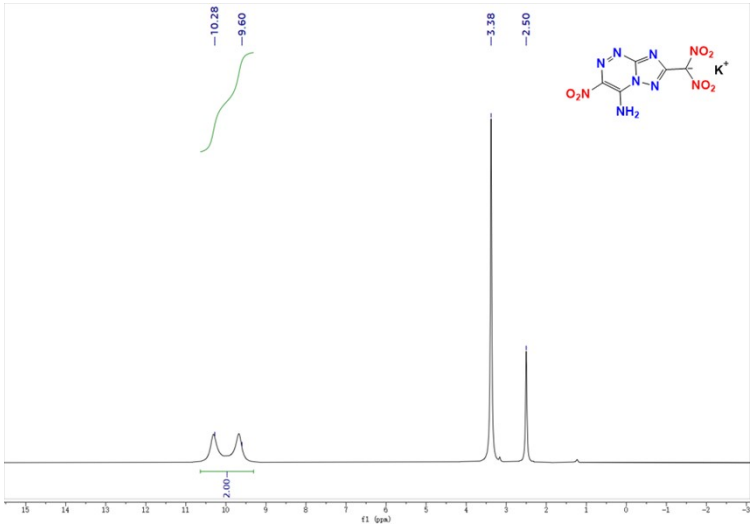
^{13}C NMR spectrum of **2** in d_6-DMSO.



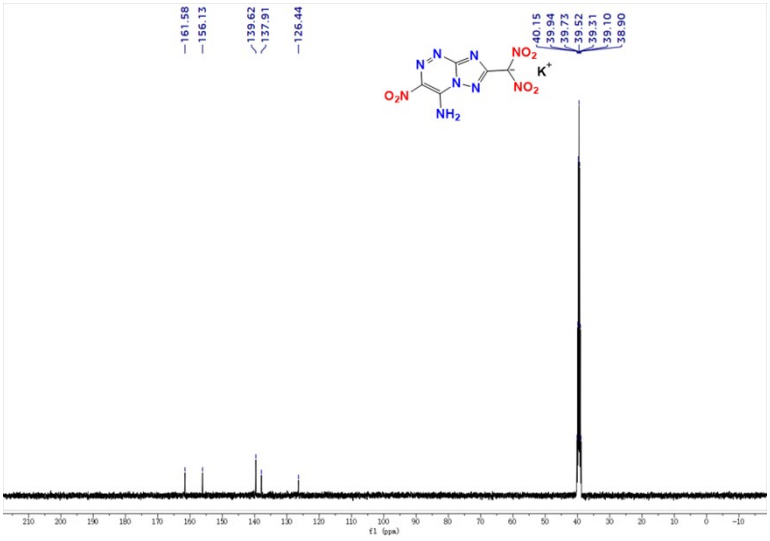
^{1}H NMR spectrum of **3** in d_6-DMSO.



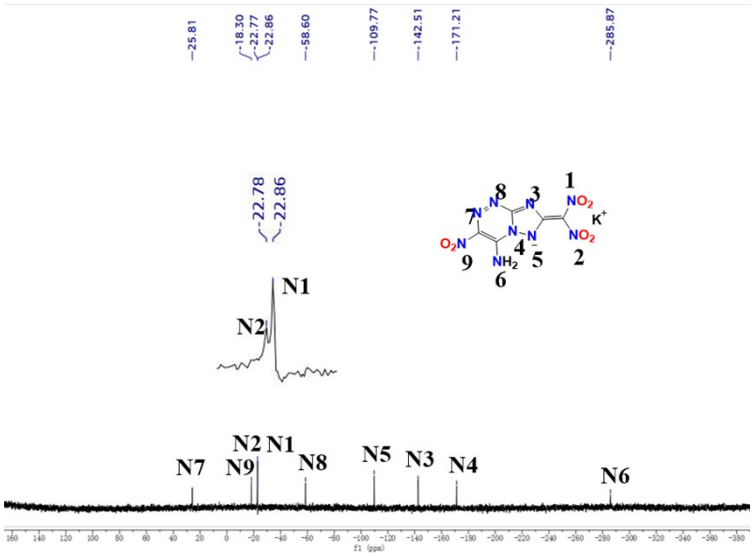
^{13}C NMR spectrum of **3** in d_6-DMSO.



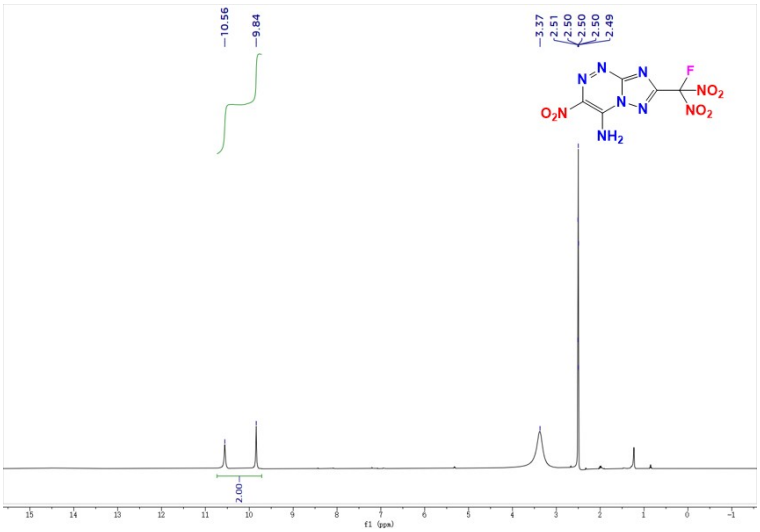
^{1}H NMR spectrum of **6** in d_6-DMSO.



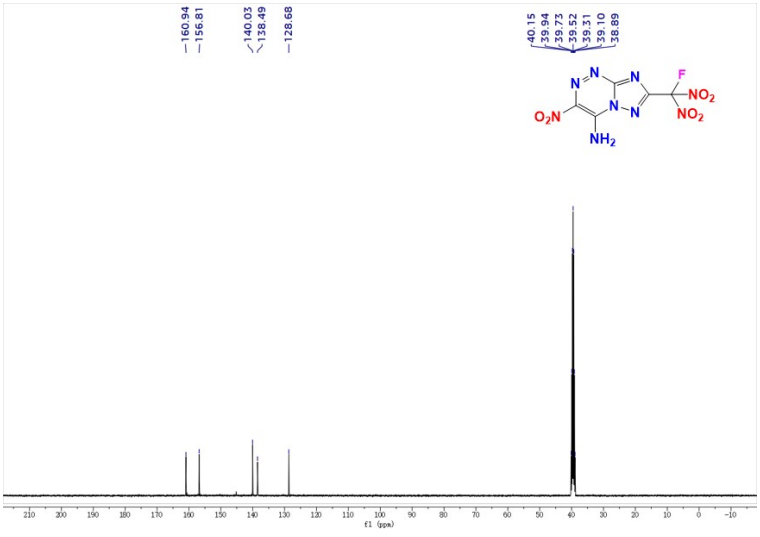
^{13}C NMR spectrum of **6** in d_6-DMSO.



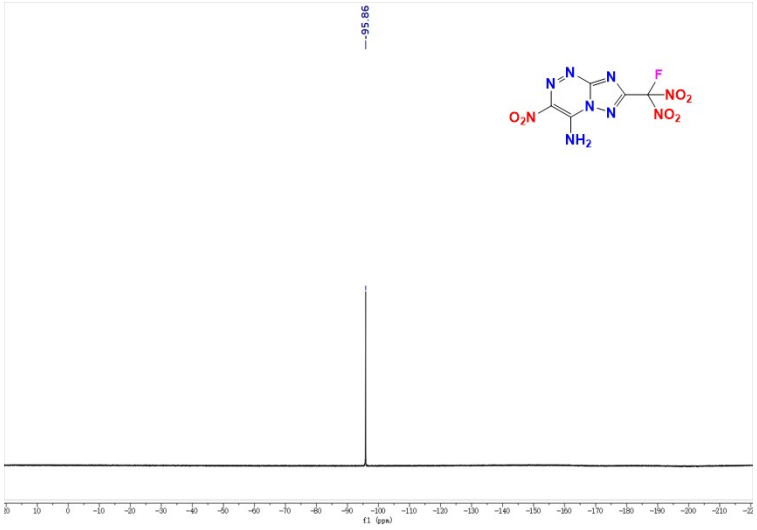
^{15}N NMR spectrum of **6** in d_6-DMSO.



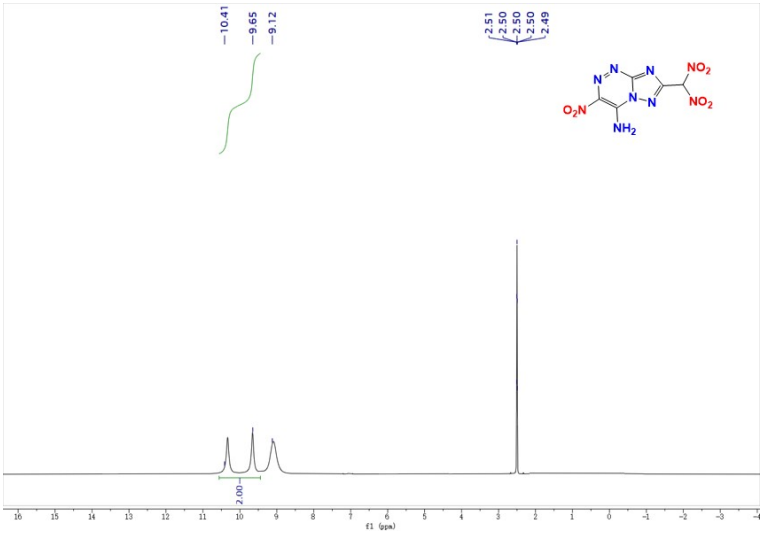
^{1}H NMR spectrum of **8** in d_6-DMSO.



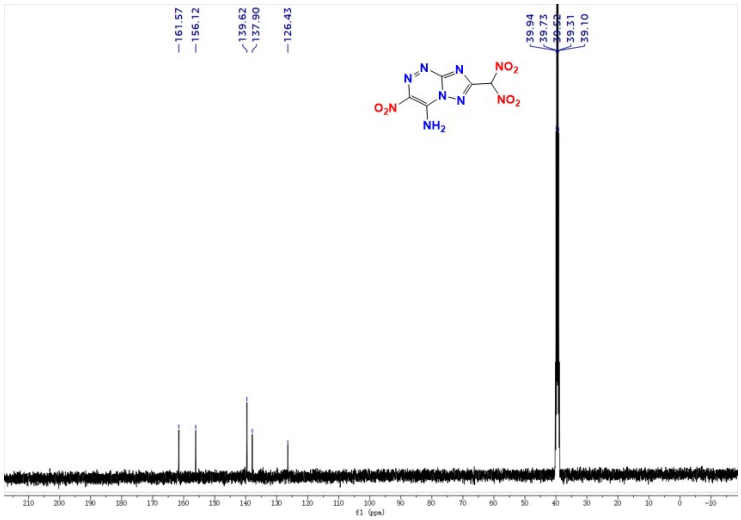
^{13}C NMR spectrum of **8** in d_6-DMSO.



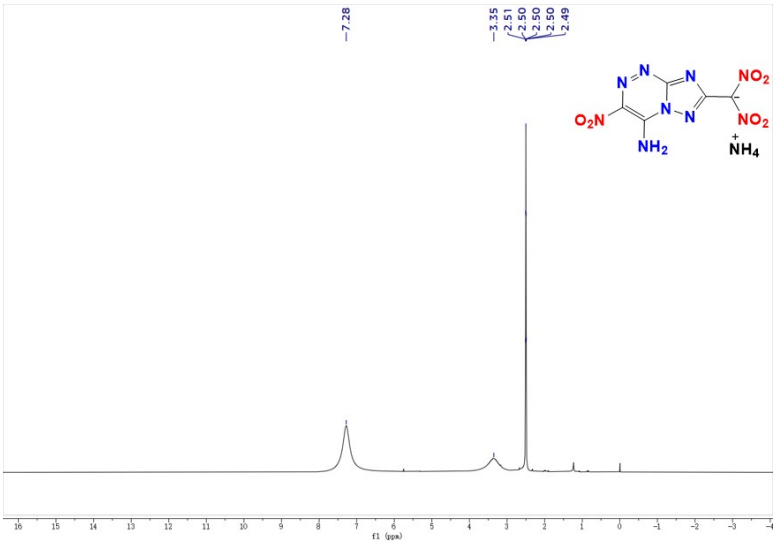
^{19}F NMR spectrum of **8** in d_6-DMSO.



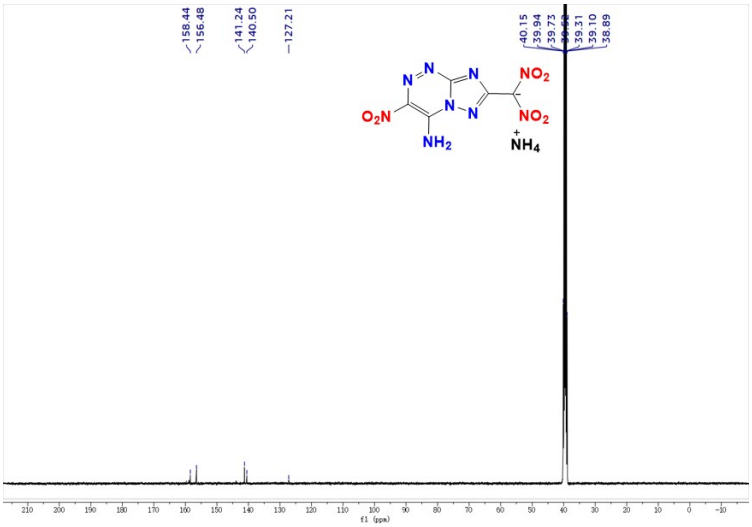
^{1}H NMR spectrum of **9** in d_6-DMSO.



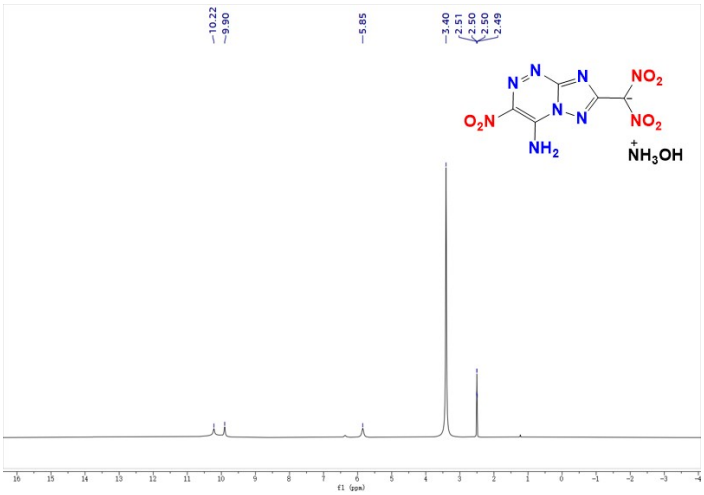
^{13}C NMR spectrum of **9** in d_6-DMSO.



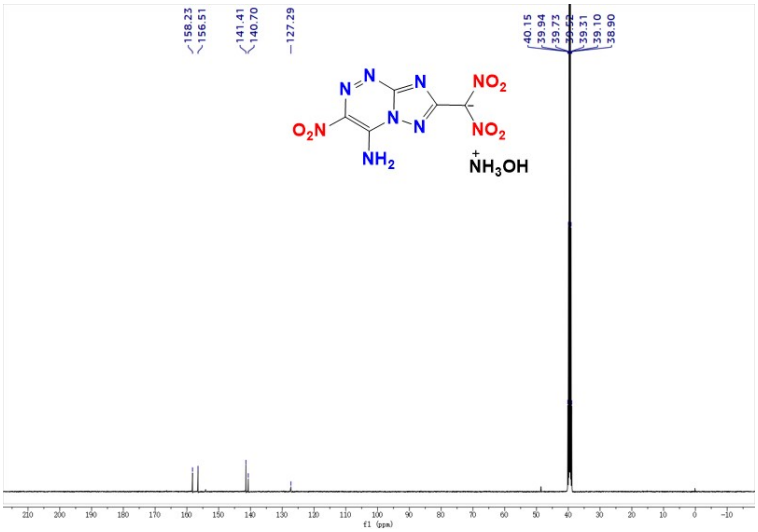
^{1}H NMR spectrum of **10** in d_6-DMSO.



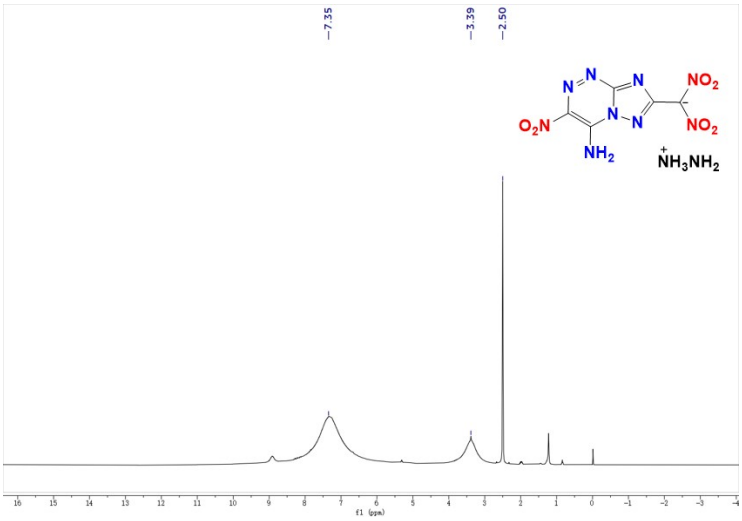
^{13}C NMR spectrum of **10** in d_6-DMSO.



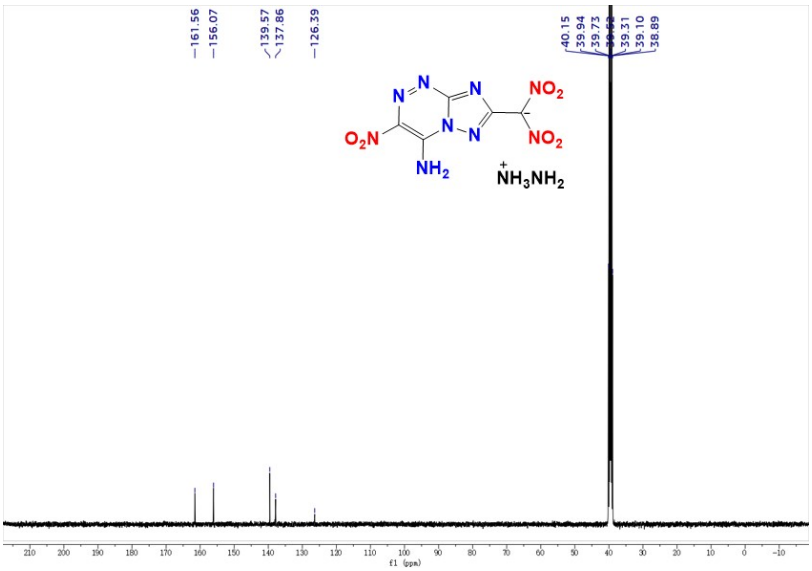
^{1}H NMR spectrum of **11** in d_6-DMSO.



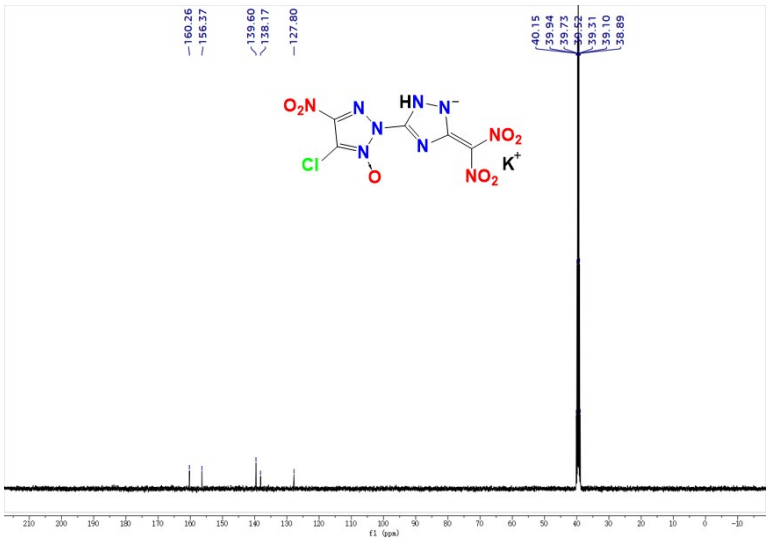
^{13}C NMR spectrum of **11** in d_6-DMSO.



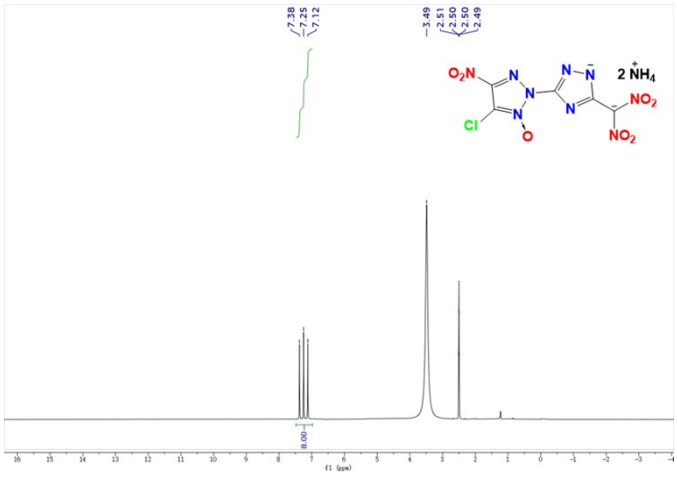
^{1}H NMR spectrum of **12** in d_6-DMSO.



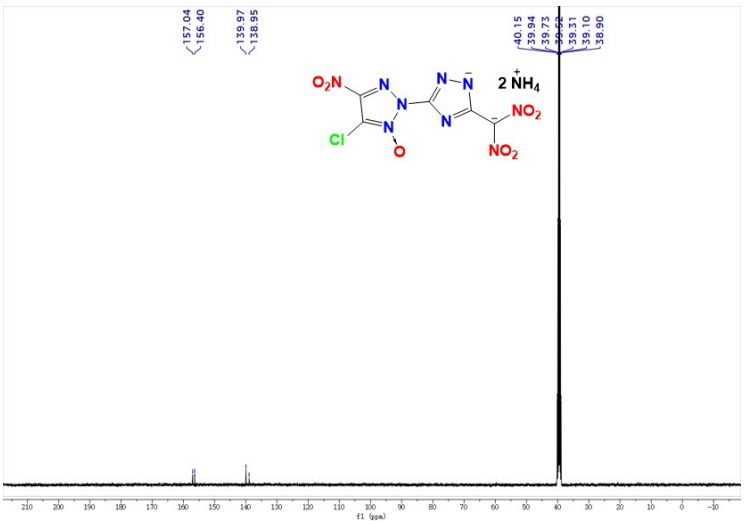
^{13}C NMR spectrum of **12** in d_6-DMSO.



^{13}C NMR spectrum of **7** in d_6-DMSO.

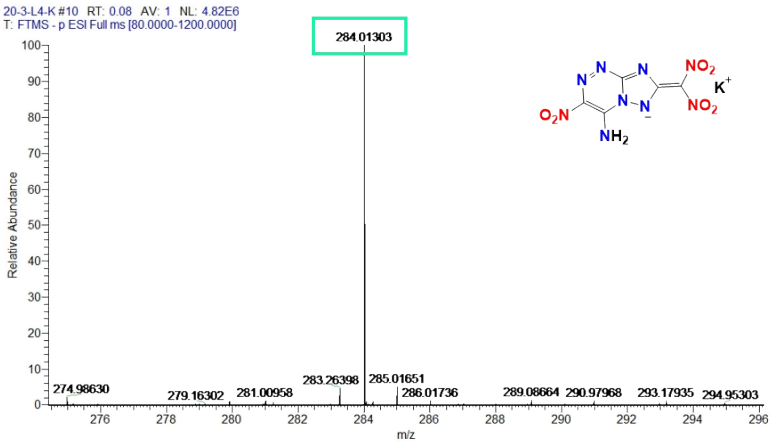


^{1}H NMR spectrum of **13** in d_6-DMSO.

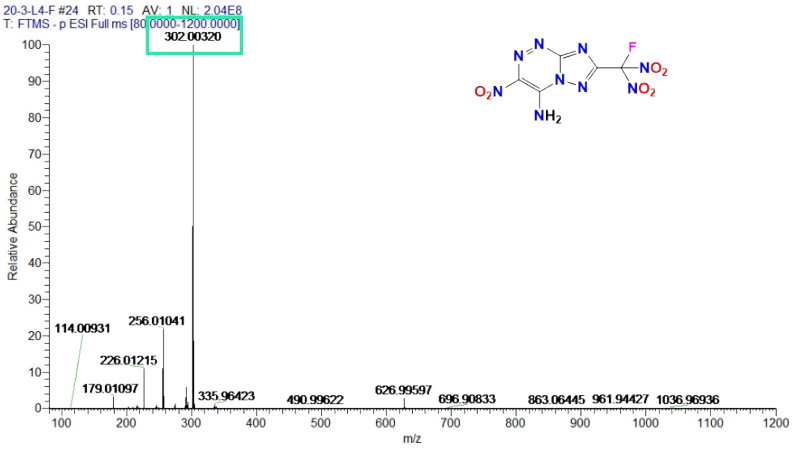


^{13}C NMR spectrum of **13** in d_6-DMSO.

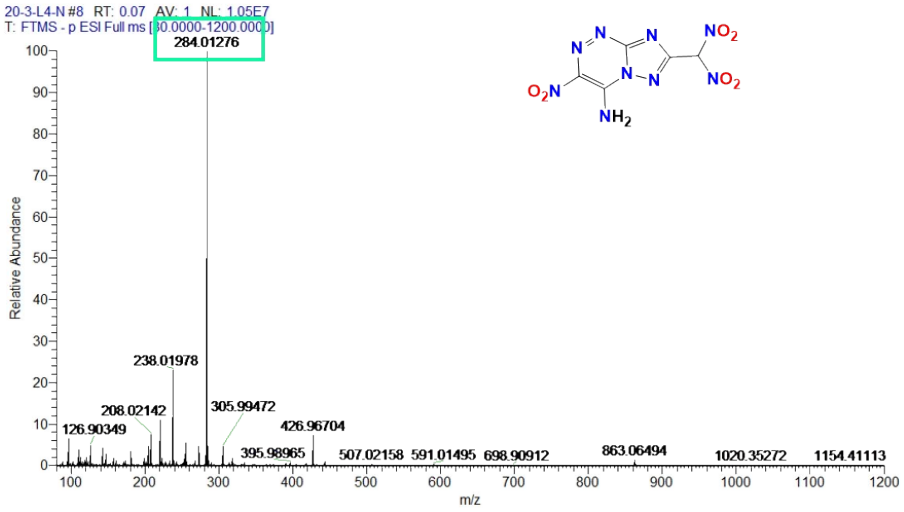
5. HRMS spectrum for 6-13



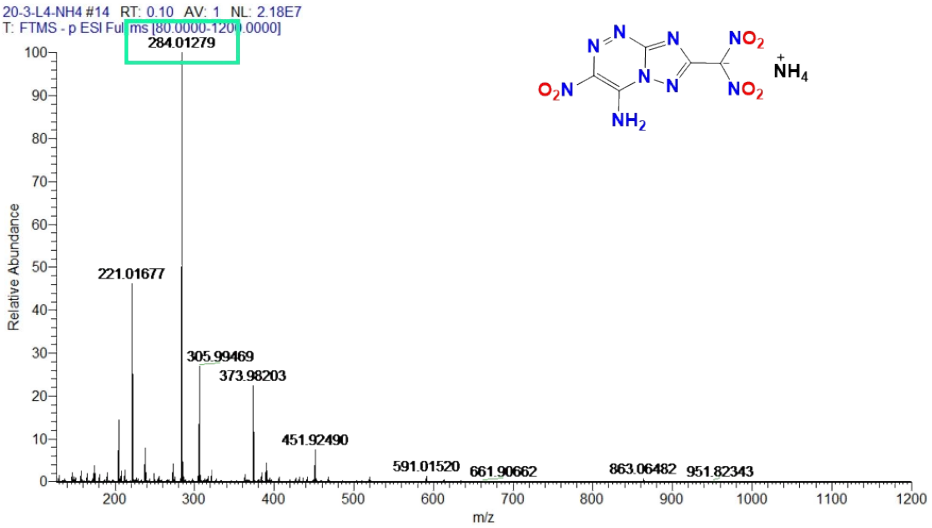
HRMS spectrum for **6**



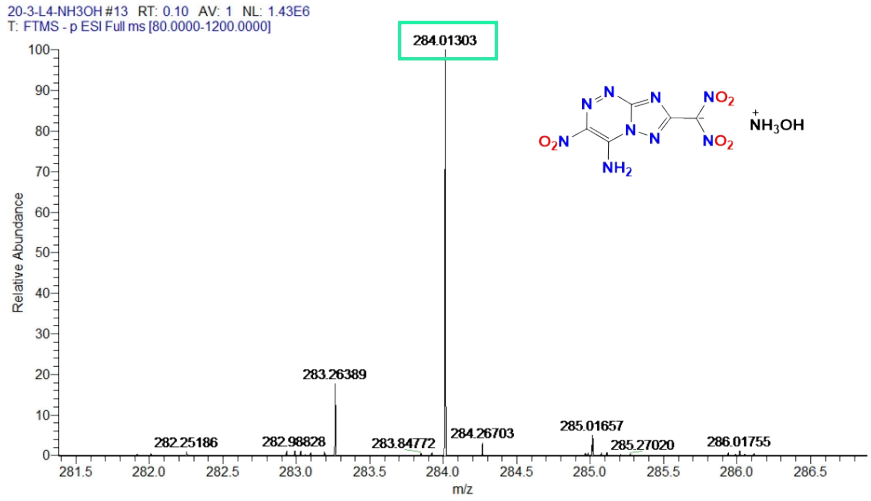
HRMS spectrum for **8**



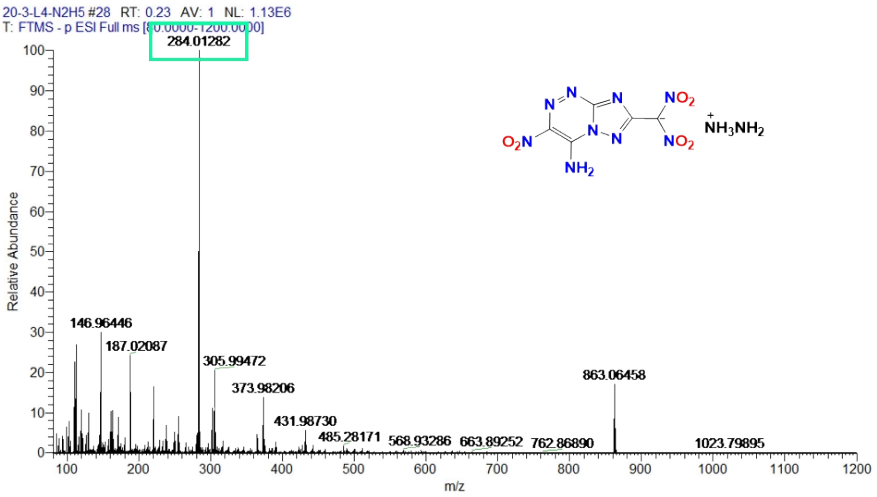
HRMS spectrum for **9**



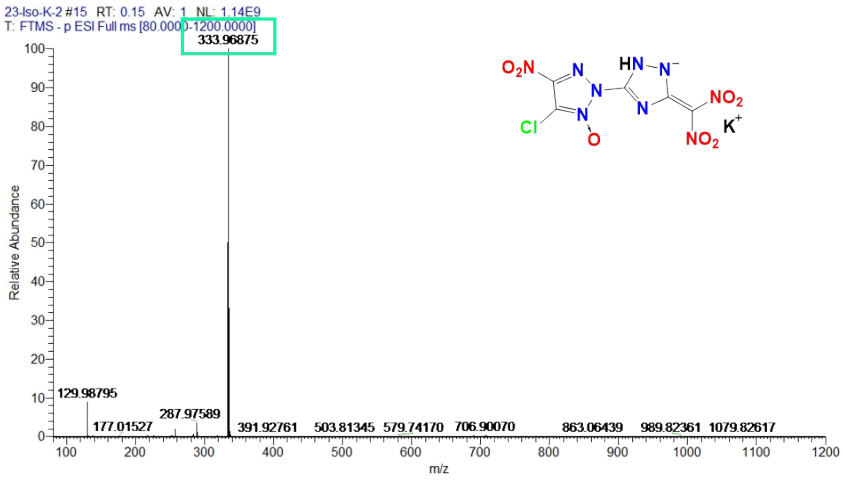
HRMS spectrum for **10**



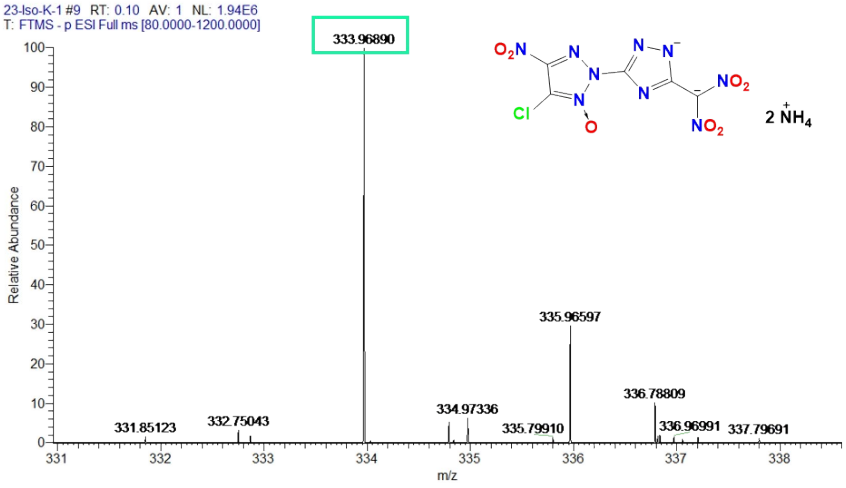
HRMS spectrum for **11**



HRMS spectrum for **12**

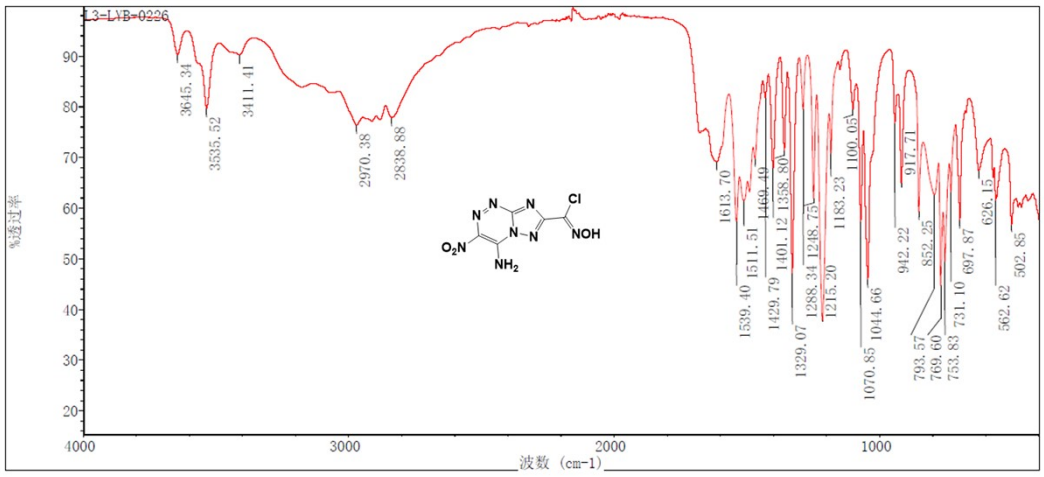


HRMS spectrum for **7**

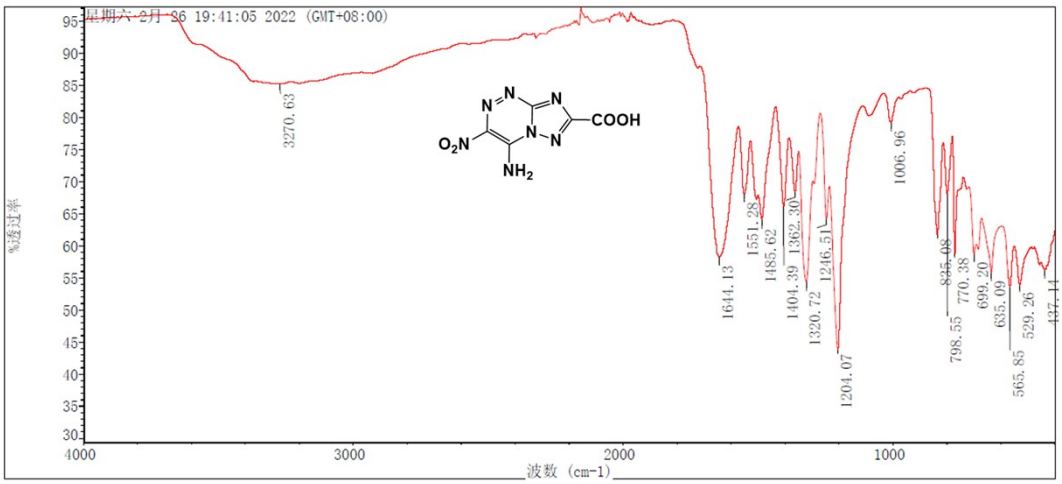


HRMS spectrum for **13**

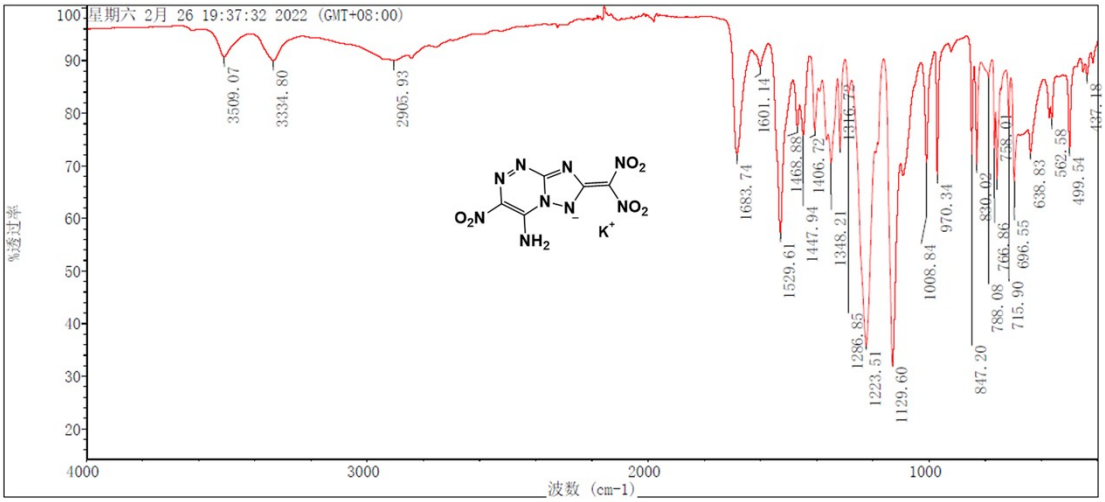
6. IR spectra of all new compounds



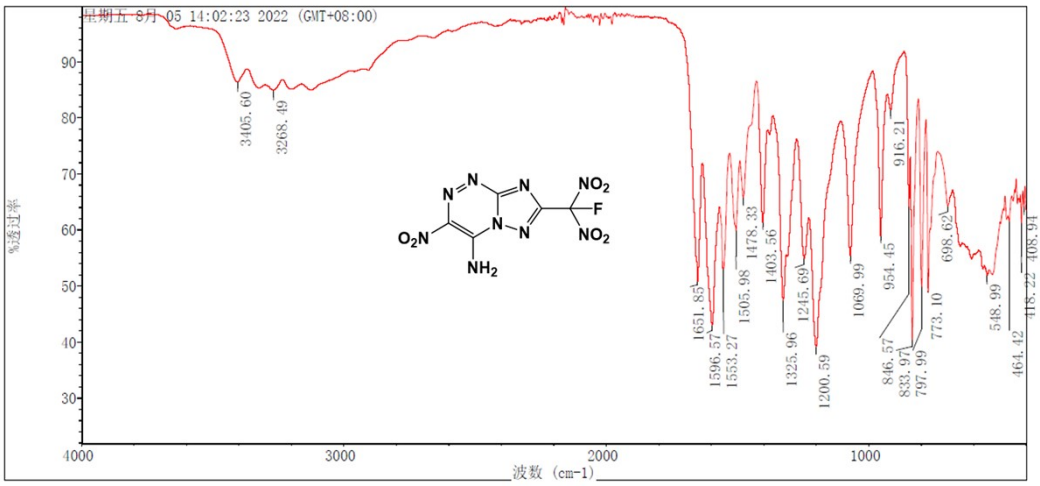
IR spectrum of compound **2**



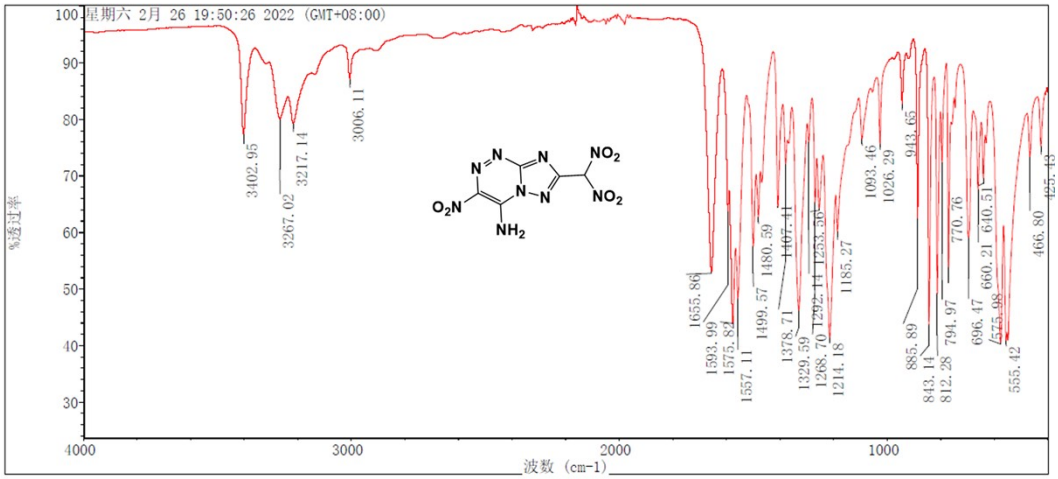
IR spectrum of compound **3**



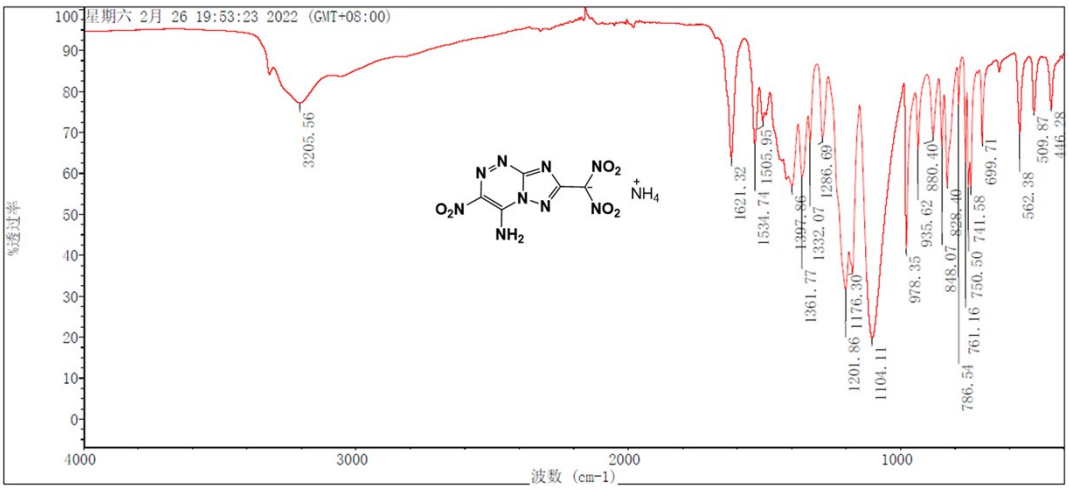
IR spectrum of compound **6**



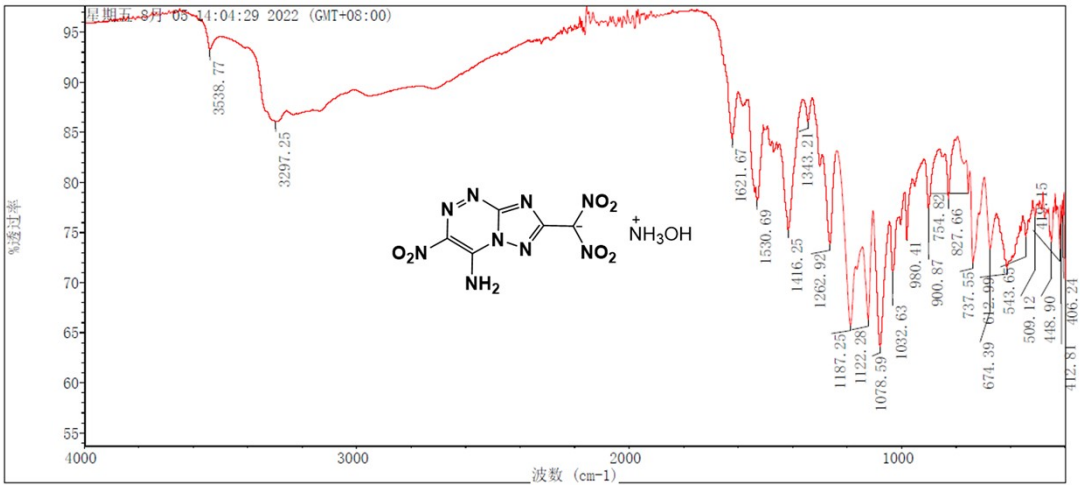
IR spectrum of compound **8**



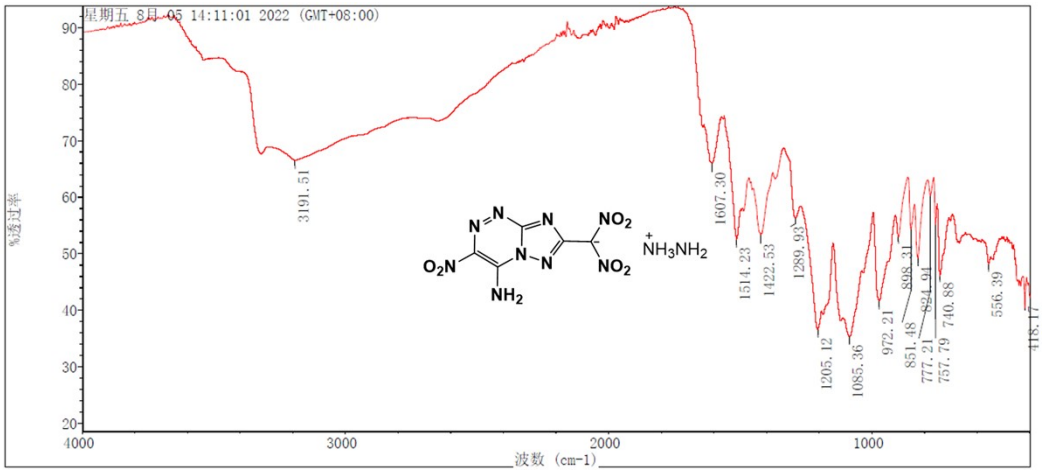
IR spectrum of compound **9**



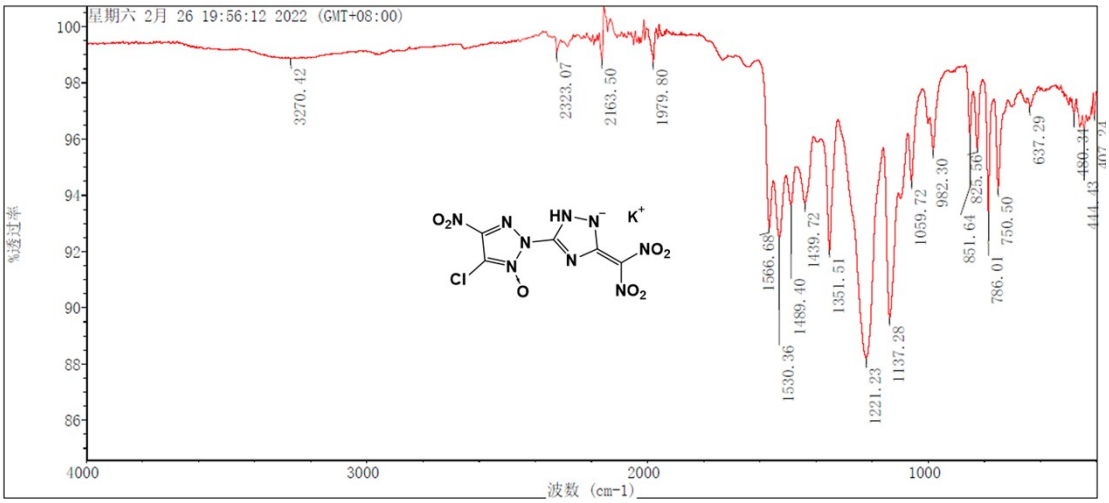
IR spectrum of compound **10**



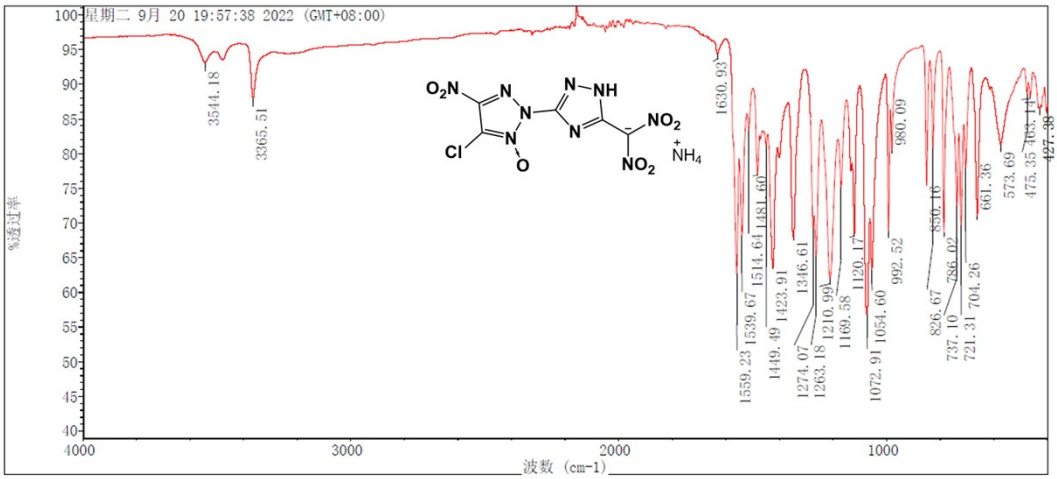
IR spectrum of compound **11**



IR spectrum of compound **12**

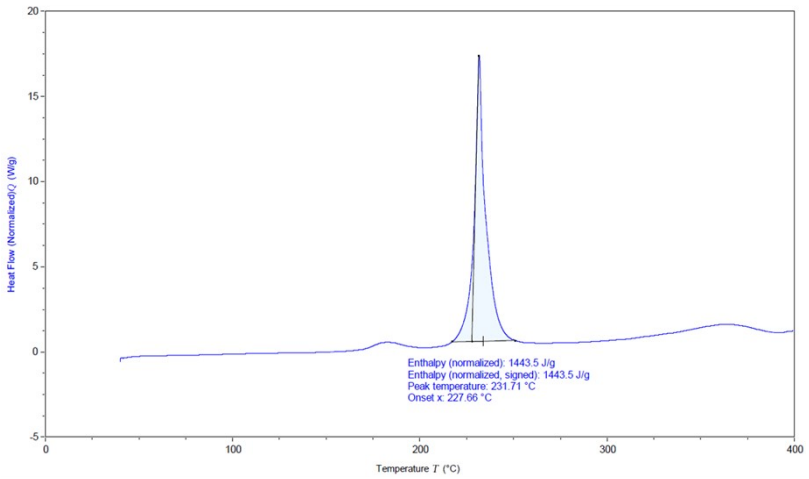


IR spectrum of compound **7**

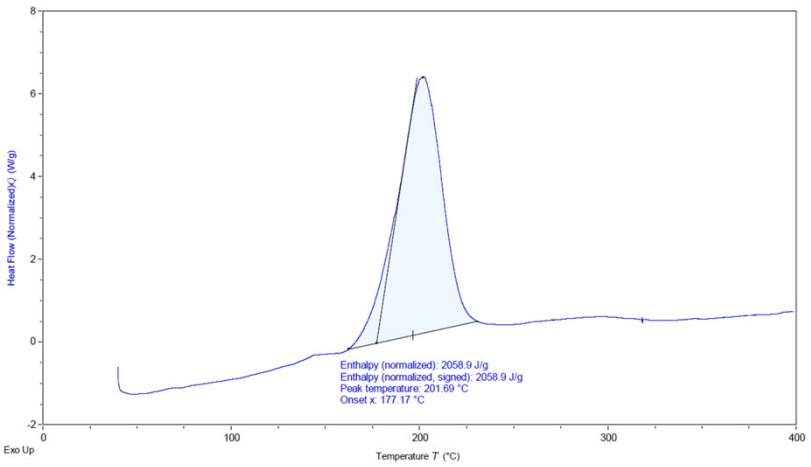


IR spectrum of compound **13**

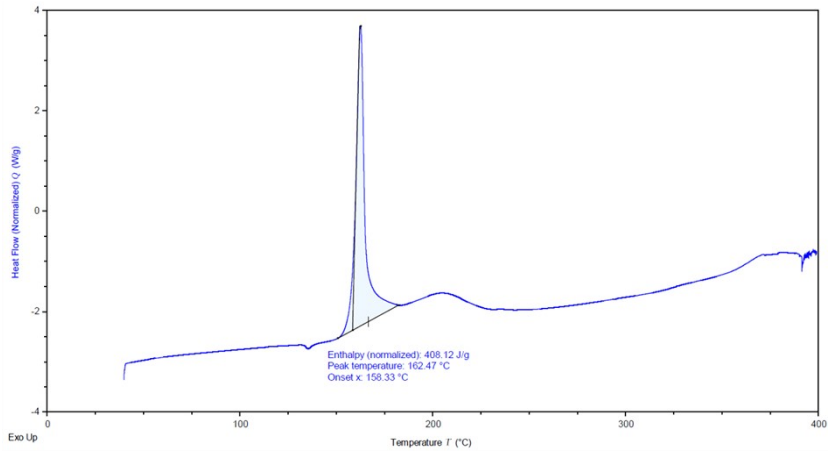
7. DSC plots for 6-13



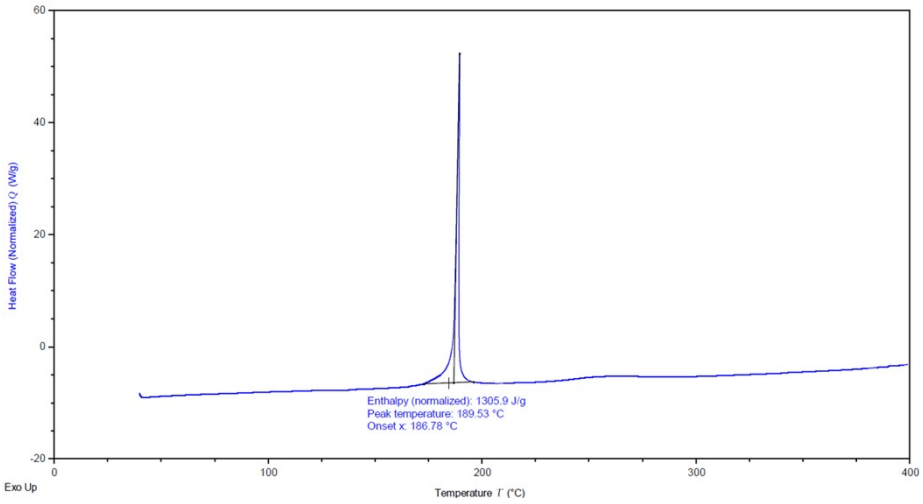
DSC curve of compound **6** at 5 °C min^{-1}



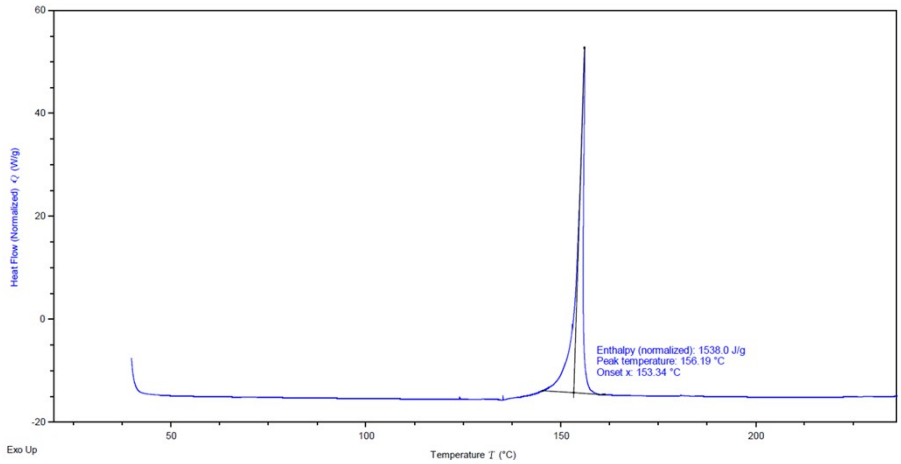
DSC curve of compound **8** at 5 °C min^{-1}



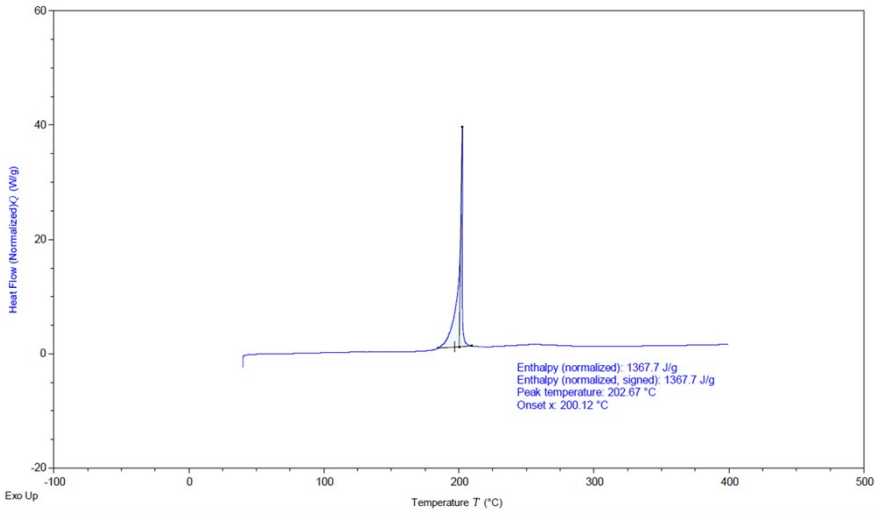
DSC curve of compound **9** at 5 °C min^{-1}



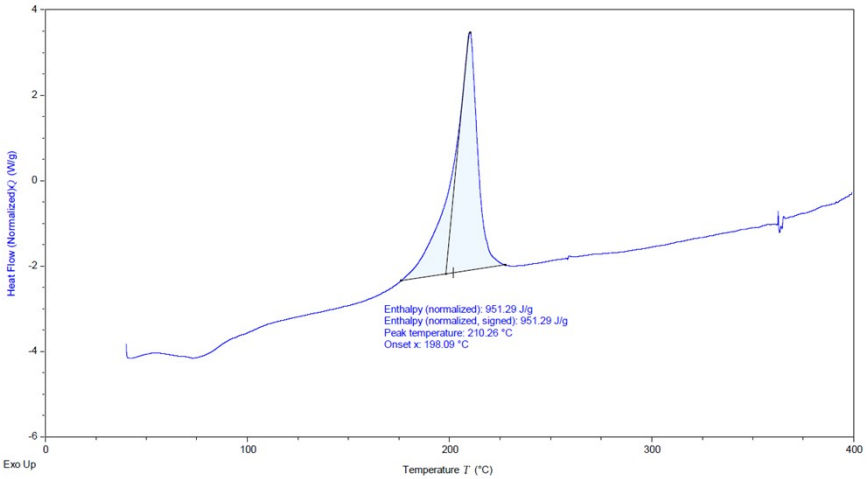
DSC curve of compound **10** at 5 °C min^{-1}



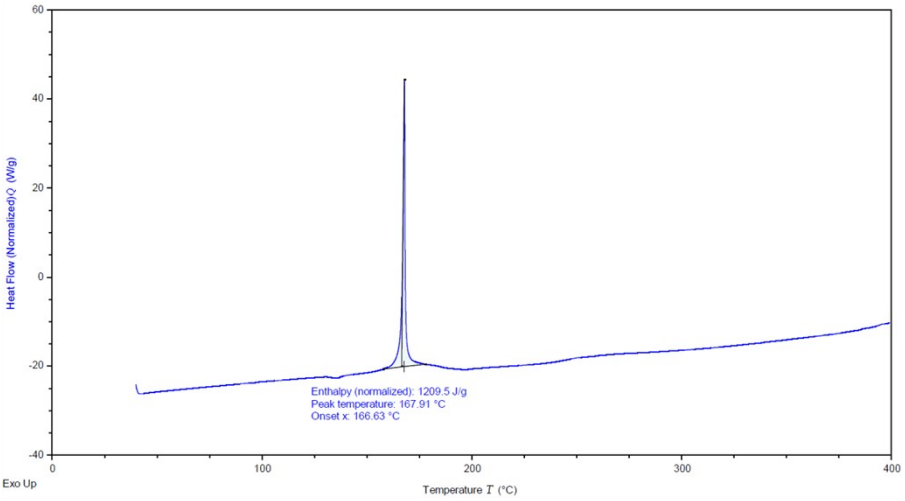
DSC curve of compound **11** at 5 °C min^{-1}



DSC curve of compound **12** at 5 °C min^{-1}



DSC curve of compound **7** at 5 °C min^{-1}



DSC curve of compound **13** at 5 °C min^{-1}

References

1 A. Strömberg, O. Gropen and U. Wahlgren, Gaussian basis sets for the fourth-row main group elements, In–Xe, *J. Comput. Chem.*, 1983, **4**, 181-186.

2 M. N. Glukhovtsev, A. Pross, M. P. McGrath and L. Radom, Extension of Gaussian-2 (G2) theory to bromine-and iodine-containing molecules: Use of effective core potentials, *J. Chem. Phys.*, 1995, **103**, 1878–1885.

3 M. S. Westwell, M. S. Searle, D. J. Wales and D. H. Williams, Empirical Correlations between Thermodynamic Properties and Intermolecular Forces. *J. Am. Chem. Soc.*, 1995, **117**, 5013–5015.