Supporting Information

A Facile Synthesis of Energetic Salts Based on Fully Nitroamino-functionalized [1,2,4]Triazolo[4,3-b][1,2,4]triazole

Chengming Bian,*[a] Wenjing Feng,[a] Qunying Lei,[a] Haifeng Huang,*[b] Xia Li,[a]

Jianlong Wang,[a] Chuan Li,[c] Zhongliang Xiao*[d]

[a]School of Science, North University of China, Taiyuan, Shanxi, 030051, P.R. China, E-mail: biancm@nuc.edu.cn
[b]CAS Key Laboratory of Energy Regulation Materials, Shanghai Institute of Organic Chemis try, Chinese Academy of Sciences, Ling Ling Road 345, Shanghai, 200032, P. R. China, E-mail: hfhuang@sioc.ac.cn
[c]School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng, 252059, P. R. China
[d]School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, J iangsu, 210094, P.R. China, E-mail: xiaozhl2019@163.com

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1 Crystallographic data

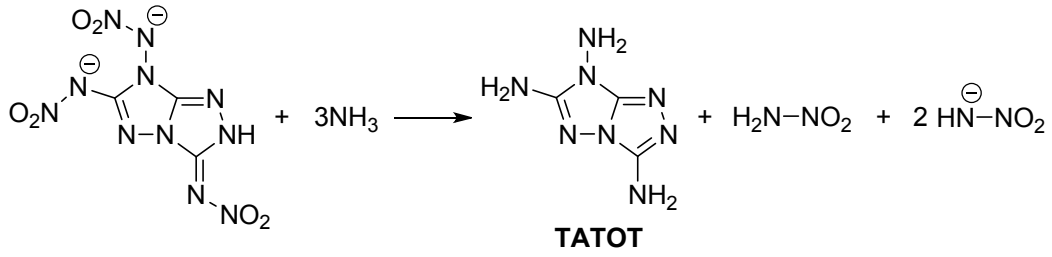
Table S1 Crystallographic data and structure refinement parameters **5**·H_2O, **6**·0.72H_2O and **7**

	5•H_2O	**6**•0.72H_2O	**7**
Formula	$C_5H_{15}N_{17}O_7$	$C_5H_{16.41}N_{19}O_{6.72}$	$C_5H_{17}N_{21}O_6$
Mw	425.34	450.37	467.39
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a[Å]	6.7723 (3)	7.3254 (7)	7.6291 (2)
b[Å]	13.1291 (5)	12.5221 (13)	13.4799 (3)
c[Å]	18.8628 (8)	19.3440 (19)	17.4739 (4)
V[Å^3]	1637.80 (12)	1743.1 (3)	1777.78 (7)
Z	4	4	4
T[K]	189.7(10)	150 (2)	150.0(1)
λ[Å]	1.54184	0.71076	1.54184
ρ_{calcd}[mg m^{-3}]	1.725	1.716	1.746
μ[mm^{-1}]	1.35	0.151	1.33
F(000)	880	933	968
Crystal size[mm^{-3}]	0.17×0.16×0.15	0.2×0.16×0.1	0.18×0.16×0.15
θ range[°]	3.4-66.6	2.7-26.3	4.2-66.6
index ranges	-8≤h≤8	-9≤h≤9	-5≤h≤9
	-15≤k≤12	-15≤k≤15	-14≤k≤16
	-22≤l≤22	-24≤l≤24	-19≤l≤20
reflns collected	9467	23305	5900
Independent reflns (R_{int})	5733[0.021]	3552[0.059]	3125[0.020]
data/retraints/parameters	5733/12/535	3552/0/307	3125/0/289
GOF on F^2	1.036	1.016	1.067
$R[F^2 > 2\sigma(F^2)]$	0.036	0.052	0.042
$wR(F^2)$	0.0989[a]	0.1378[b]	0.1136[c]

[a] $w = 1/[\sigma^2(F_o^2) + (0.0579P)^2 + 0.4072P]$; [b] $w = 1/[\sigma^2(F_o^2) + (0.056P)^2 + 1.514P]$; [c] $w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 1.2413\ P]$, where $P = (F_o^2 + 2F_c^2)/3$

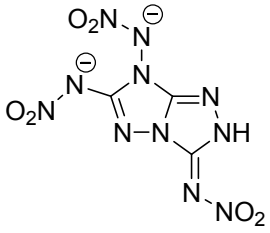
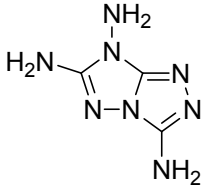
2 Computational Details

The ΔH_f of the 3,6,7-trinitroimino-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]triazolate anion is 460.18 kJ mol^{-1}. Calculations were carried out by using the Gaussian 09 (Revision A.02) suite of programs based on isodesmic reactions (Scheme S1). The geometric optimization of the structures and frequency analyses were carried out by using the B3LYP functional with the 6-31+G**basis set, and single-point energies were calculated at the MP2(full)/6-311++G**level (Table S2). All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

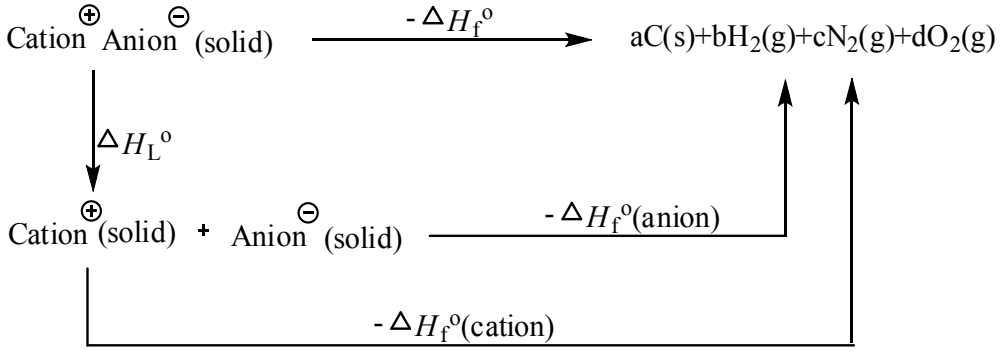


Scheme S1 Isodesmic reactions for anion

Table S2 Ab Initio computional data (gas phase)

Compound	E_0 (Hartree)	ZPE (Hartree)	ΔH_T (Hartree)	HOF (kJ mol^{-1})
	-1166.036172	0.106774	0.015633	460.1821
NH_3	-56.4346163	0.034372	0.002874	-45.9[a]
	-554.7484114	0.126854	0.009685	540.1[b,c]
NH_2NO_2	-260.5541502	0.038259	0.0034	-6.1
	-260.0119686	0.026168	0.003332	-84

[a] *Angew. Chem. Int. Ed.*, 2017, **56**, 5877–5881. [b] *Chem. Eur. J.*, 2015, **21**, 9219–9228. [c] Based on the literature, the heat of sublimation is estimated with Trouton's rule. The gas phase heat of formation of **TATOT** was calculated with equation, in which T_d represents the decomposition temperature. $\Delta H_f(g) = \Delta H_f(s) + \Delta H_{sub} = \Delta H_f(s) - 188[J\ mol\text{-}1\ K^{-1}] \times T_d$



Scheme S2 Born-Haber cycle for the formation for energetic salts.

Based on the Born-Haber energy cycle (Scheme S2), the heat of formation of salts **2** to **7** can be simplified according to Equation. (1), where ΔH_L is the lattice energy of the salt.

ΔH_f^o(ionic salt, 298K)=ΔH_f^o(cation, 298K) + ΔH_f^o(anion, 298K) — ΔH_L (1)

The ΔH_L value could be predicted by the formula suggested by Jenkins et al. [Eq. 2], in which U_{POT} is the lattice potential energy; and n_M and n_X depend on the nature of the ions M_p^+ and X_q^-, respectively (equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions).

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

The equation for the lattice potential energy, U_{POT}, takes the form of Equation (3), where ρ_m is the density (g cm^{-3}), M_m is the chemical formula mass of the ionic material (g), and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.

U_{POT} (kJ mol^{-1}) = $\gamma (\rho_m/M_m)^{1/3} + \delta$ (3)

3 Spectrums

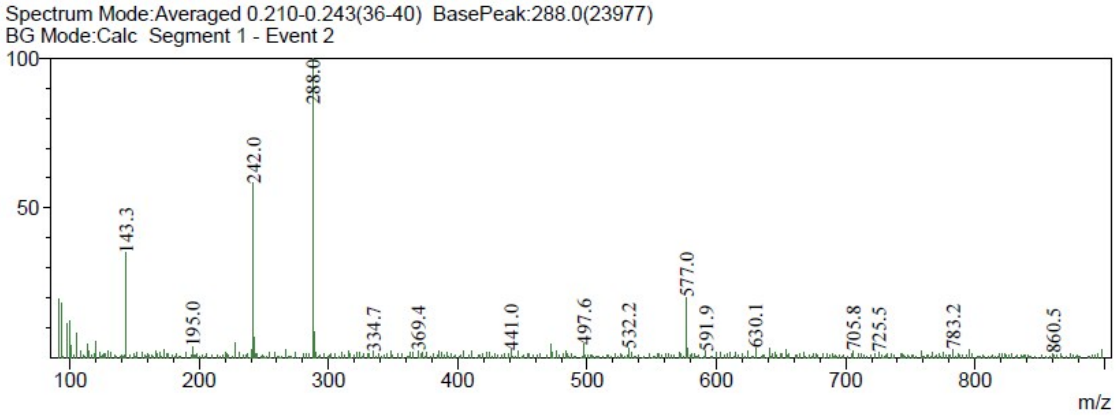


Figure S1 Mass Spectrum of compound **1**

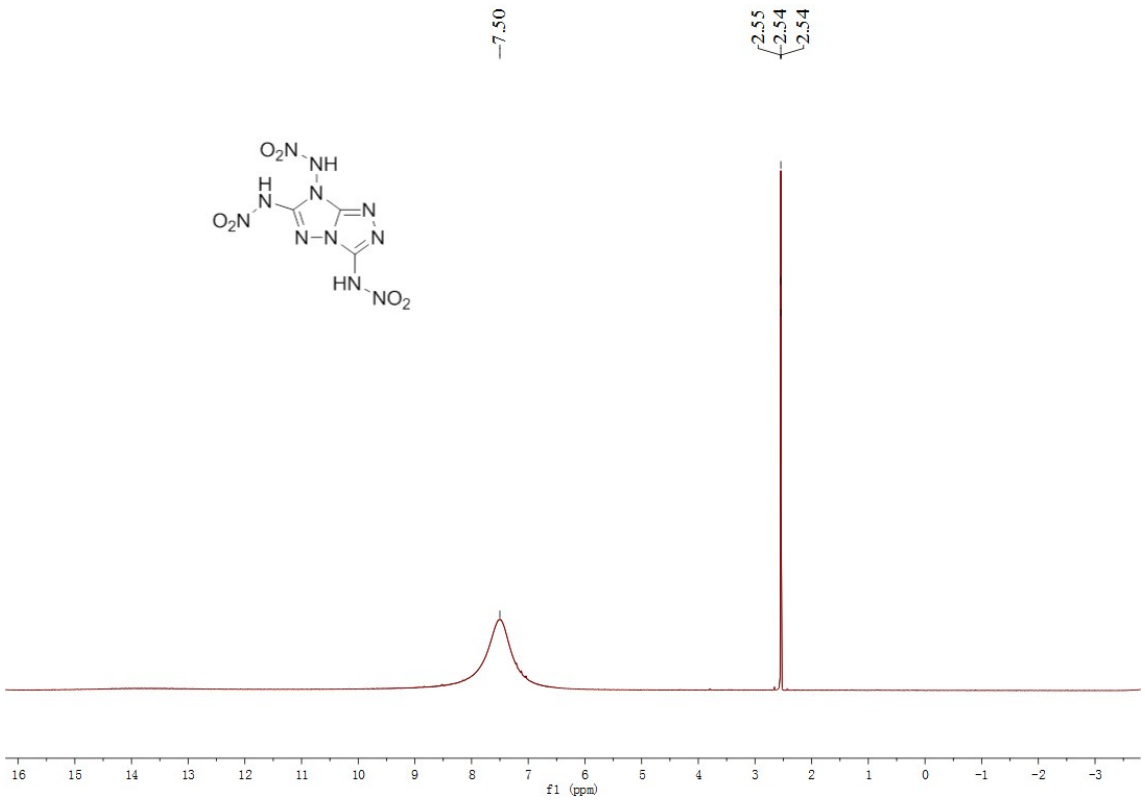


Figure S2 ^{1}H NMR Spectrum of compound **1**

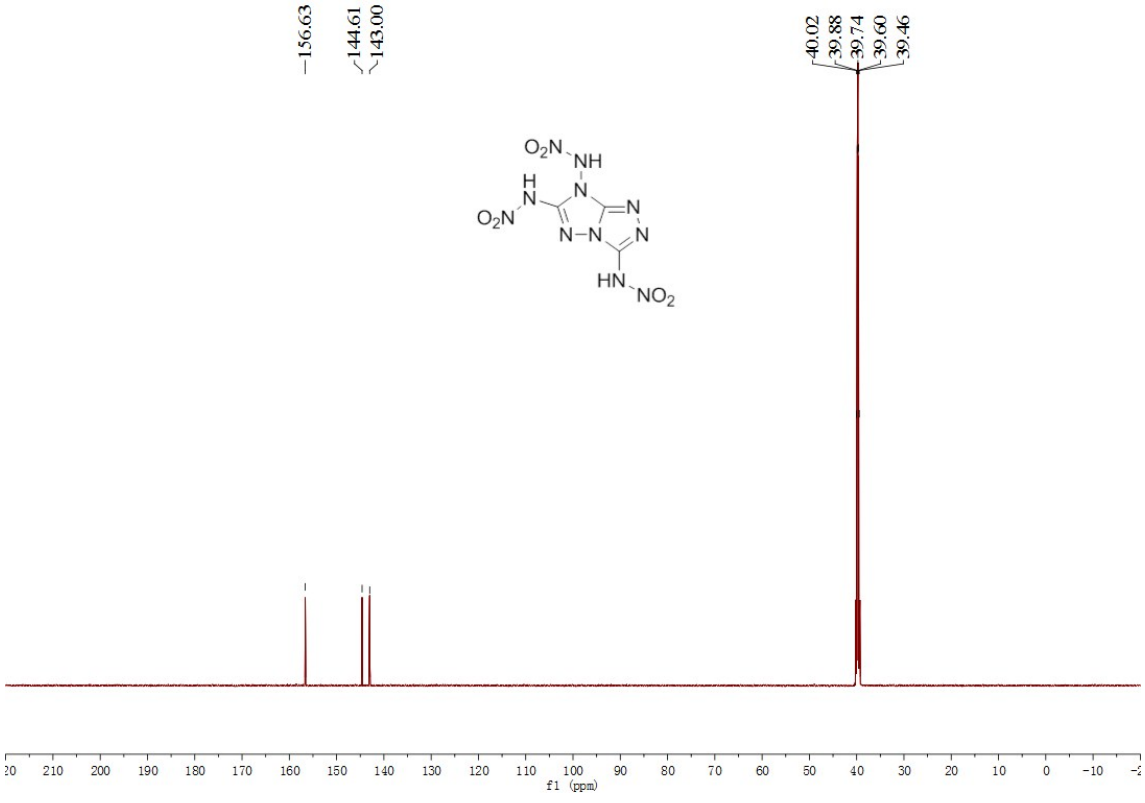


Figure S3 ^{13}C NMR Spectrum of compound **1**

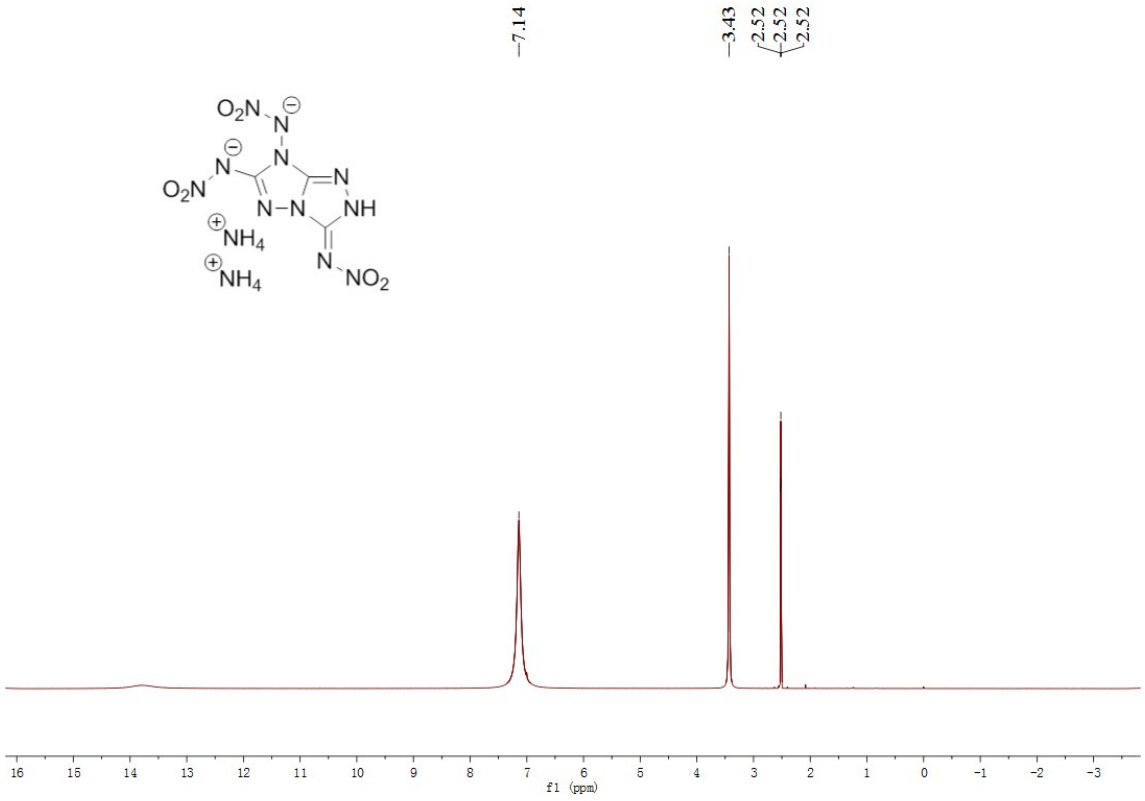


Figure S4 ^{1}H NMR Spectrum of salt **2**

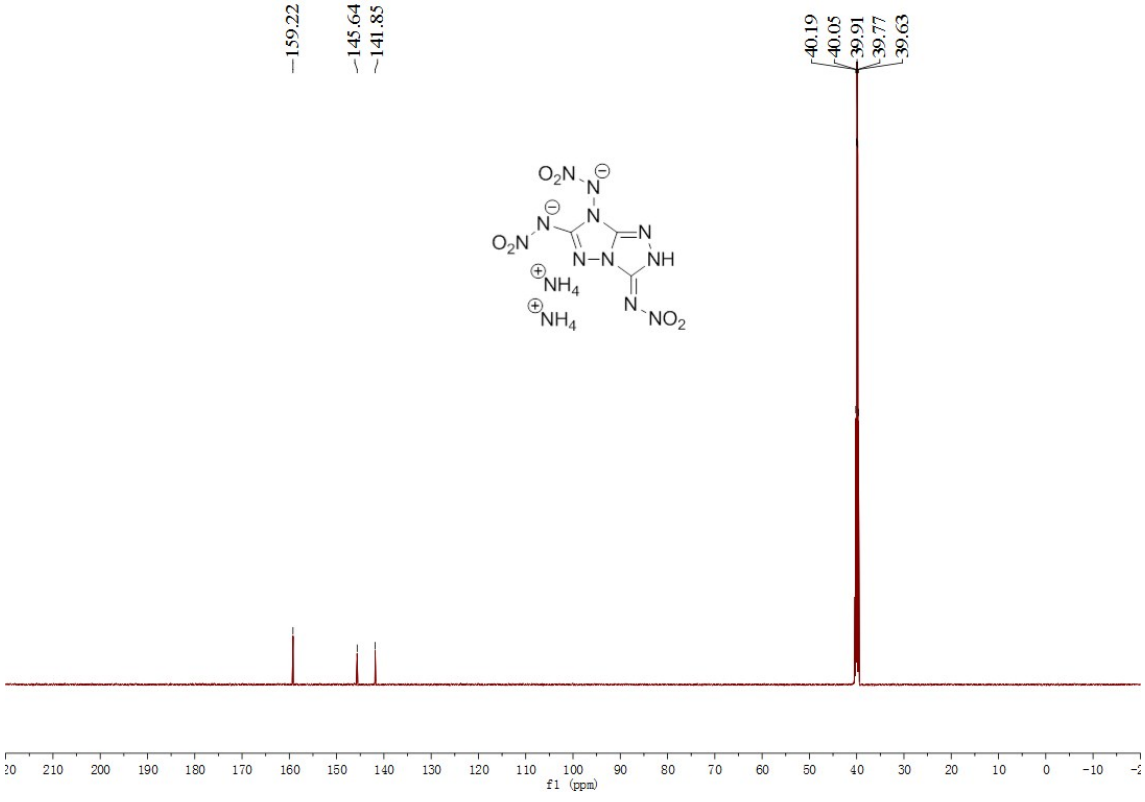


Figure S5 ^{13}C NMR Spectrum of salt **2**

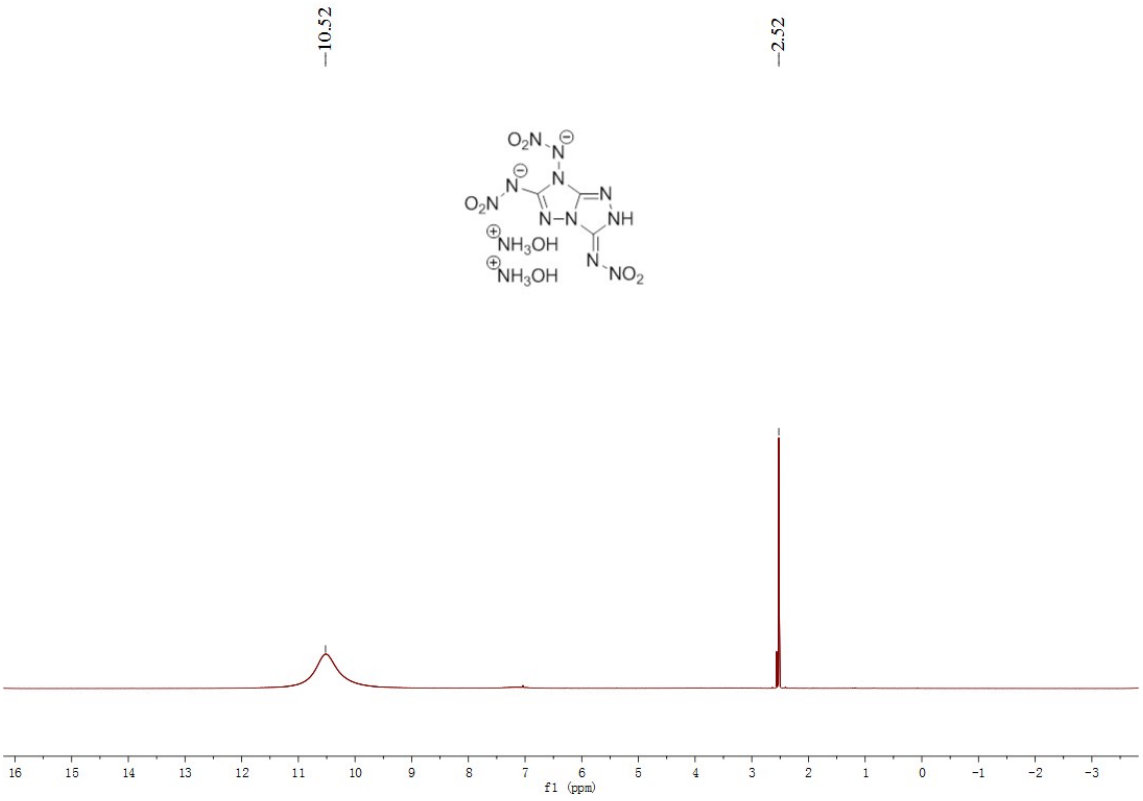


Figure S6 ^{1}H NMR Spectrum of salt **3**

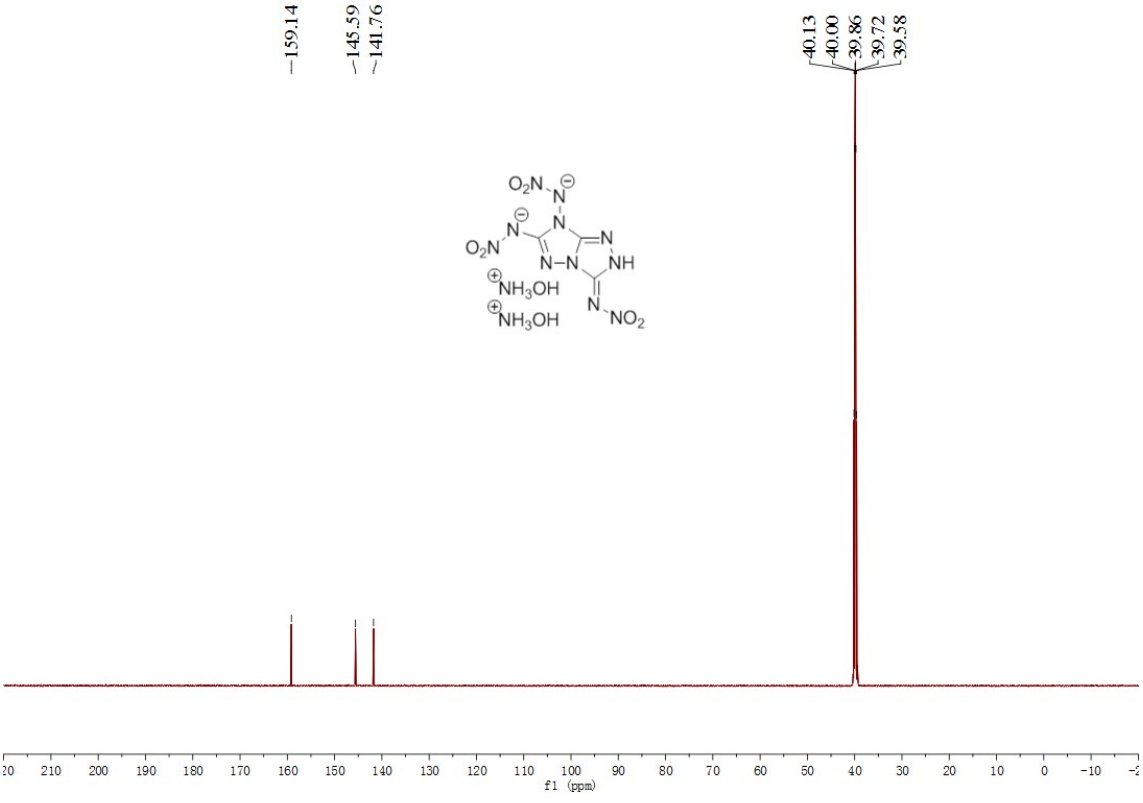


Figure S7 ^{13}C NMR Spectrum of salt **3**

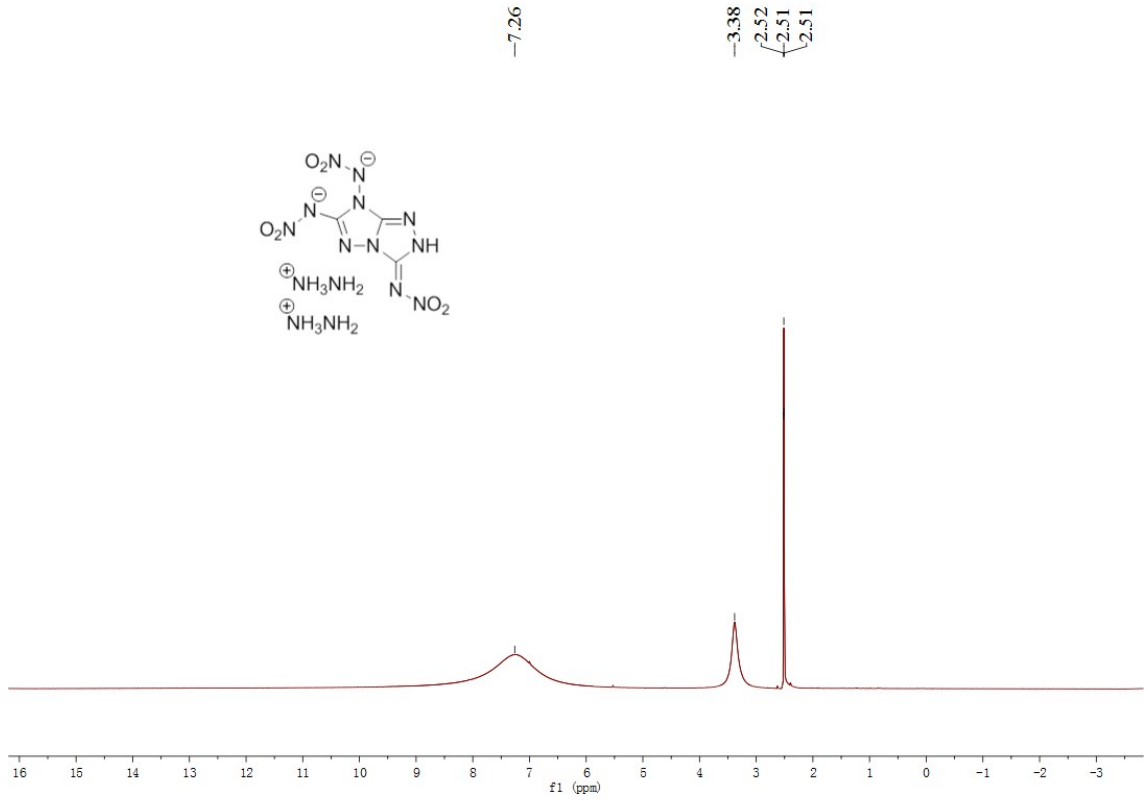


Figure S8 ^{1}H NMR Spectrum of salt **4**

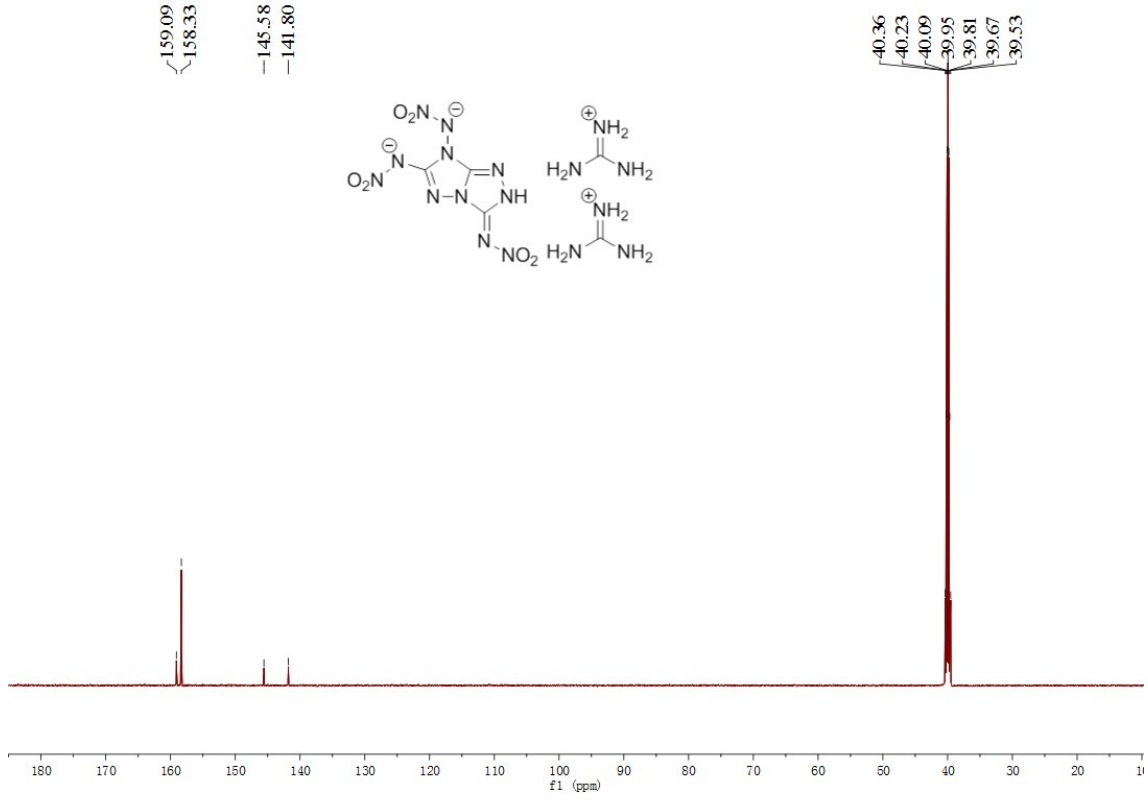


Figure S9 ^{13}C NMR Spectrum of salt **4**

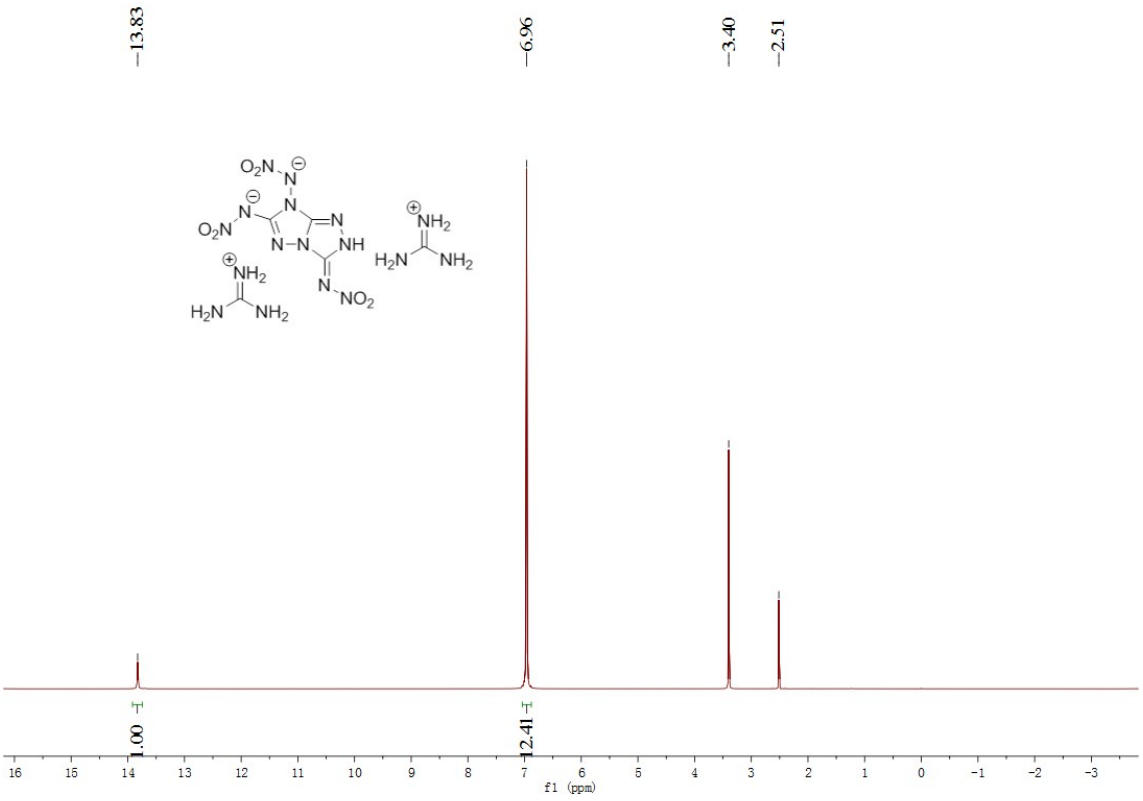


Figure S10 ^{1}H NMR Spectrum of salt **5**

Figure S11 ^{13}C NMR Spectrum of salt **5**

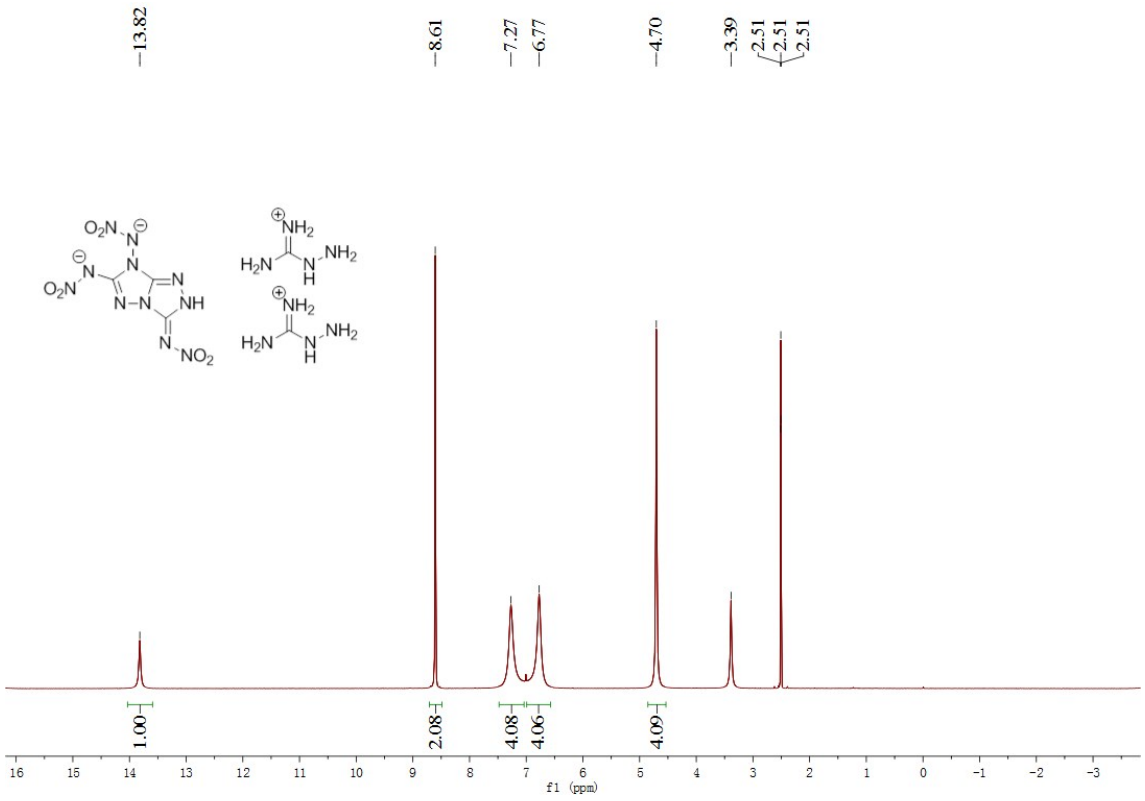


Figure S12 ^{1}H NMR Spectrum of salt **6**

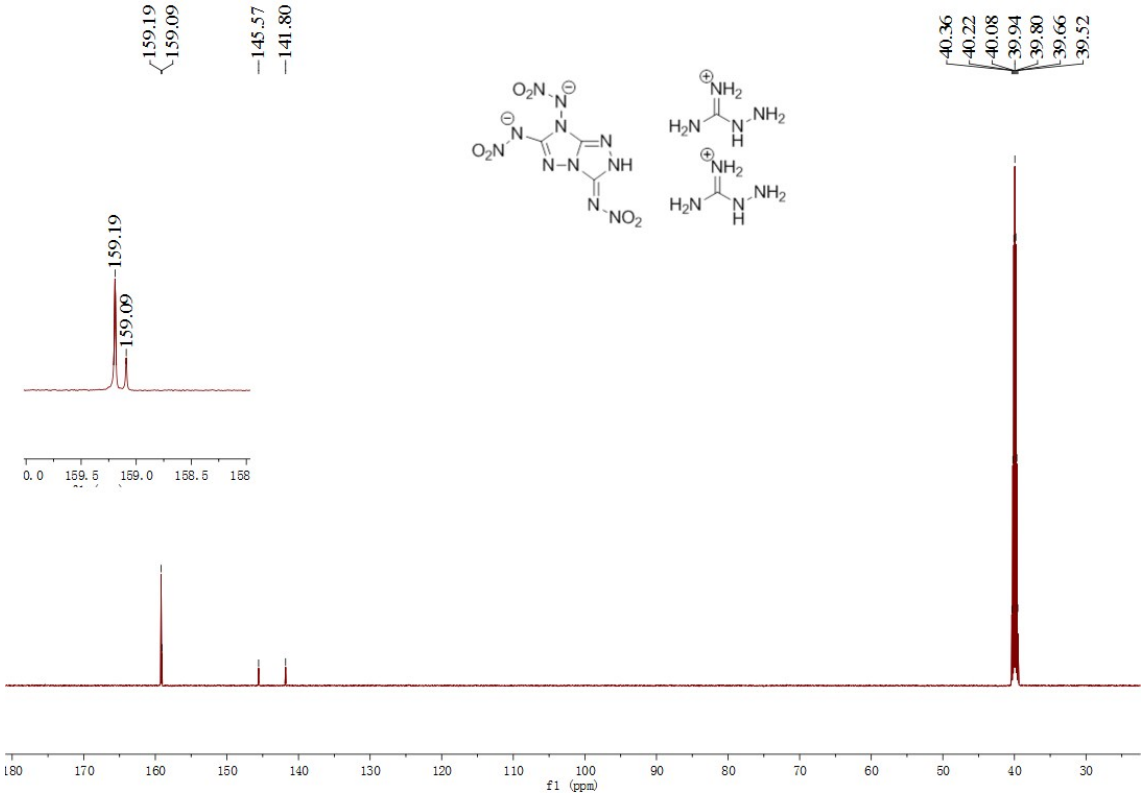


Figure S13 ^{13}C NMR Spectrum of salt **6**

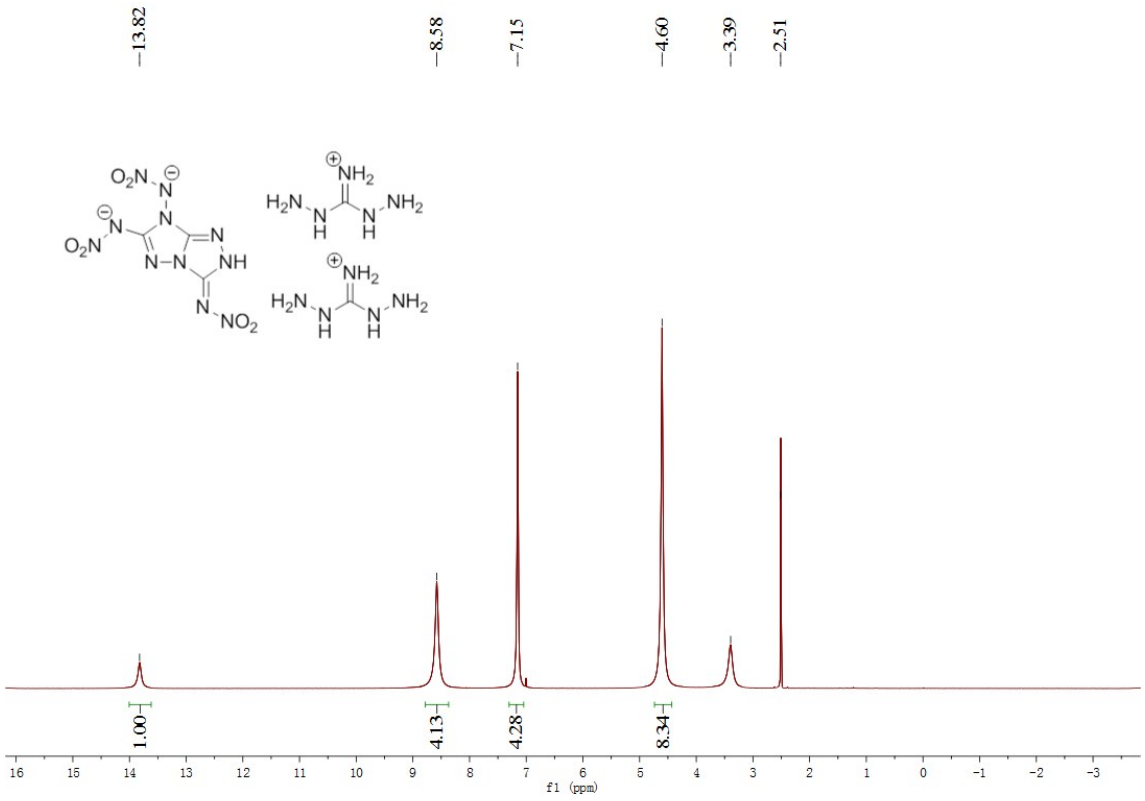


Figure S14 ^{1}H NMR Spectrum of salt **7**

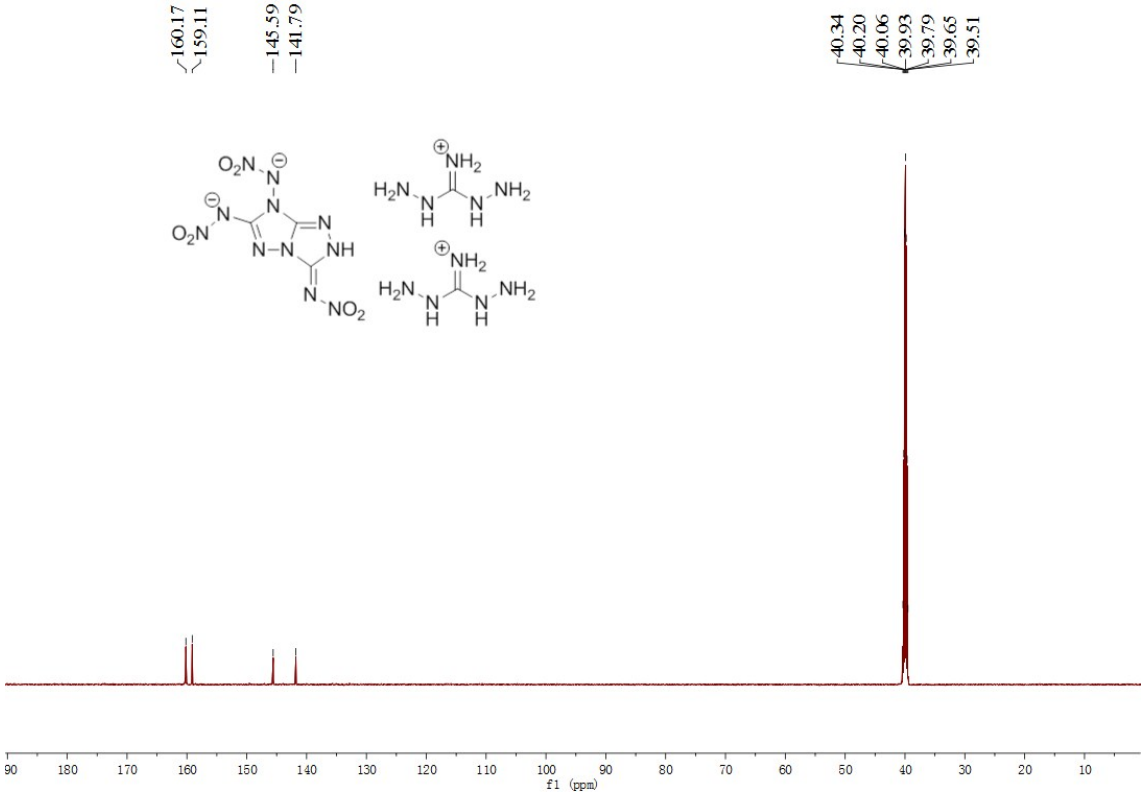


Figure S15 ^{13}C NMR Spectrum of salt **7**

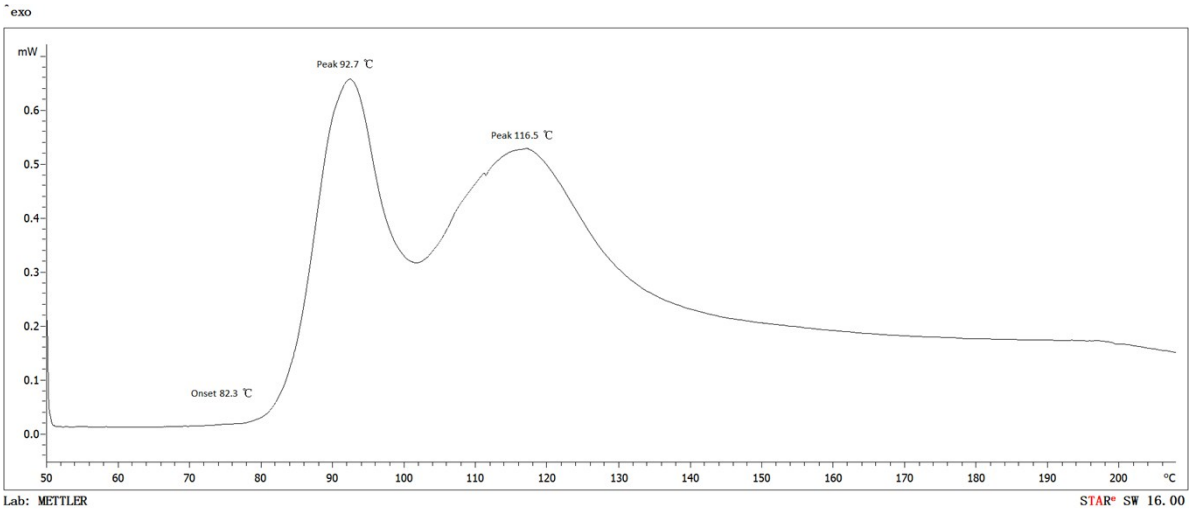


Figure S16 DSC plot of compound **1**

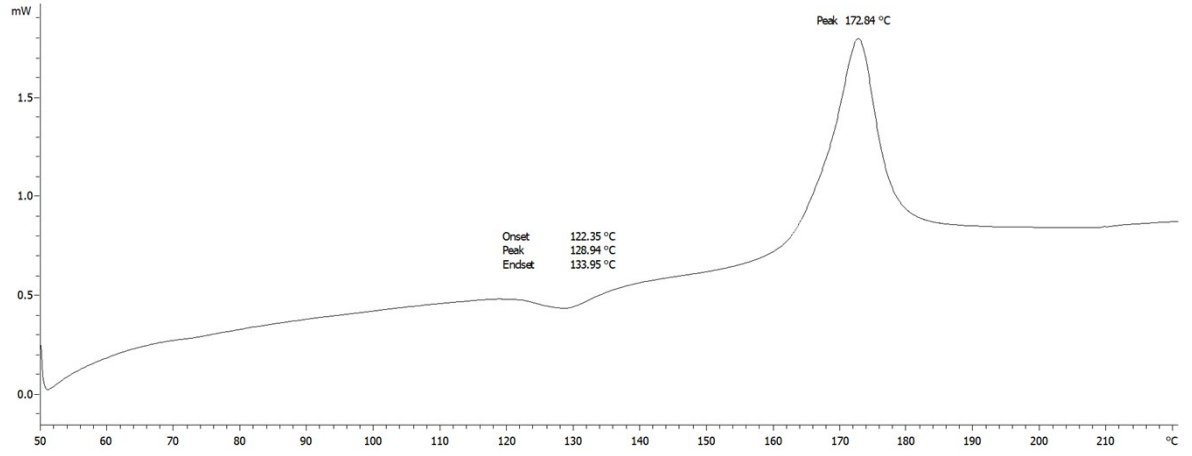


Figure S17 DSC plot of salt **2**

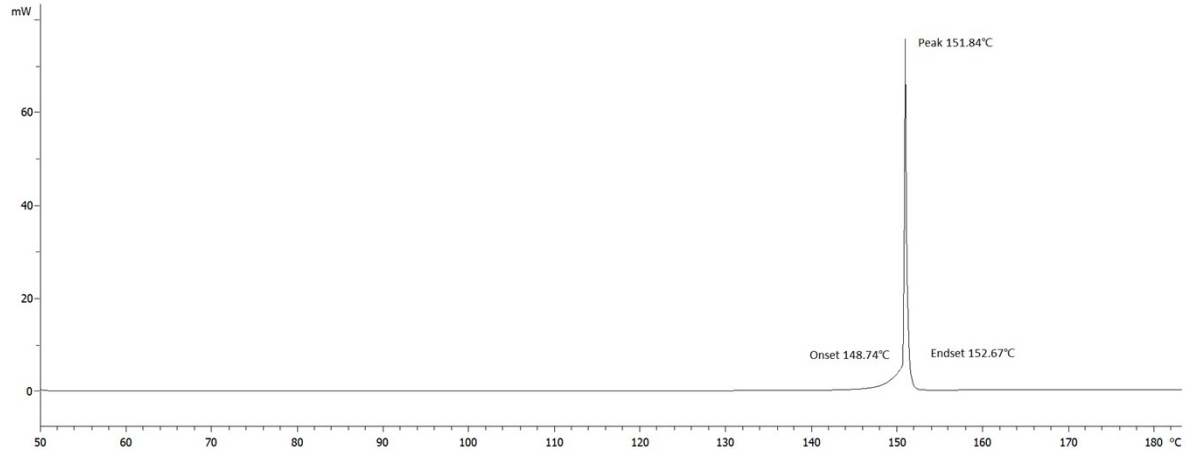


Figure S18 DSC plot of salt **3**

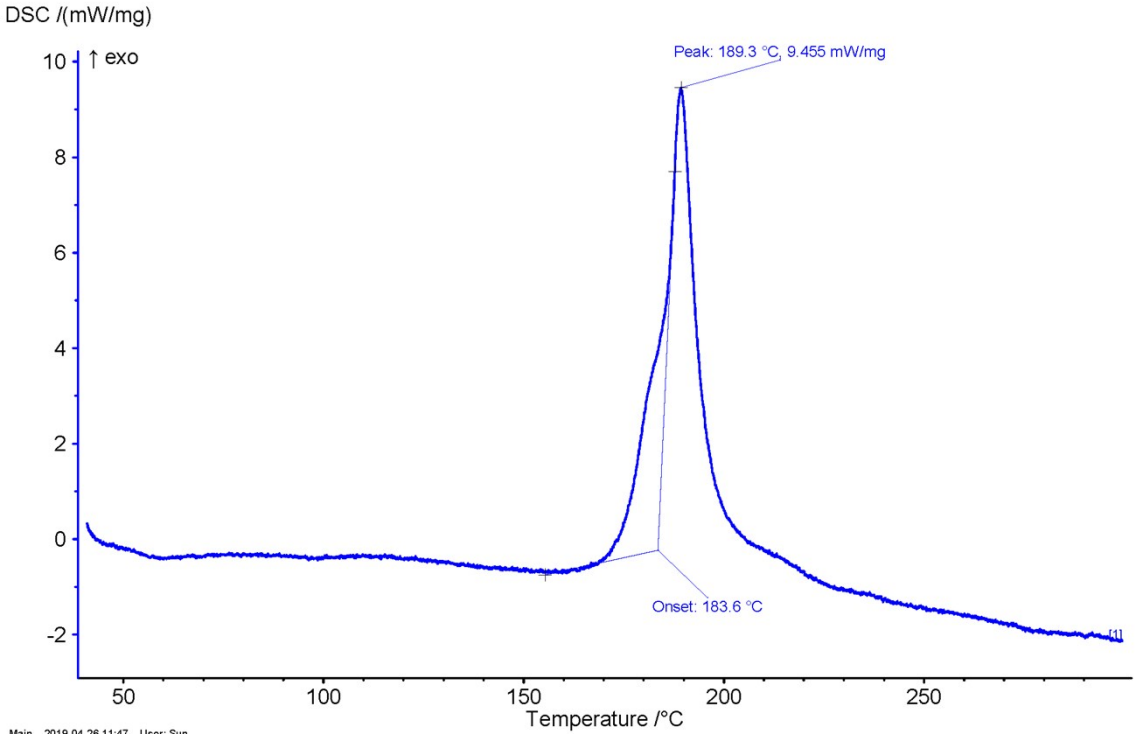


Figure S19 DSC plot of salt **4**

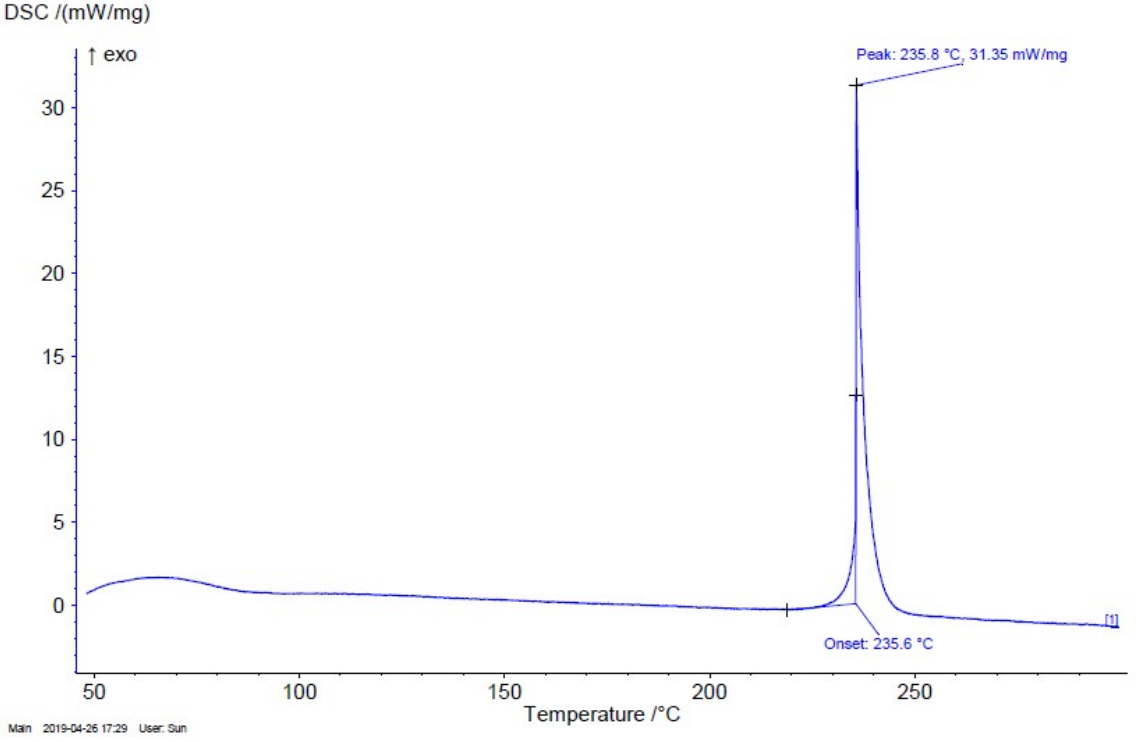


Figure S20 DSC plot of salt **5**

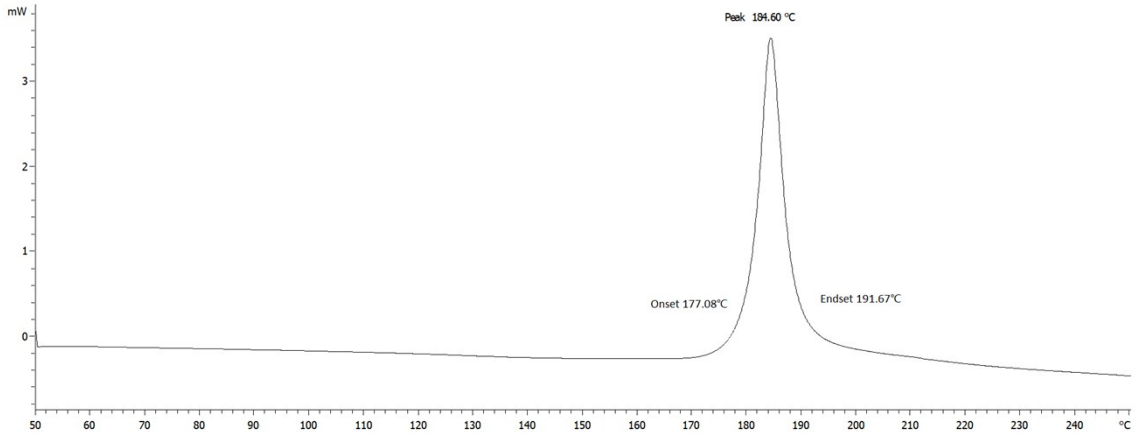


Figure S21 DSC plot of salt **6**

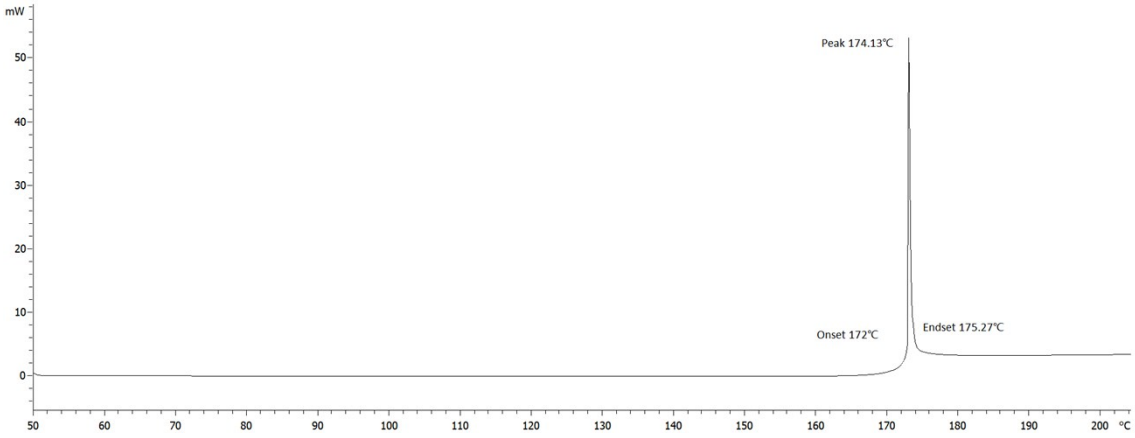


Figure S22 DSC plot of salt **7**

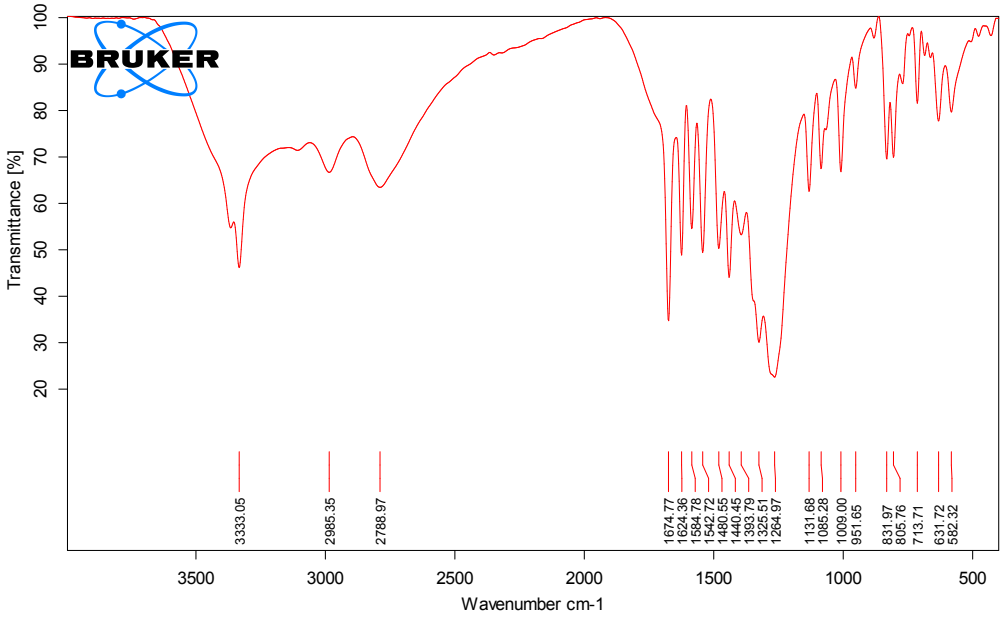


Figure S23 IR spectrum of compound **1**

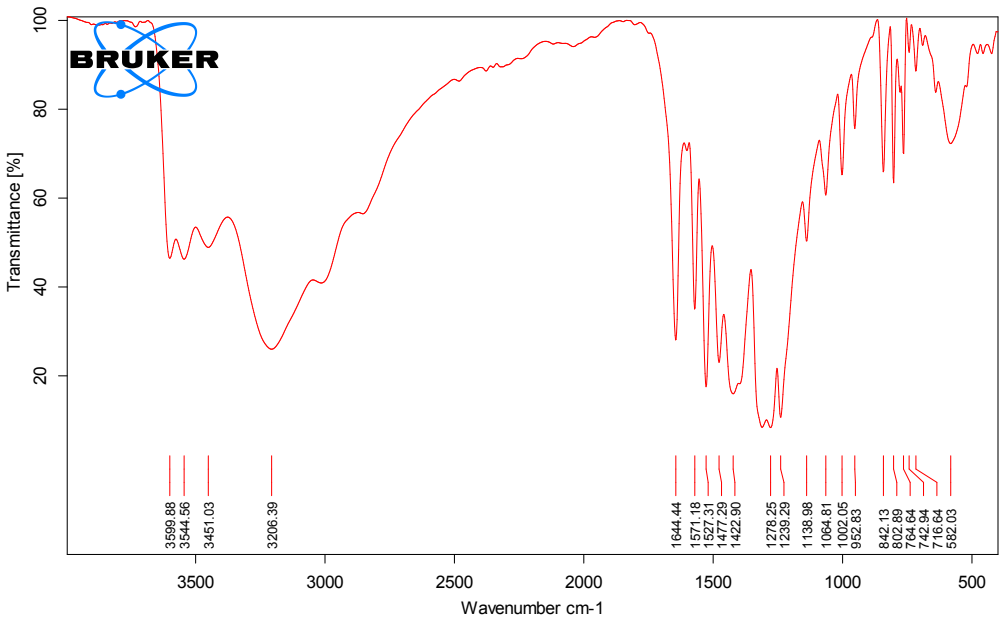


Figure S24 IR spectrum of salt **2**

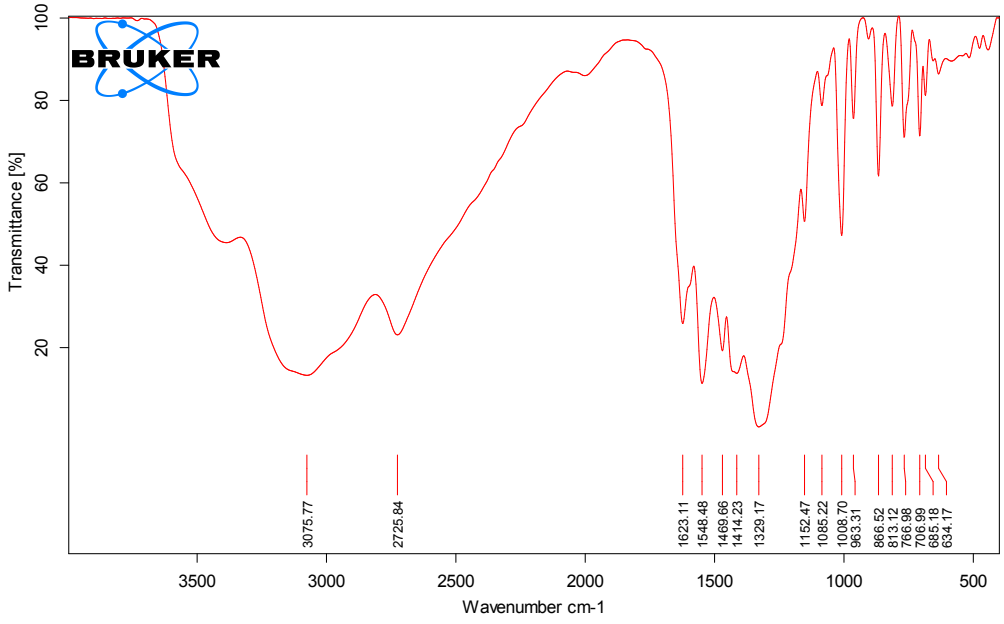


Figure S25 IR spectrum of salt **3**

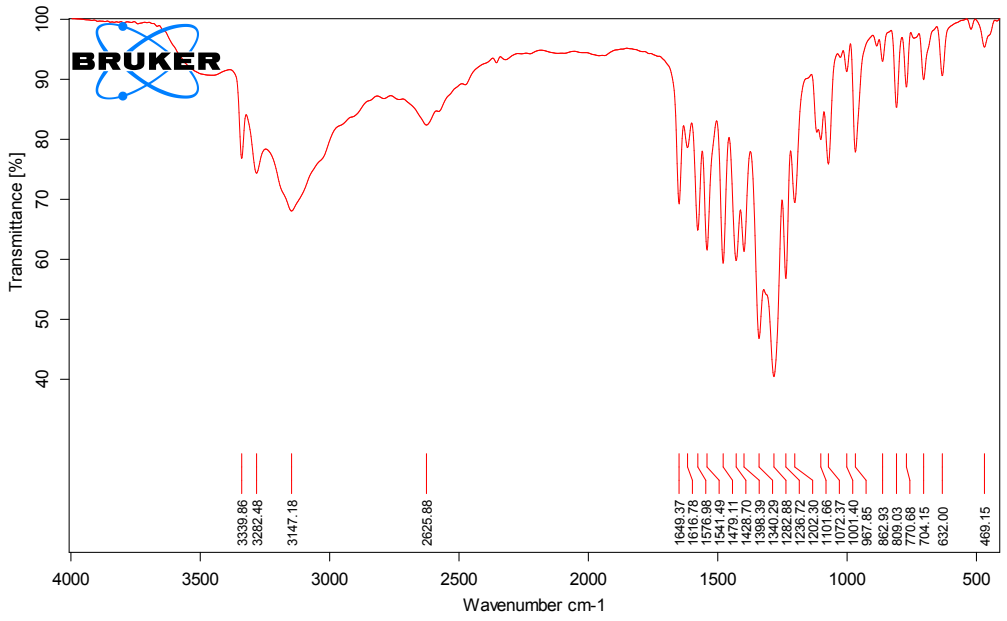


Figure S26 IR spectrum of salt **4**

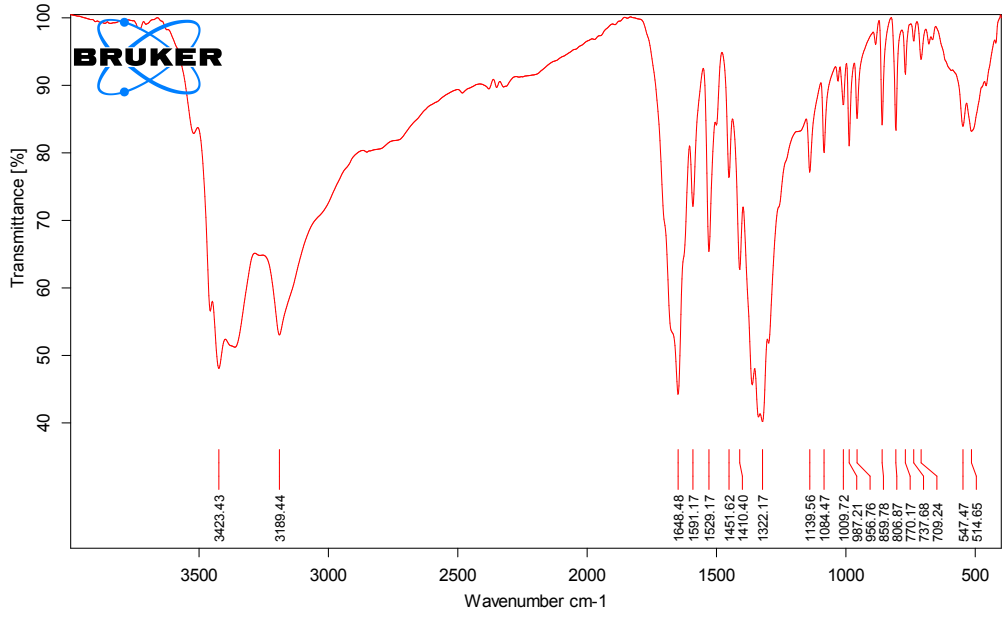


Figure S27 IR spectrum of salt **5**

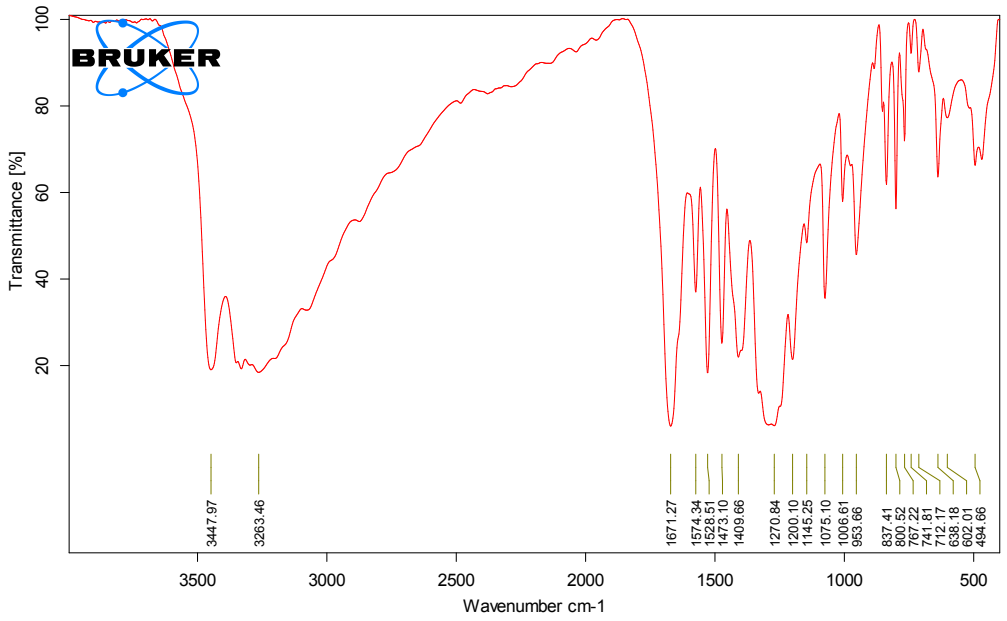


Figure S28 IR spectrum of salt **6**

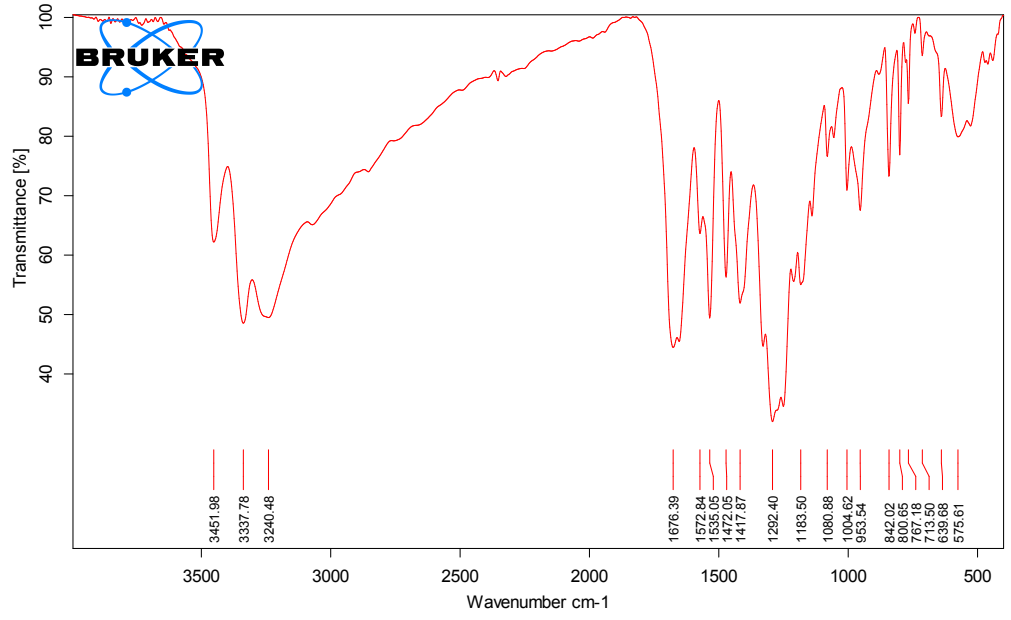


Figure S29 IR spectrum of salt **7**