

Fused triazolotriazine bearing gem–dinitro group – a promising high energy density material

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1. Experimental section

Caution All the nitrogen-rich compounds may explode under certain conditions although no explosion was encountered in the procedure of preparing these energetic materials. Thus, it is indispensable to keep safeguard procedures and keep experiments in a small scale at the same time.

General ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz (Bruker Avance 400) nuclear magnetic resonance spectrometers operating at 400 and 100 MHz, respectively. Chemical shifts are reported in ppm relative to Me_4Si . Differential scanning calorimeter (DSC, Shimadzu TA-60ws) was used to measure the melting temperatures and decomposition temperatures at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under argon atmosphere. IR spectra were recorded using KBr pellets for solids on a Bruker ALPHA FT-IR Spektrometer. HRMS was recorded on Bruker Apex IV FTMS. All chemicals were bought from commercial companies and used directly unless otherwise noted. The sensitivities towards impact and friction were determined using a drop hammer and a BAM friction tester.

5-Amino-1H-1,2,4-triazole-3-carbonitrile (**1**) was synthesized according to the literature^[S1].

4-Amino-[1,2,4]triazolo[5,1-c][1,2,4]triazine-3,7-dicarbonitrile (2): The mixture of 6.2 mL H_2O and 5.4 mL concentrated HCl containing 5-amino-1H-1,2,4-triazole-3-carbonitrile (**1**, 1.630 g, 14.9 mmol, 1 equiv) was slowly dripped with 20.0 mL H_2O sodium nitrite (1.255 g, 17.9 mmol, 1.2 equiv) solution and kept at $0\text{ }^\circ\text{C}$ for 20 min. Then, 36.0 mL mixed aqueous solution of malononitrile (1.184 g, 17.9 mmol, 1.2 equiv, 50% concentration) and sodium acetate (6.131 g, 74.7 mmol) was added to maintain the low temperature reaction, and slowly recovered to room temperature for 2 h. The yellow solid powder is then filtered (2.504 g, 91.07%). $T_{\text{onset}}=229.4\text{ }^\circ\text{C}$. ^1H NMR (400 MHz, DMSO-d_6): $\delta_{\text{H}} = 10.28$ (s, 2H, NH_2) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): $\delta_{\text{C}} = 155.4$ (s, 1C), 144.6 (s, 1C), 141.9 (s, 1C), 114.6 (s, 1C), 112.4 (s, 1C), 112.3 (s, 1C) ppm. IR: 3572.17 (s), 3323.35 (m), 2243.21 (s), 1689.64 (m), 1606.70 (m), 1556.55 (m), 1431.18 (m), 1381.03 (m), 1344.38 (m), 1290.38 (m), 1215.15 (m) cm^{-1} . HRMS: calc. for $\text{C}_6\text{H}_2\text{N}_8$ [$\text{M} - \text{H}$] $^-$: 185.0324, found: 185.0307.

(3Z,7Z)-4-Amino- N^3, N^7 -dihydroxy-[1,2,4]triazolo[5,1-c][1,2,4]triazine-3,7-bis(carboximidamide) (3): adding hydroxylamine aqueous solution (1.4 mL, 20.8 mmol, 2.2 equiv, 50% concentration) at room temperature to the ethanol solution (90.0 mL) of **2** (1.757 g, 9.4 mmol, 1 equiv), the clear yellow solution immediately become turbid yellow solution. After 2 h of stirring at room temperature, the yellow solid **3** was obtained by vacuum remove of drying ethanol (2.165 g, 91.32%). $T_{\text{onset}}=304.9\text{ }^\circ\text{C}$. ^1H NMR (400 MHz, DMSO-d_6): $\delta_{\text{H}} = 10.17$ (s, 2H, NH_2), 9.70 (s, 1H, OH), 9.35 (s, 1H, OH), 6.36 (s, 2H, NH_2), 5.89 (s, 2H, NH_2) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): $\delta_{\text{C}} = 160.6$ (s, 1C), 155.9 (s, 1C), 151.3 (s, 1C), 144.9 (s, 1C), 140.4 (s, 1C), 123.8 (s, 1C) ppm. IR: 3450.68 (m), 3421.75 (m), 1666.99 (s), 1629.38 (m), 1599.94 (m), 1496.29

(m), 1403.71 (s), 1360.18 (m), 1282.67 (m), 1191.05 (m), 1161.64 (m) cm^{-1} . HRMS: calc. for $\text{C}_6\text{H}_8\text{N}_{10}\text{O}_2$ [$\text{M} + \text{H}$] $^{+}$: 253.0904, found: 253.0907.

(3Z,7Z)-4-amino- N^3, N^7 -dihydroxy-[1,2,4]triazolo[5,1-c][1,2,4]triazine-3,7-bis(carbimido-yl)dichloride (4): The aqueous solution (11.0 mL) of sodium nitrite (0.698 g, 9.9 mmol, 2.4 equiv) was slowly dropped into hydrochloric acid solution (11.0 mL) of **3** (1.048 g, 4.2 mmol, 1 equiv). After stirring at 0 °C for 2 h, the solution was filtered to obtain a yellow solid (**4**, 0.957 g, 76.01%). $T_{\text{(onset)}}$ = 237.8 °C. ^1H NMR (400 MHz, DMSO-d_6): δ_{H} = 13.24 (s, 1H, OH), 12.77 (s, 1H, OH), 9.93 (s, 1H, NH), 8.64 (s, 1H, NH) ppm. ^{13}C NMR (400 MHz, DMSO-d_6): δ_{C} = 160.2 (s, 1C), 155.6 (s, 1C), 140.6 (s, 1C), 136.0 (s, 1C), 128.8 (s, 1C), 125.6 (s, 1C) ppm. IR: 3628.10 (s), 1653.00 (s), 1566.20 (s), 1402.25 (s), 1307.74 (s), 1201.65 (s), 1087.85 (m), 1028.06 (s) cm^{-1} . HRMS: calc. for $\text{C}_6\text{H}_4\text{Cl}_2\text{N}_8\text{O}_2$ [$\text{M} + \text{H}$] $^{+}$: 290.9907, found: 290.9908.

Potassium (4-amino-[1,2,4]triazolo[5,1-c][1,2,4]triazine-3,7-diyl)bis(dinitromethanide) (5): **4** (0.728 g, 2.5 mmol, 1 equiv) was added to the mixture of fuming nitric acid (7.0 mL) and TFAA (5.5 mL) and reacted at 0 °C for 8 h, then the reaction mixture was poured into ice water bath for quenching and extracted with CHCl_3 . The chloro-dinitro intermediate was obtained. Subsequently dissolved with methanol (4.0 mL), the reaction was carried out by adding KI solution (0.400 g, 2.4 mmol, 2.2 equiv) of methanol (4.0 mL) to produce compound **5** (0.422 g, 40.16%). $T_{\text{(onset)}}$ = 128.8 °C. ^1H NMR (400 MHz, DMSO-d_6): none. ^{13}C NMR (400 MHz, DMSO-d_6): δ_{C} = 159.0 (s, 1C), 151.6 (s, 1C), 148.5 (s, 1C), 136.8 (s, 1C), 127.2 (s, 1C), 126.6 (s, 1C) ppm. IR: 3414.00 (s), 1616.35 (s), 1494.83 (s), 1400.32 (m), 1246.02 (s), 1136.00 (s) cm^{-1} . HRMS: calc. for $\text{C}_6\text{H}_2\text{N}_{10}\text{O}_8\text{K}_2$ [$1/2(\text{M} - 2\text{H})$] $^{-}$: 171.0034, found: 171.0030.

General method for preparing compounds 6–8:

The neutral compound was obtained by acidification of potassium salt (**5**), and then reacted with aqueous ammonia, 50 % hydroxylamine aqueous solution and 80 % hydrazine hydrate to prepare the corresponding ammonium salt, hydroxylamine salt and hydrazine salt, respectively.

Ammonium (4-amino-[1,2,4]triazolo[5,1-c][1,2,4]triazine-3,7-diyl)bis(dinitromethanide) (6): $T_{\text{d(onset)}}$ = 152.3 °C. ^1H NMR (400 MHz, DMSO-d_6): δ_{H} = 7.16 (s, 8H, NH_4^{+}). ^{13}C NMR (400 MHz, DMSO-d_6): δ_{C} = 157.4 (s, 1C), 155.8 (s, 1C), 147.2 (s, 1C), 133.6 (s, 1C), 128.8 (s, 1C), 116.4 (s, 1C) ppm. IR: 3199.91 (m), 1653.00 (m), 1521.84 (s). HRMS: calc. for $\text{C}_6\text{H}_{10}\text{N}_{12}\text{O}_8$ [$1/2(\text{M} - 2\text{e})$] $^{-}$: 172.0112, found: 172.0120.

Hydroxylammonium (4-amino-[1,2,4]triazolo[5,1-c][1,2,4]triazine-3,7-diyl)bis(dinitromethanide) (7): $T_{\text{d(onset)}}$ = 145.2 °C. ^1H NMR (400 MHz, DMSO-d_6): δ_{H} = 8.130 (s, 6H, NH_2OH^{+}). ^{13}C NMR (400 MHz, DMSO-d_6): δ_{C} = 158.495 (s, 1C), 155.415 (s, 1C), 148.848 (s, 1C), 136.367 (s, 1C), 128.850 (s, 1C), 127.343 (s, 1C) ppm. IR: 3178.69 (m), 1521.84 (m), 1236.37 (s), 1128.36 (m). HRMS: calc. for $\text{C}_6\text{H}_{10}\text{N}_{12}\text{O}_{10}$ [$1/2(\text{M} - 2\text{e})$] $^{-}$:

172.0112, found: 172.0108.

Hydrazinium (4-amino-[1,2,4]triazolo[5,1-c][1,2,4]triazine-3,7-diyl)bis(dinitromethanide) (8): $T_{d(onset)}=127.4$ °C. ^1H NMR (400 MHz, DMSO- d_6): $\delta_{\text{H}} = 6.34$ (s, 10H, NH_2NH_3^+). ^{13}C NMR (400 MHz, DMSO- d_6): $\delta_{\text{C}} = 158.6$ (s, 1C), 154.3 (s, 1C), 148.8 (s, 1C), 136.5 (s, 1C), 128.5 (s, 1C), 127.2 (s, 1C) ppm. IR: 3307.92 (m), 1597.06 (m), 1517.98 (m), 1340.53 (m), 1267.23(m). HRMS: calc. for $\text{C}_6\text{H}_{10}\text{N}_{12}\text{O}_{10}$ [$1/2(\text{M} - 2\text{e})$] $^-$: 172.0112, found: 172.0107.

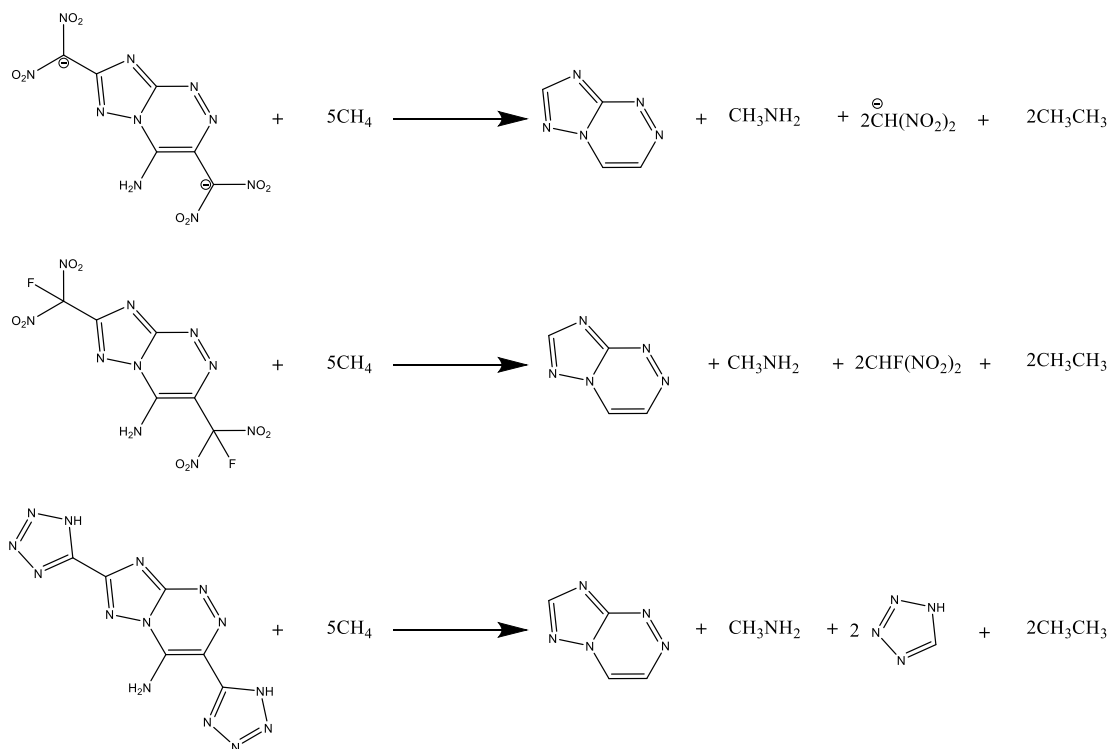
3,7-Bis(fluorodinitromethyl)-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amine (9): Selectfluor[®] (0.087 g, 0.2 mmol, 2 equiv) was added to the acetonitrile solvent containing potassium salt 5 (0.047 g, 0.1 mmol, 1 equiv). After stirring at room temperature for 3 h, acetonitrile was dried in vacuum, and then ethyl acetate and water were added for extraction. The organic phase was combined and the solvent was dried to obtain yellow solid (0.028 g, 66.67%). $T_{d(onset)}=139.1$ °C. ^1H NMR (400 MHz, DMSO- d_6): none. ^{13}C NMR (400 MHz, DMSO- d_6): $\delta_{\text{C}} = 156.0$ (s, 1C), 152.9 (s, 1C), 138.5 (s, 1C), 130.1 (s, 1C), 122.6 (s, 1C), 122.4 (s, 1C) ppm. ^{19}F NMR (400 MHz, DMSO- d_6): $\delta_{\text{F}} = -96.798$ (s, 1F), -97.051 (s, 1F). IR: 3500.80 (m), 1712.79 (m), 1616.35 (m), 1494.83 (s), 1238.30(m), 1130.29(m), 970.19(m). HRMS: calc. for $\text{C}_6\text{H}_2\text{F}_2\text{N}_{10}\text{O}_8$ [(M - e)] $^-$: 380.0031, found: 379.9989.

3,7-Di(1H-tetrazol-5-yl)-[1,2,4]triazolo[5,1-c][1,2,4]triazin-4-amine (10): Compound 2 (0.093 g, 0.5 mmol) was dissolved in 5 mL H_2O , then added NaN_3 (0.072 g, 1.1 mmol) and ZnCl_2 (0.161 g, 1.2 mmol), heated to 100 °C, refluxed for 0.5 h. Then recover to room temperature, add HCl to adjust pH to 1-2, filter to get milky white solid (0.124 g, 91.15%). $T_{d(onset)}=283.7$ °C. ^1H NMR (400 MHz, DMSO- d_6): $\delta_{\text{H}} = 10.42$ (s, 1H, NH), 10.42 (s, 1H, NH), 9.00 (s, 2H, NH_2) ppm. ^{13}C NMR (400 MHz, DMSO- d_6): $\delta_{\text{C}} = 156.4$ (s, 1C), 155.6 (s, 1C), 153.3 (s, 1C), 151.5 (s, 1C), 141.0 (s, 1C), 121.5 (s, 1C) ppm. IR: 3396.64 (m), 3273.20 (m), 1662.64 (s), 1589.34 (s), 1489.05 (m), 1417.68 (m), 1381.03 (s), 1259.52 (s) cm^{-1} . HRMS: calc. for $\text{C}_6\text{H}_4\text{N}_{14}$ [M + H] $^+$: 273.0816, found: 273.0820.

2. Gaussian Calculations

The density and heats of formation (HOF) of 5–10 were calculated by the Gaussian09 suite of programs.^[S2] First, the geometric optimization of the structures and frequency analyses were accomplished by using the B3LYP with the 6-311+G** basis set and optimized structures were used to calculate the density and heats of formation.

The HOF was determined by using an isodesmic reaction (Scheme S1). The HOF of other compounds in Scheme S1 were available in the NIST WebBook^[S3] and literature references^[S4].



Scheme S1 Isodesmic reactions for anions of **5-8**, and compound **9,10**.

For the ionic salt **5-8**, the HOF can be simplified by the formula given in Eq (1) based on a Born-Haber energy cycle (Scheme S2),

$$\Delta H (\text{salts}, 298K) = \Delta H (\text{cation}, 298K) + \Delta H (\text{anion}, 298K) - \Delta H_L (1)$$

where ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al [Eq (2)]^[S5].

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

In this equation, n_M and n_X depend on the nature of the ions M_{p^+} and X_{q^-} , respectively, and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions. The equation for lattice potential energy U_{pot} [Eq (3)] has the form:

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

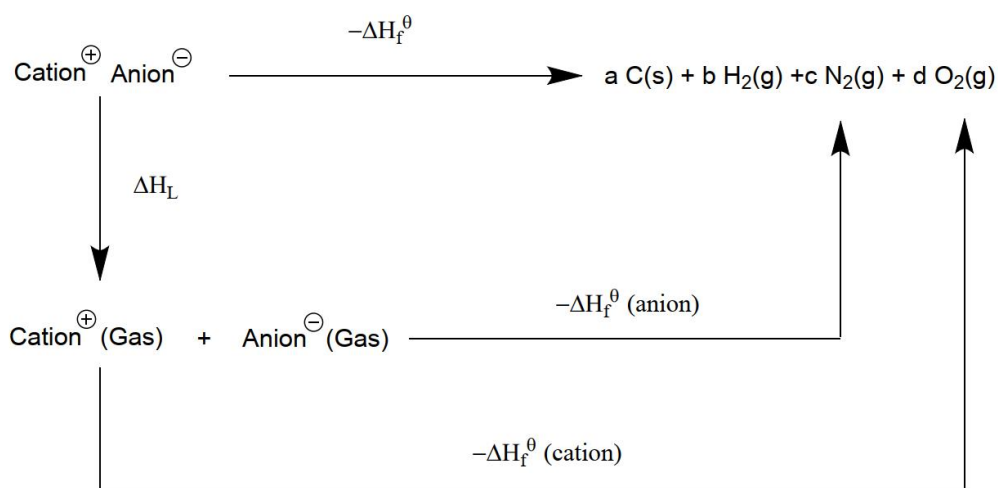
Where values for the coefficients γ (kJ mol⁻¹ cm) and δ (kJ mol⁻¹) are taken from the literature^[S6].

ρ_m [g cm⁻³] is the density obtained by the formula given in [Eq (4)]. M_m is the molecular weight, and V_m is the molar volume of the compound.

$$\rho_m = M_m / V_m (4)$$

For ionic salts with hydrogen atoms, Eq (5) is utilized to get the corrected ionic volume. We can get a correction factor by the density of crystal to get the more accurate volume of anion.

$$V_m(\text{ionic}) = pV_{M^+} + qV_{X^-} - [0.6763 + 0.9418 \times (\text{no. of hydrogen atoms in the ionic})] (5)$$



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

Table S1 The molar volume, molecular weight and calculated densities for the title compounds at B3LYP/6-311+G** level.

Compounds	$V_{M+} [\text{cm}^3 \text{mol}^{-1}]$	$V_{X-} [\text{cm}^3 \text{mol}^{-1}]$	$V_m [\text{cm}^3 \text{mol}^{-1}]$	$M [\text{g mol}^{-1}]$	$\rho_m [\text{g mol}^{-1}]$
6	18.272	186.222	231.2281	408.252	1.78
7	28.492	186.222	212.6717	378.222	1.80
8	26.118	186.222	228.3637	410.222	1.77
9	—	—	195.159	380.1408	1.95
10	—	—	163.389	272.196	1.67

Table S2 Total energy and heat of formation for the title compounds at B3LYP/6-311+G** level.

Name	E ₀ ^a [hartree]	ZPE ^b [hartree]	H _{corr} ^c [hartree]	HOF ^d [kJ·mol ⁻¹]
CH ₄	−40.3984876	0.044793	0.048605	−74.6 ^e
CH ₃ CH ₃	−79.6094381	0.074599	0.079027	−84.0 ^e
CH ₃ NH ₂	−95.6318757	0.064027	0.068396	−22.5 ^e
[1,2,4]triazolo[5,1-c][1,2,4]triazine	−427.0474732	0.087270	0.051817	196.8 ^e
CH(NO ₂) ₂ anion	−448.0247376	0.038238	0.045623	−217.0 ^f
5-8 anion	−1376.0393800	0.137856	0.158846	−189.1 ^g
5 cation	—	—	—	501.1 ^g
6 cation	—	—	—	626.4 ^g
7 cation	—	—	—	669.5 ^g
8 cation	—	—	—	770.0 ^g
CHF(NO ₂) ₂	−547.7888670	0.044535	0.051715	−238.1 ^f
9	−1575.5451020	0.145956	0.169067	−176.8 ^g
1H-tetrazole	−257.7488167	0.046864	0.051293	333.2 ^e
10	−995.4927589	0.153559	0.110758	741.8

[a] Total energy calculated by B3LYP/6-31+G**//MP2/6-311++G** method; [b] Zero-point correction; [c] Thermal correction to enthalpy; [d] Heat of formation (1 hartree = 2625.499748 kJ·mol⁻¹). [e]Data are from Ref. [S7]. [f]Data are from Ref. [S8]. [g]Data calculated from G2 calculation.

3. References

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4. Spectroscopy

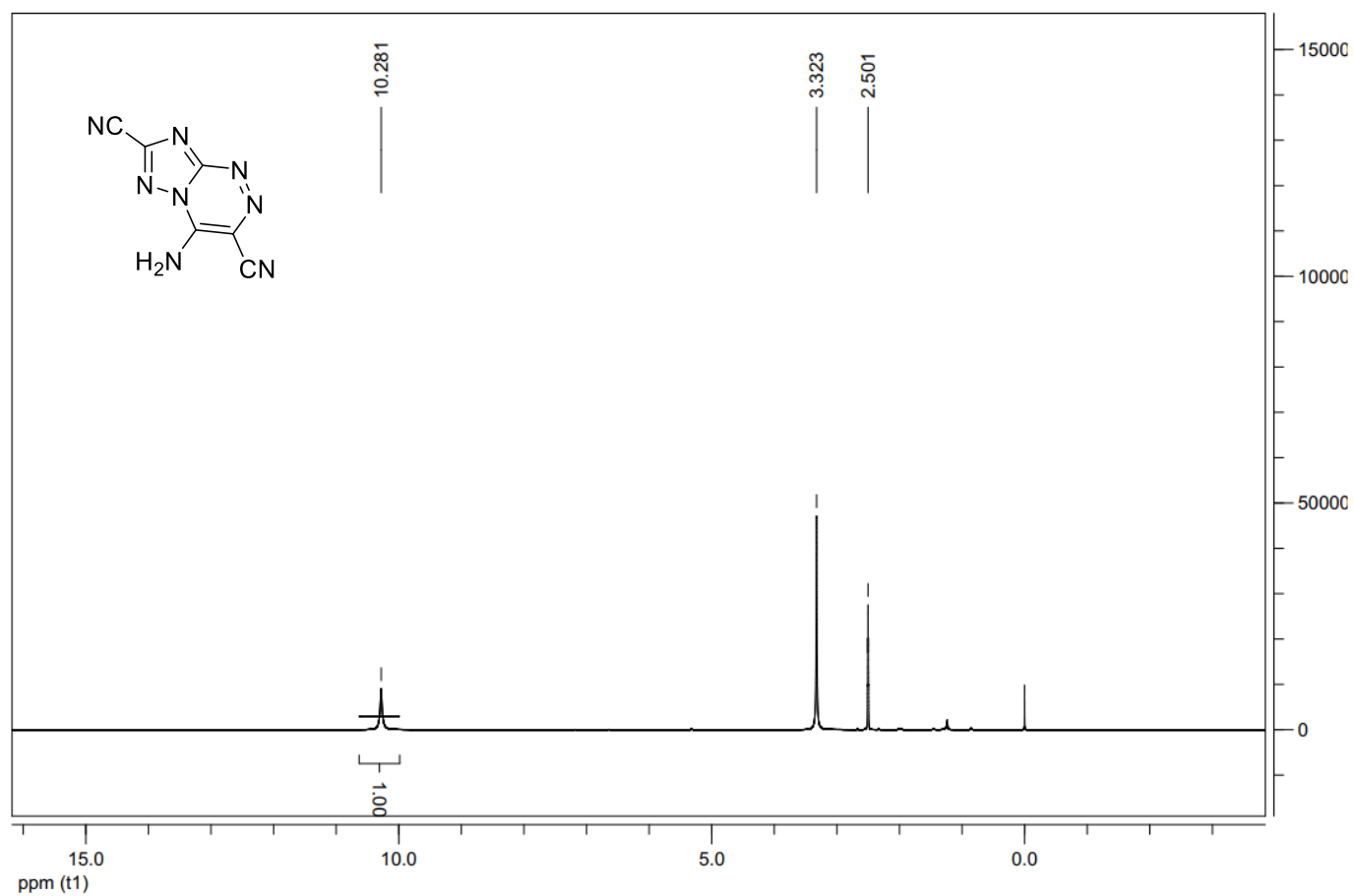


Figure S1 ¹H NMR spectrum of 2.

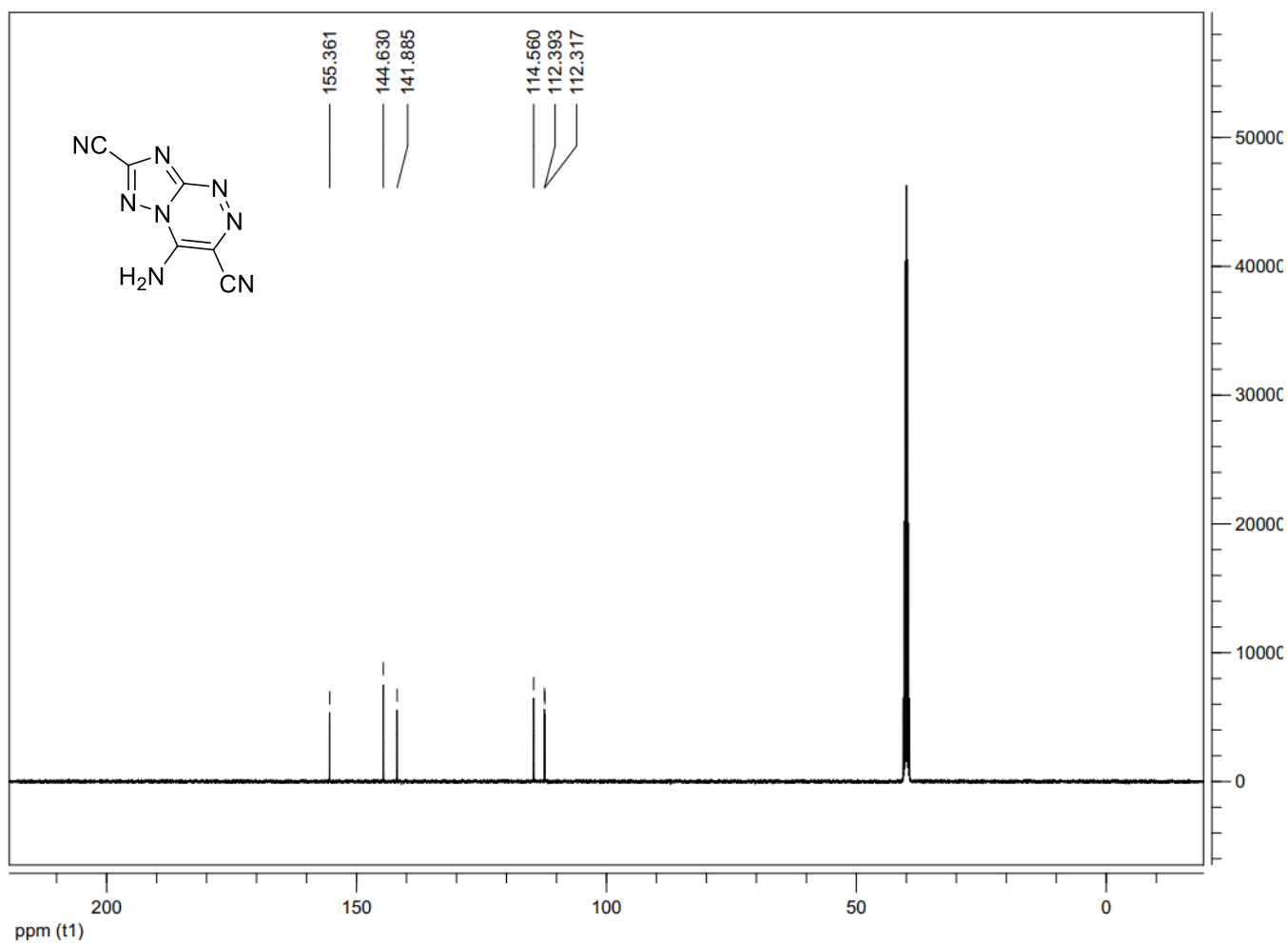


Figure S2 ^{13}C NMR spectrum of 2.

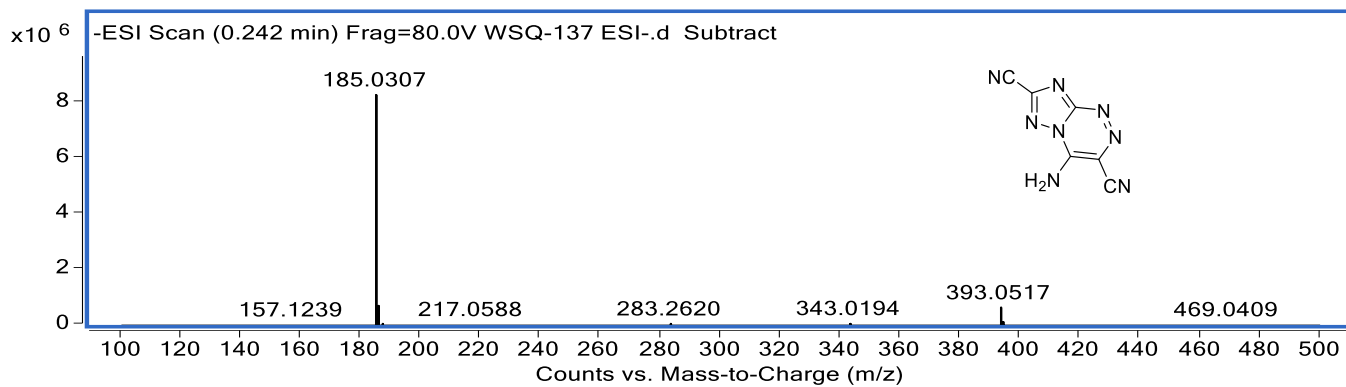


Figure S3 ESI-MS spectrum of 2.

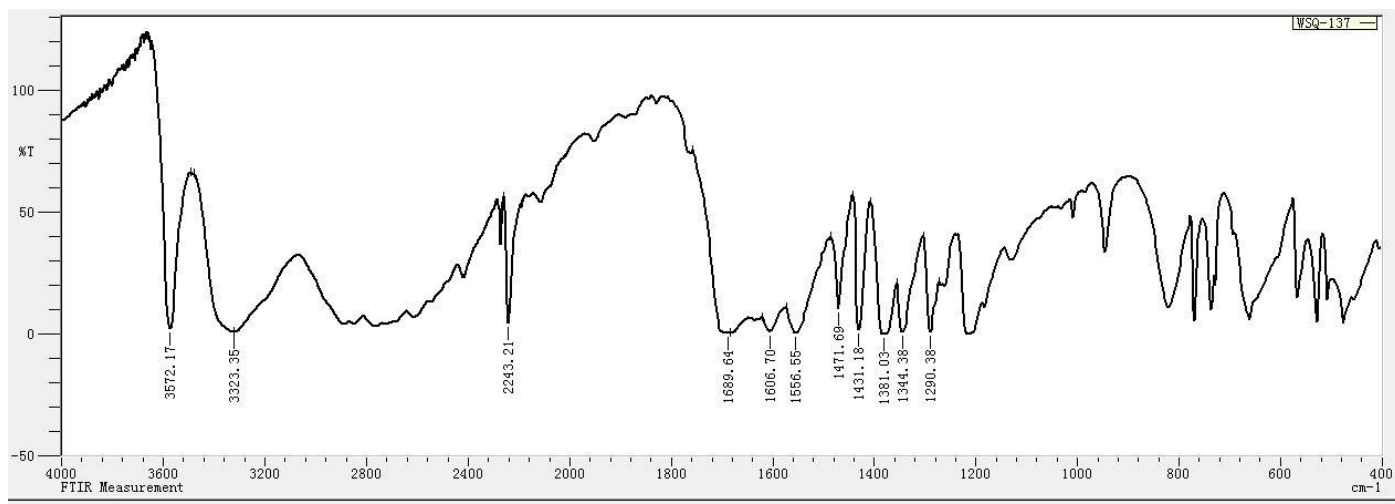


Figure S4 IR spectrum of **2**.

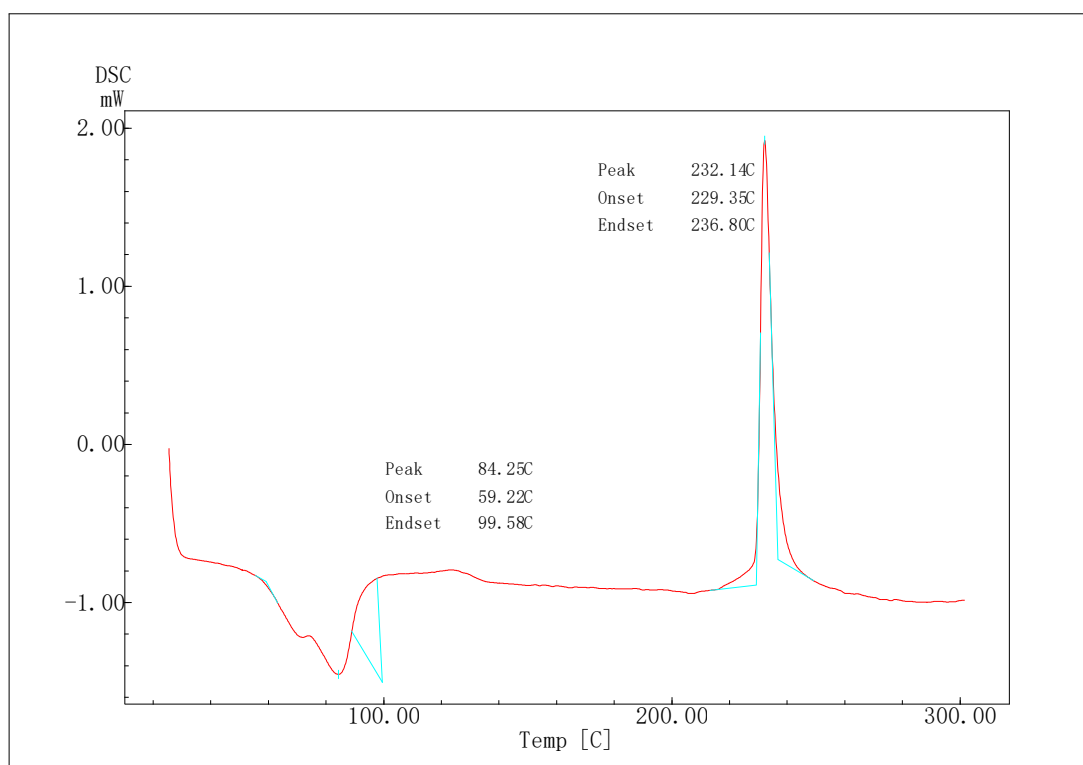


Figure S5 DSC curve of **2** (10 °C min⁻¹).

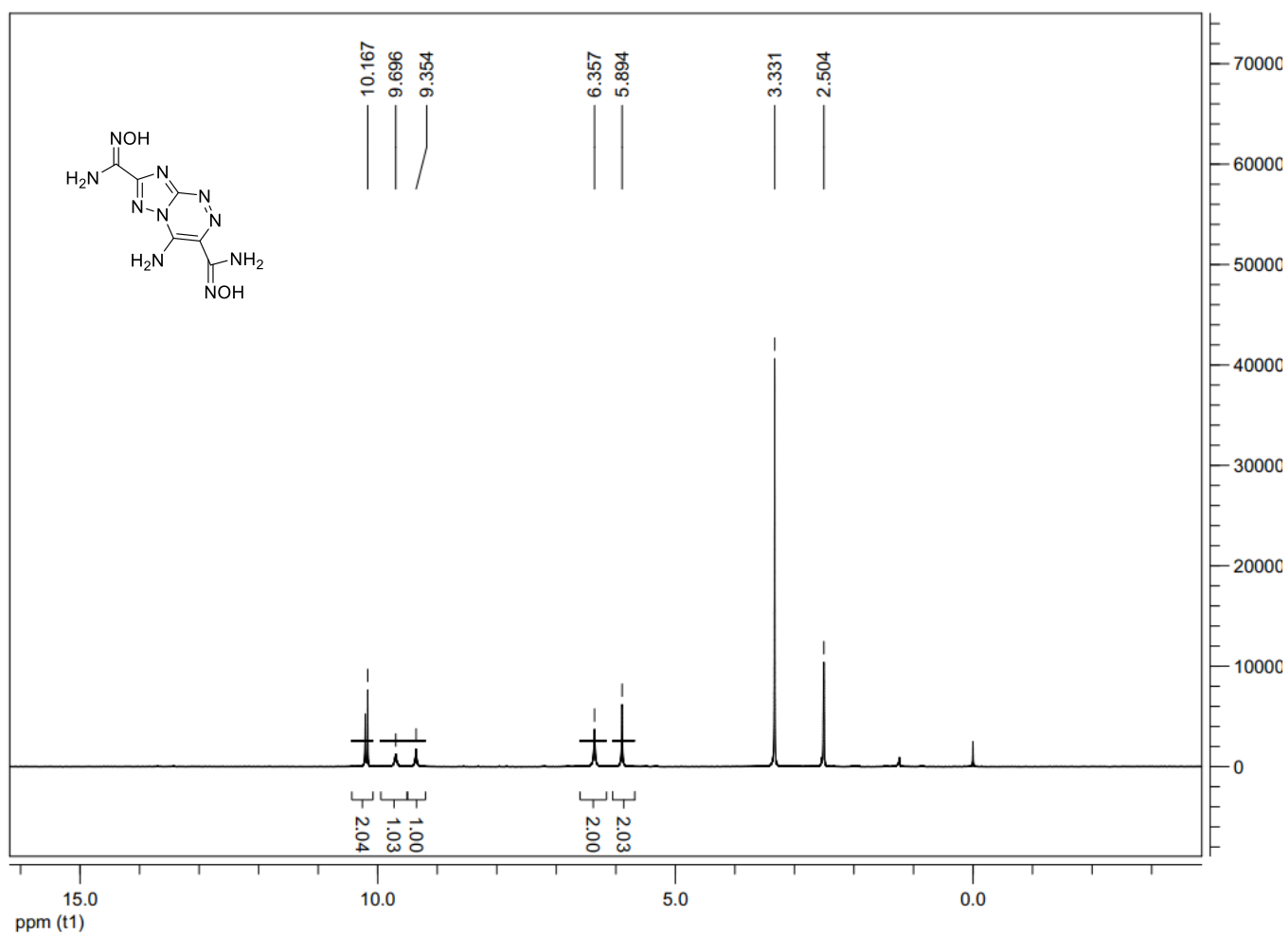


Figure S6 ¹H NMR spectrum of 3.

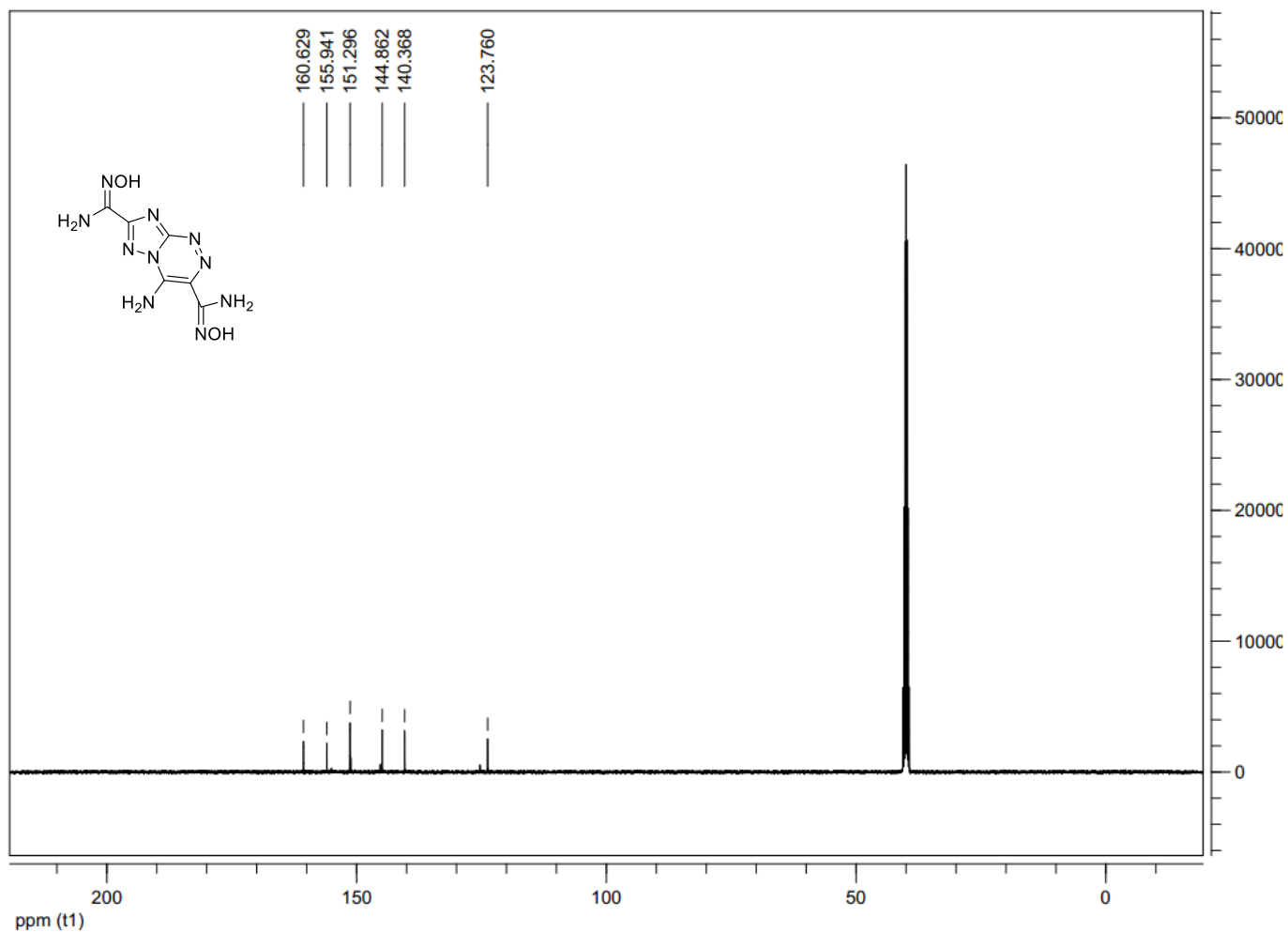


Figure S7 ¹³C NMR spectrum of 3.

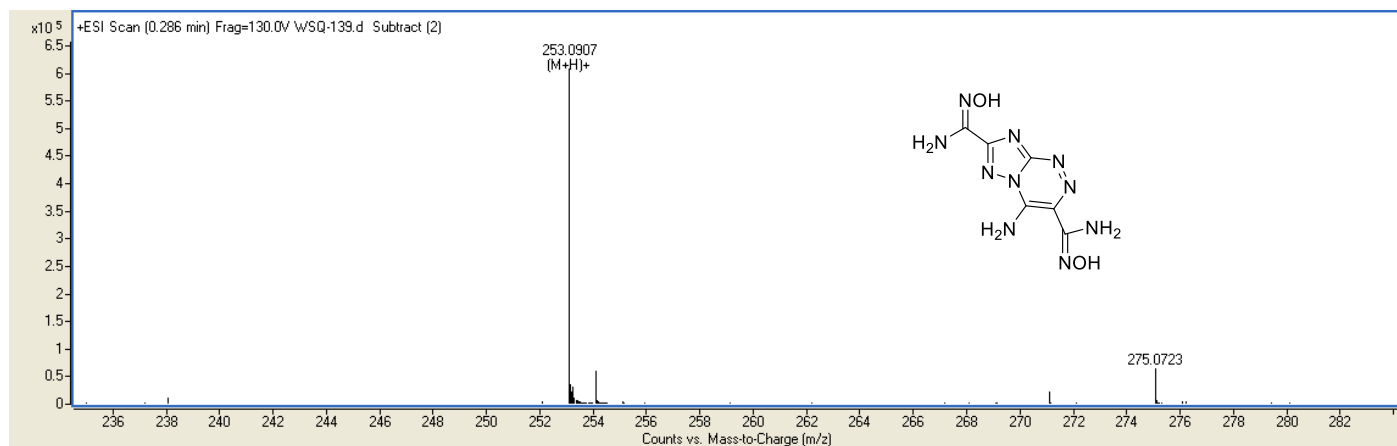


Figure S8 ESI-MS spectrum of 3.

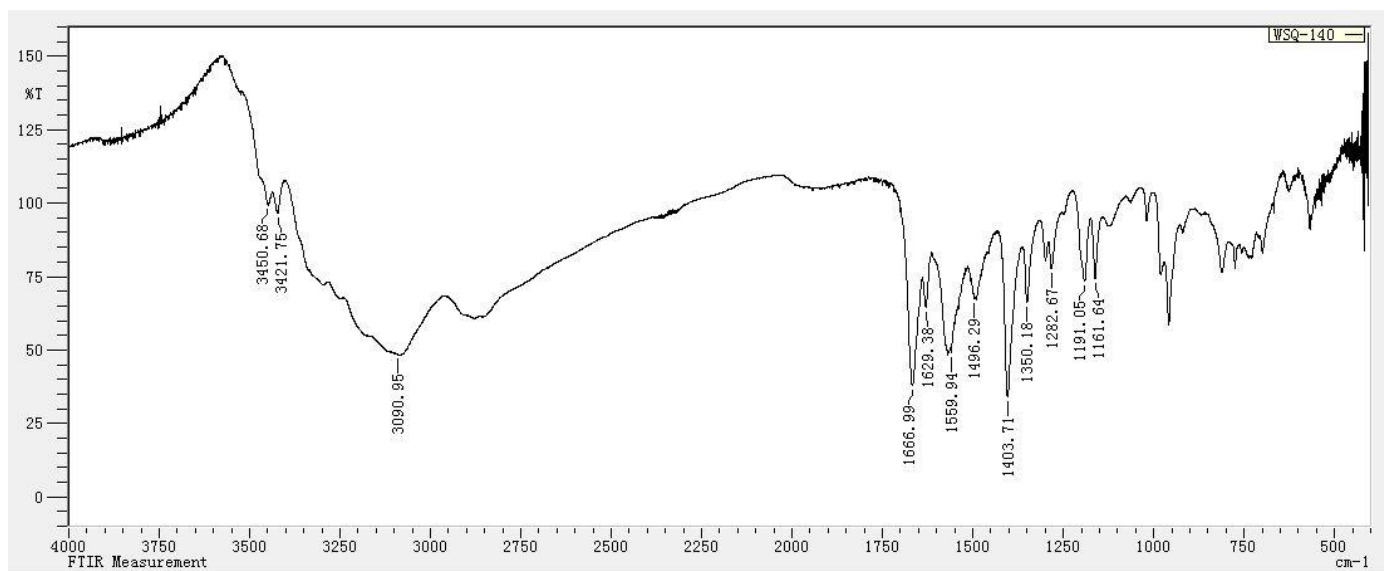


Figure S9 IR spectrum of **3**.

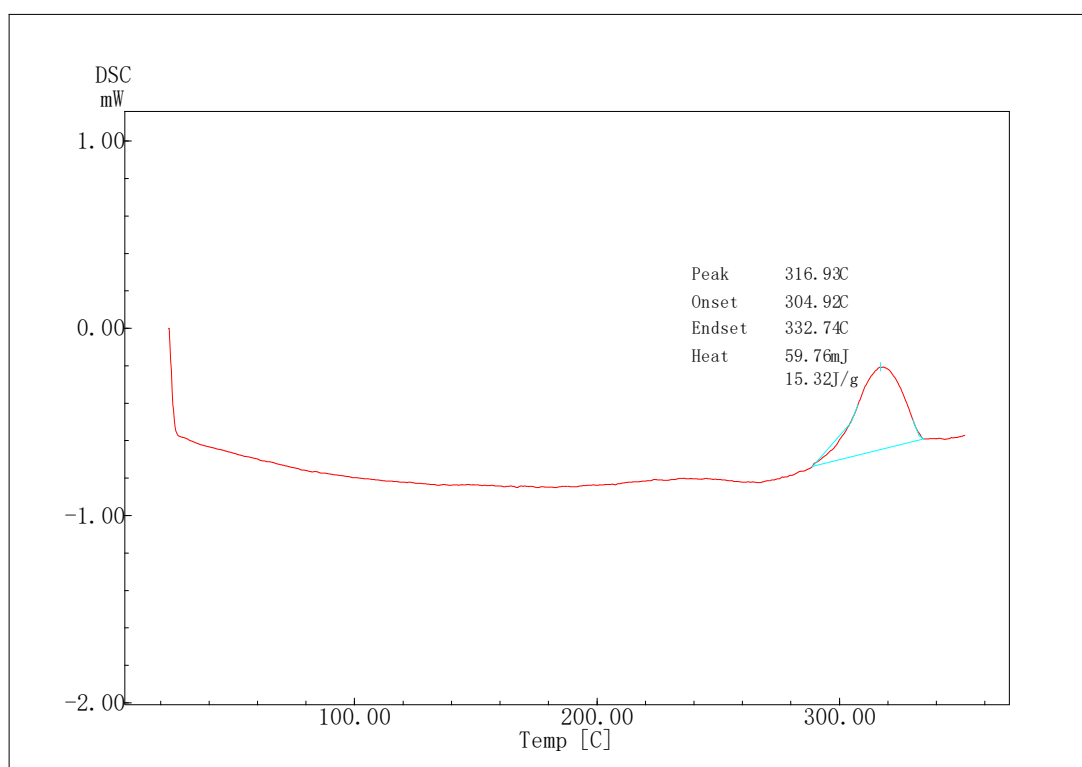


Figure S10 DSC curve of **3** (10 °C min⁻¹).

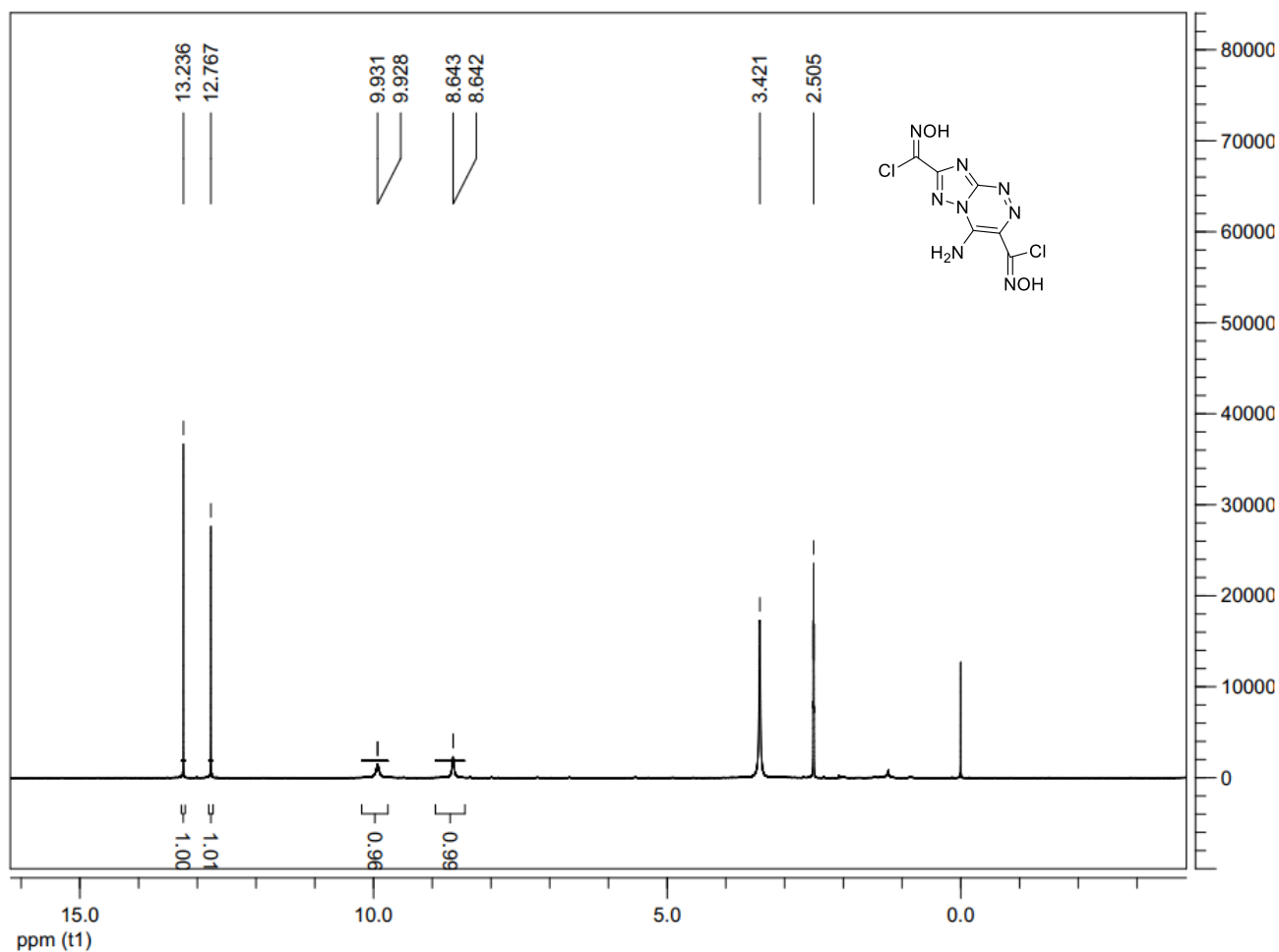


Figure S11 ^1H NMR spectrum of **4**.

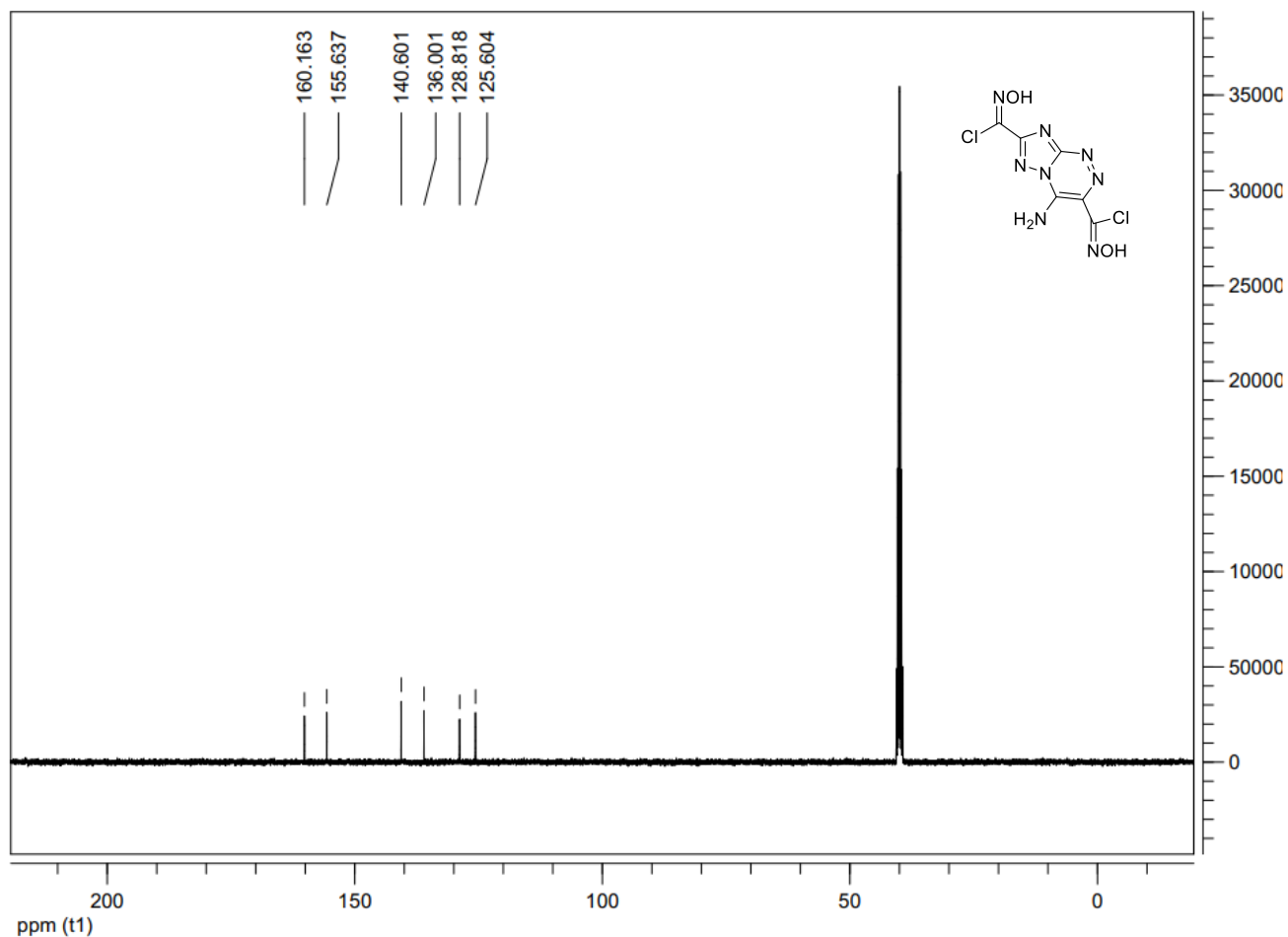


Figure S12 ¹³C NMR spectrum of **4**.

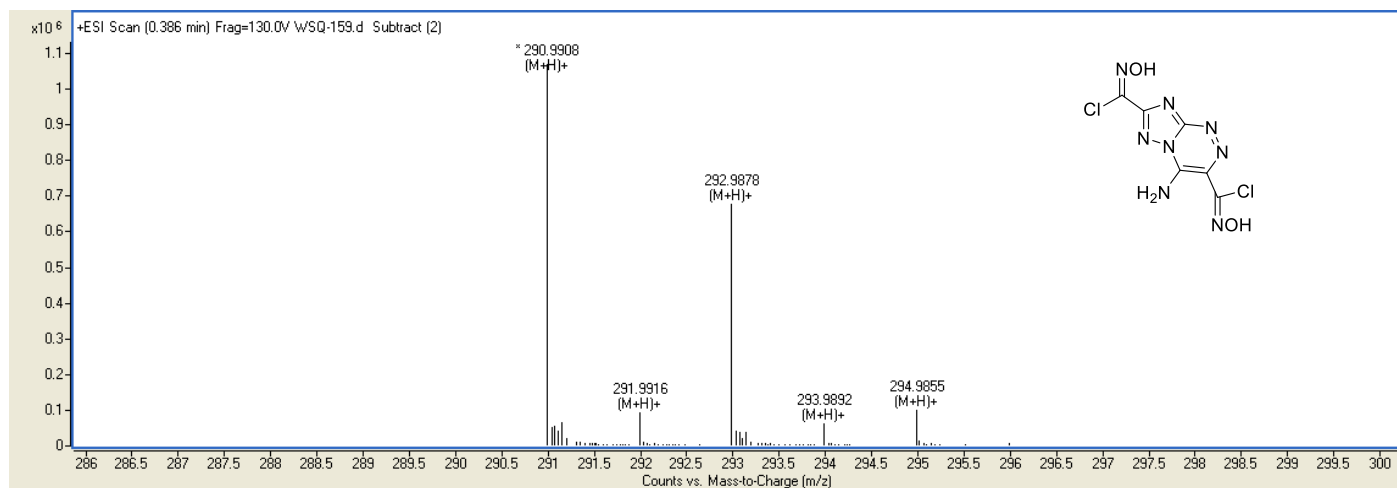


Figure S13 ESI-MS spectrum of **4**.

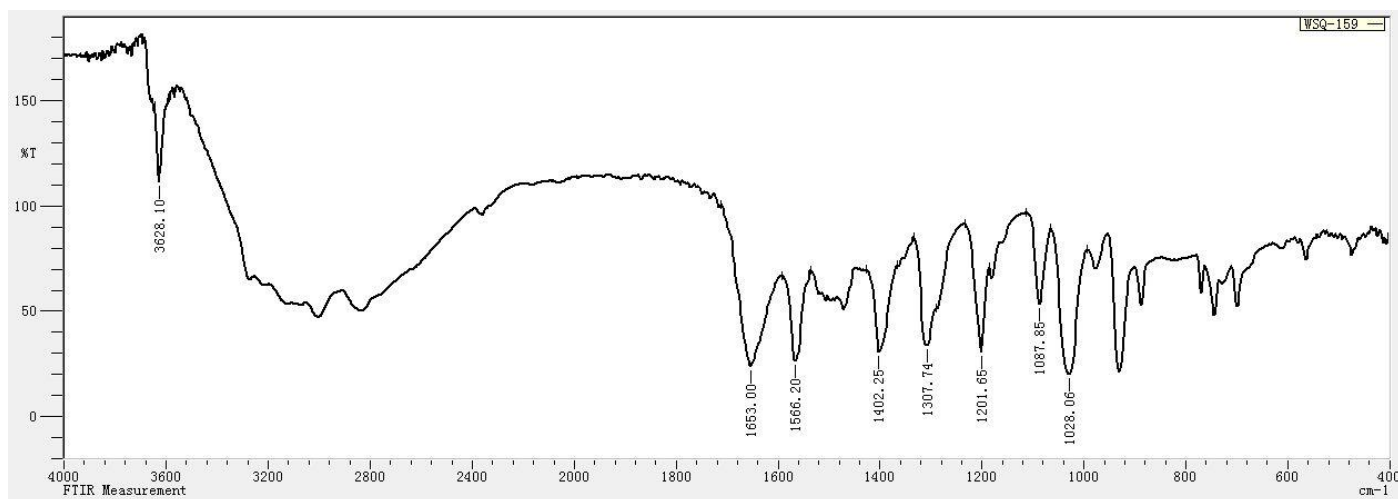


Figure S14 IR spectrum of **4**.

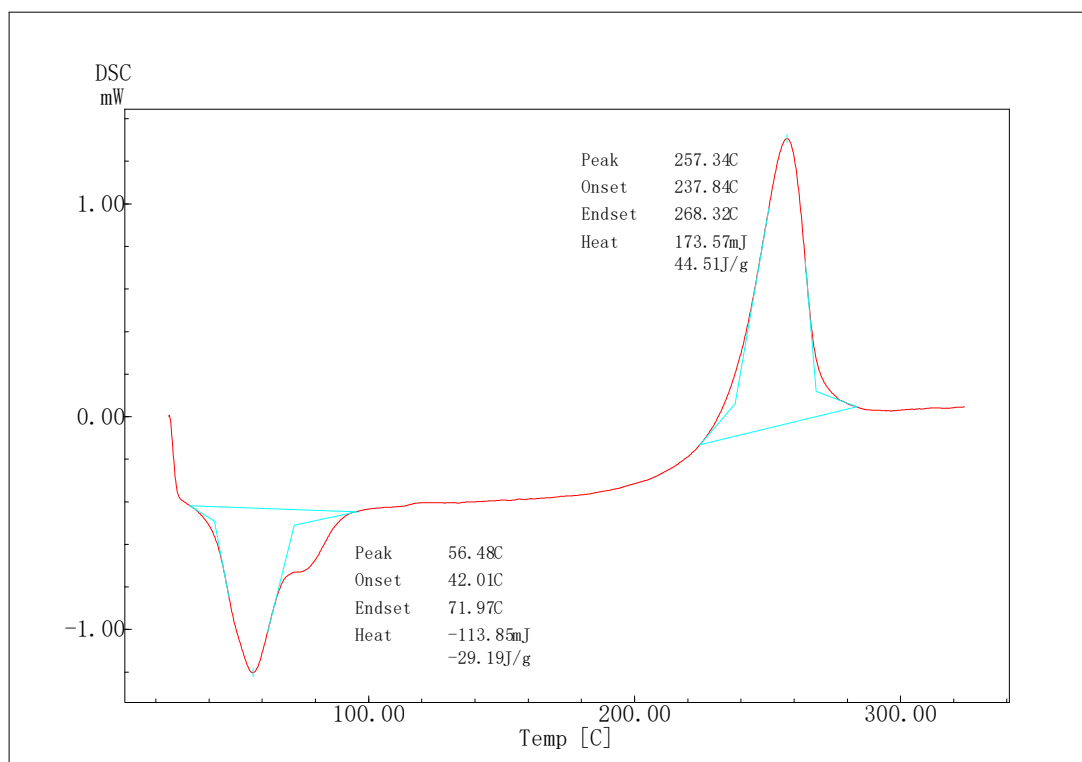


Figure S15 DSC curve of **4** ($10^{\circ}\text{C min}^{-1}$).

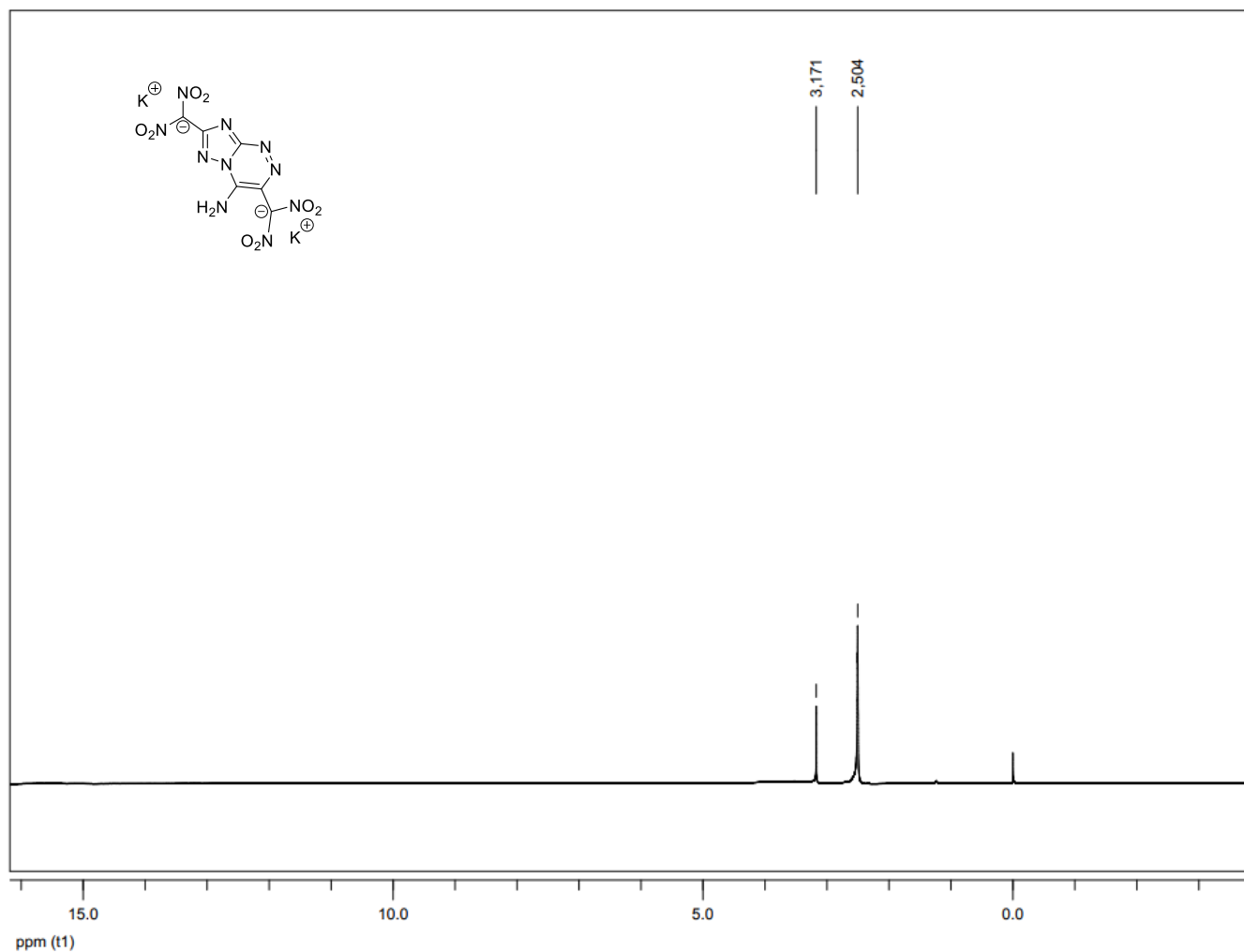


Figure S16 ^1H NMR spectrum of 5.

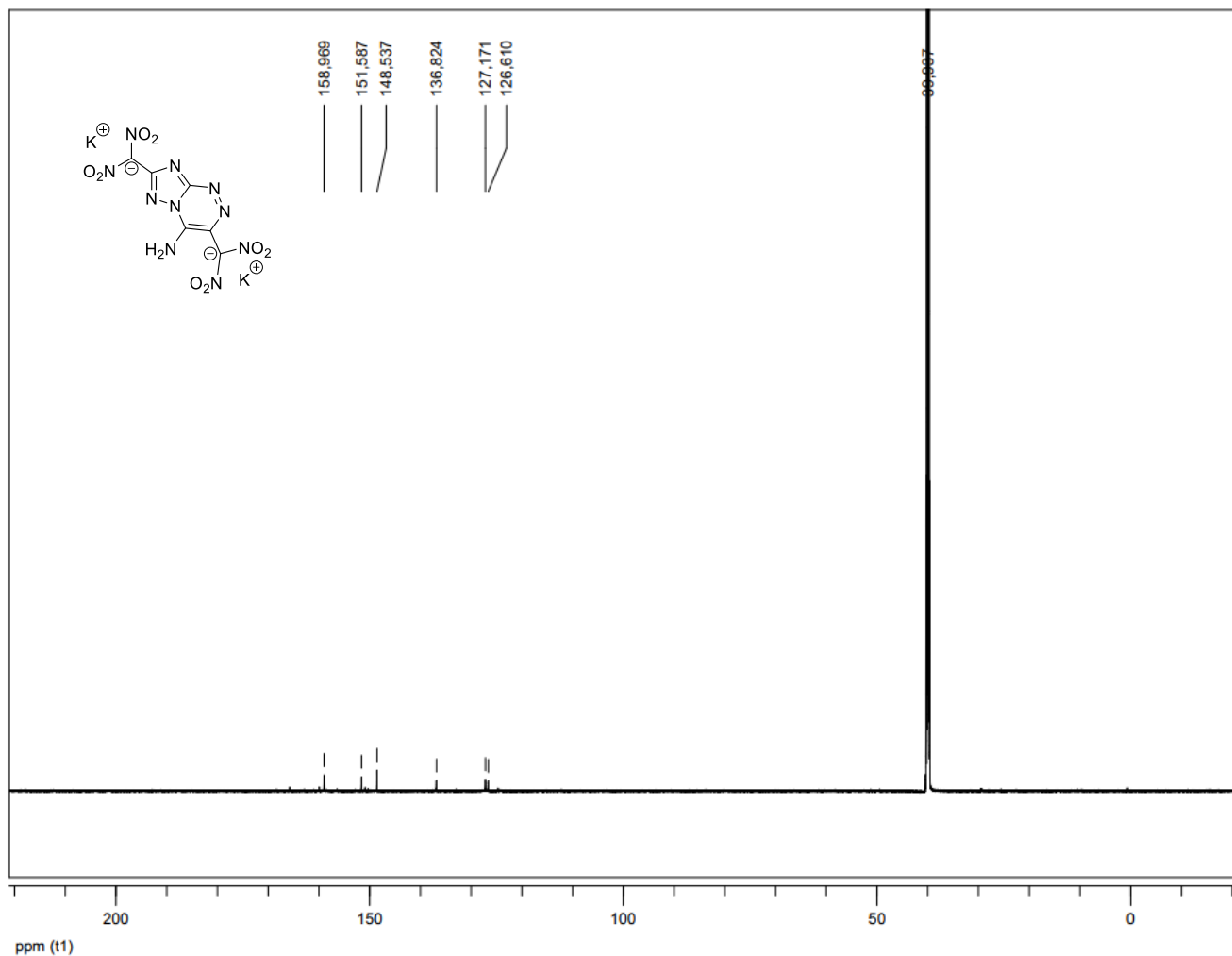


Figure S17 ^{13}C NMR spectrum of 5.

WSQ200 #368 RT: 3.59 AV: 1 NL: 6.82E7
T: FTMS - p ESI Full ms [100.0000-1500.0000]

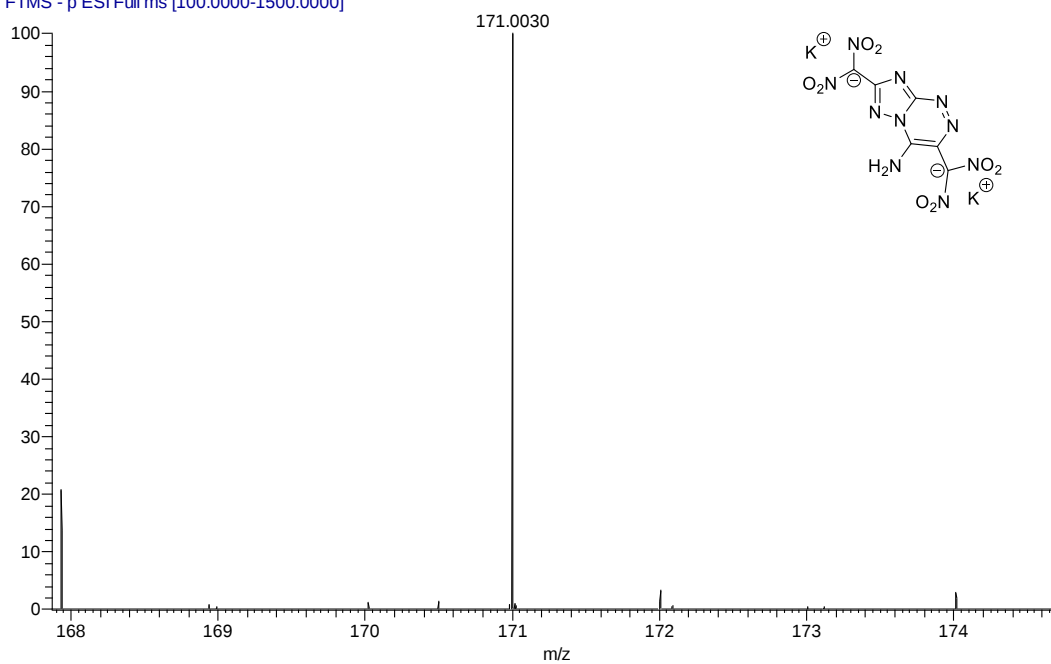


Figure S18 ESI-MS spectrum of 5.

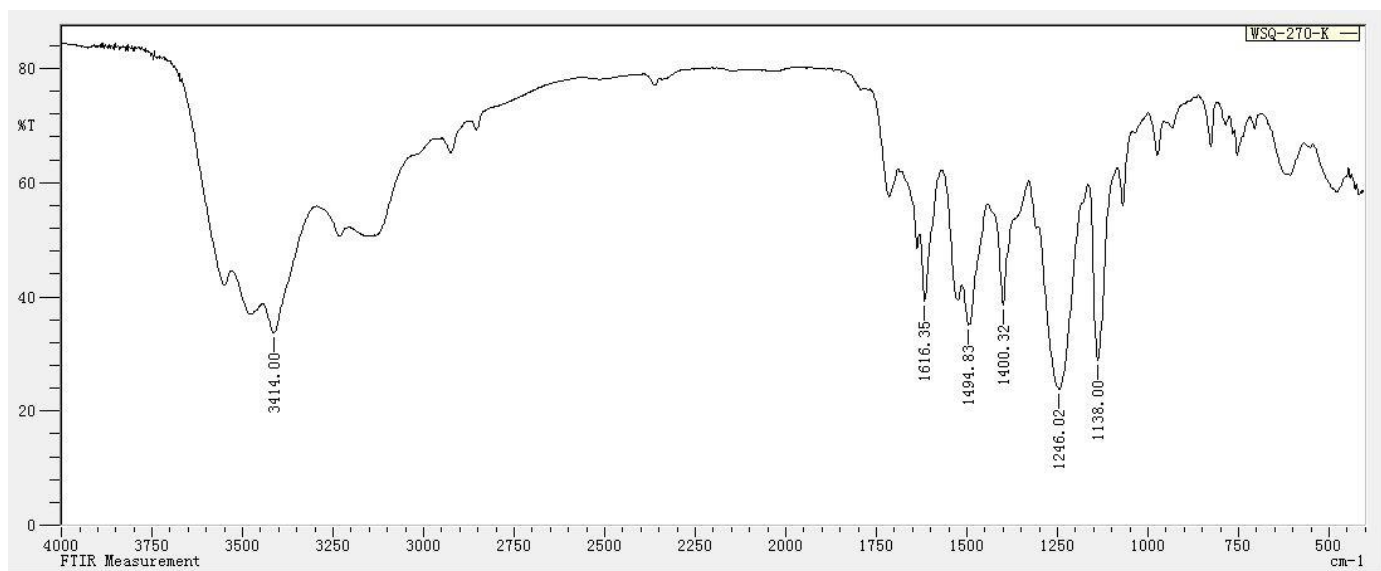


Figure S19 IR spectrum of **5**.

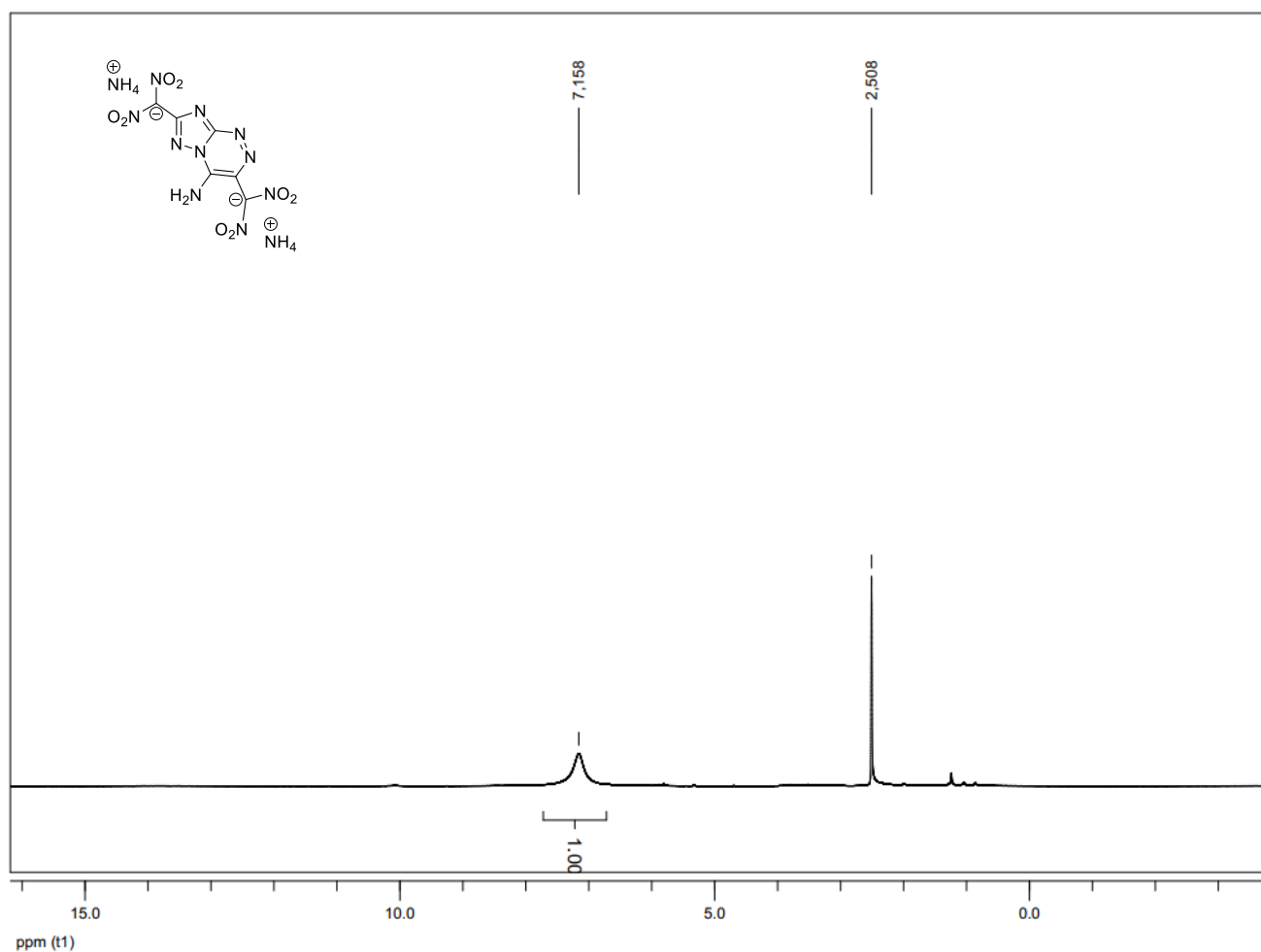


Figure S20 ¹H NMR spectrum of **6**.

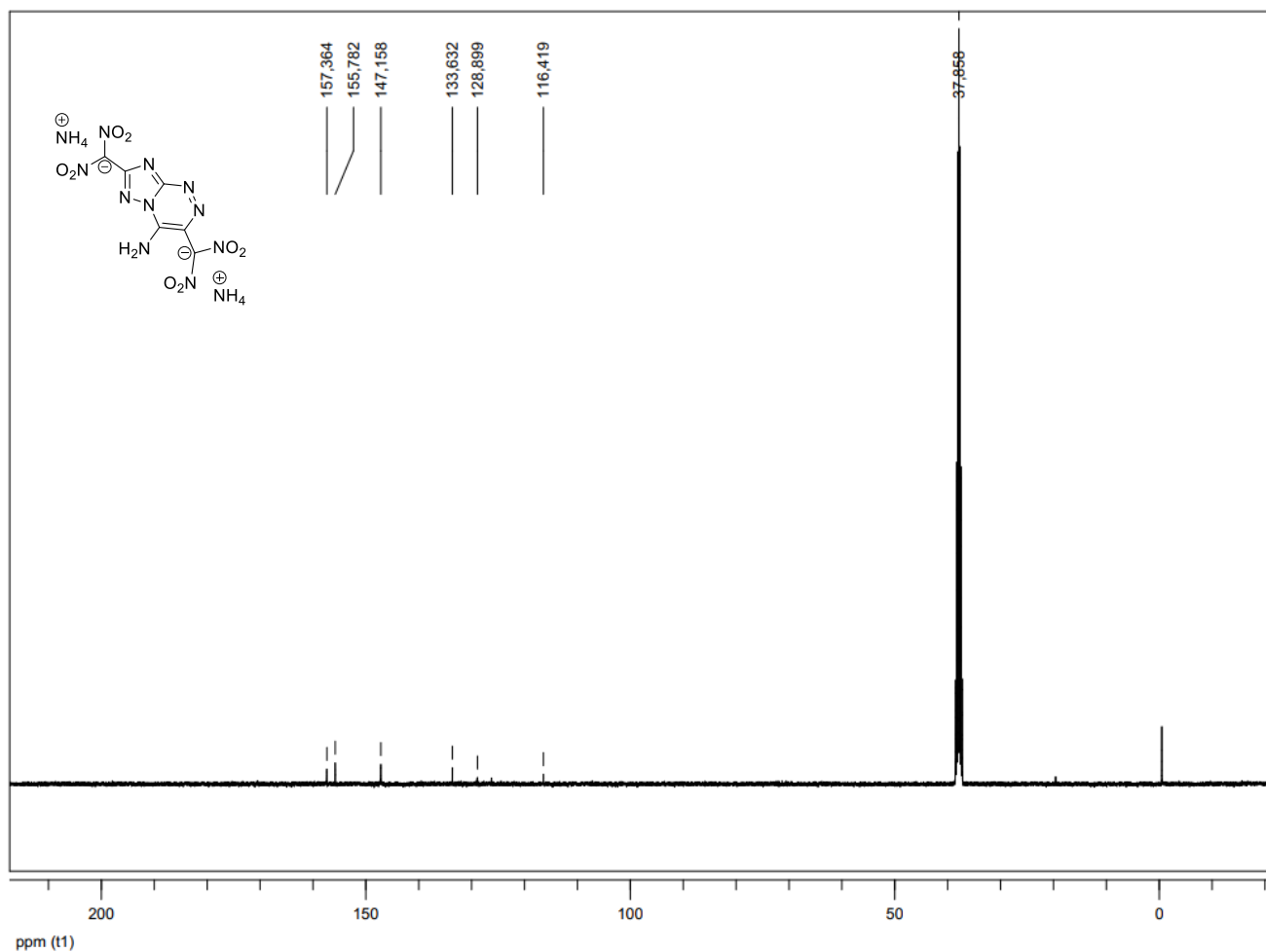


Figure S21 ¹³C NMR spectrum of **6**.

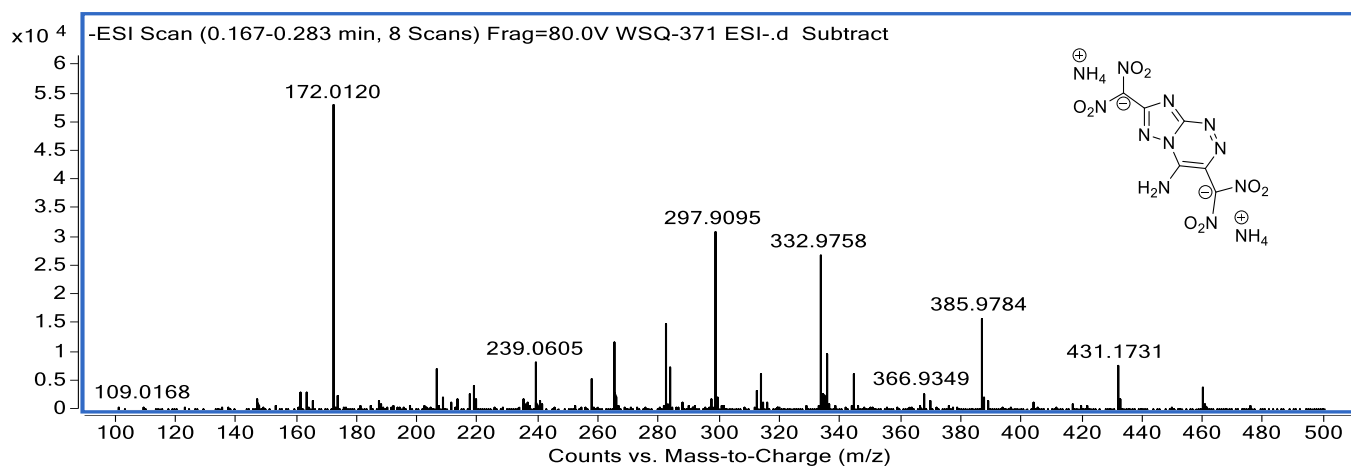


Figure S22 ESI-MS spectrum of **6**.

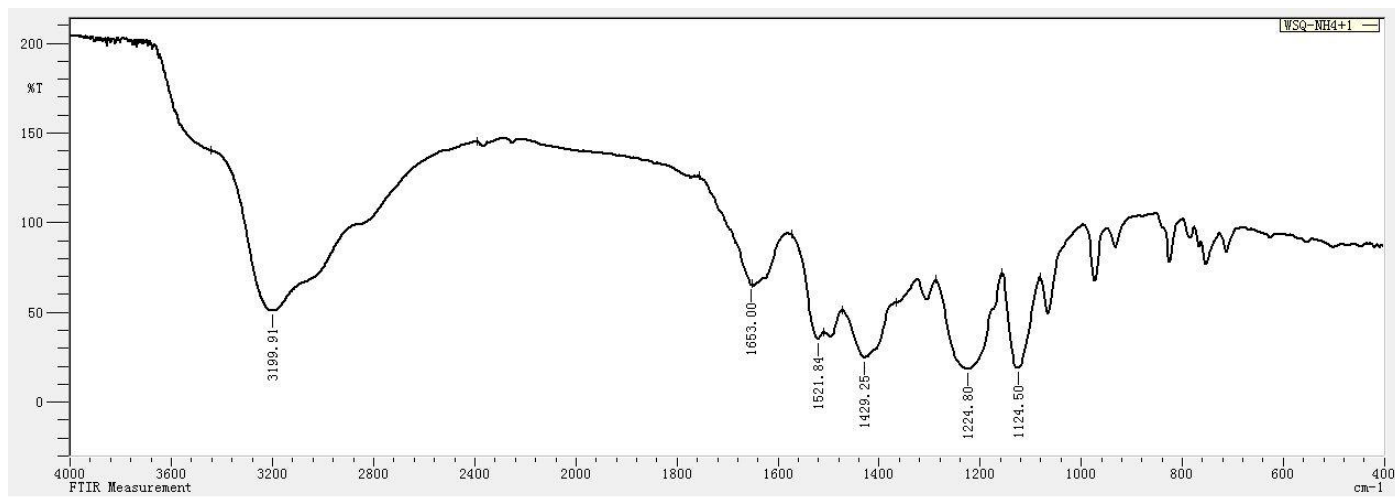


Figure S23 IR spectrum of **6**.

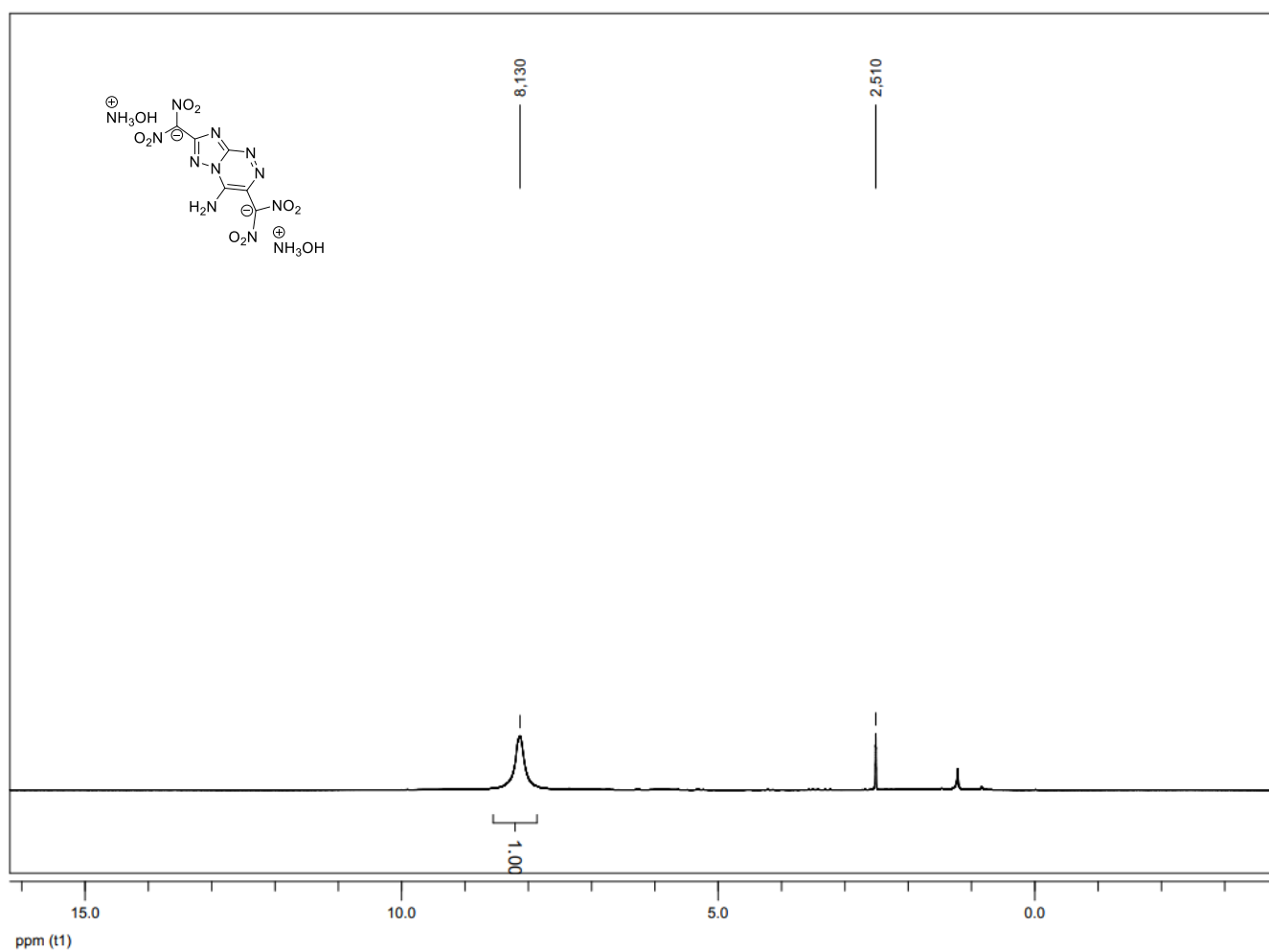


Figure S24 ¹H NMR spectrum of **7**.

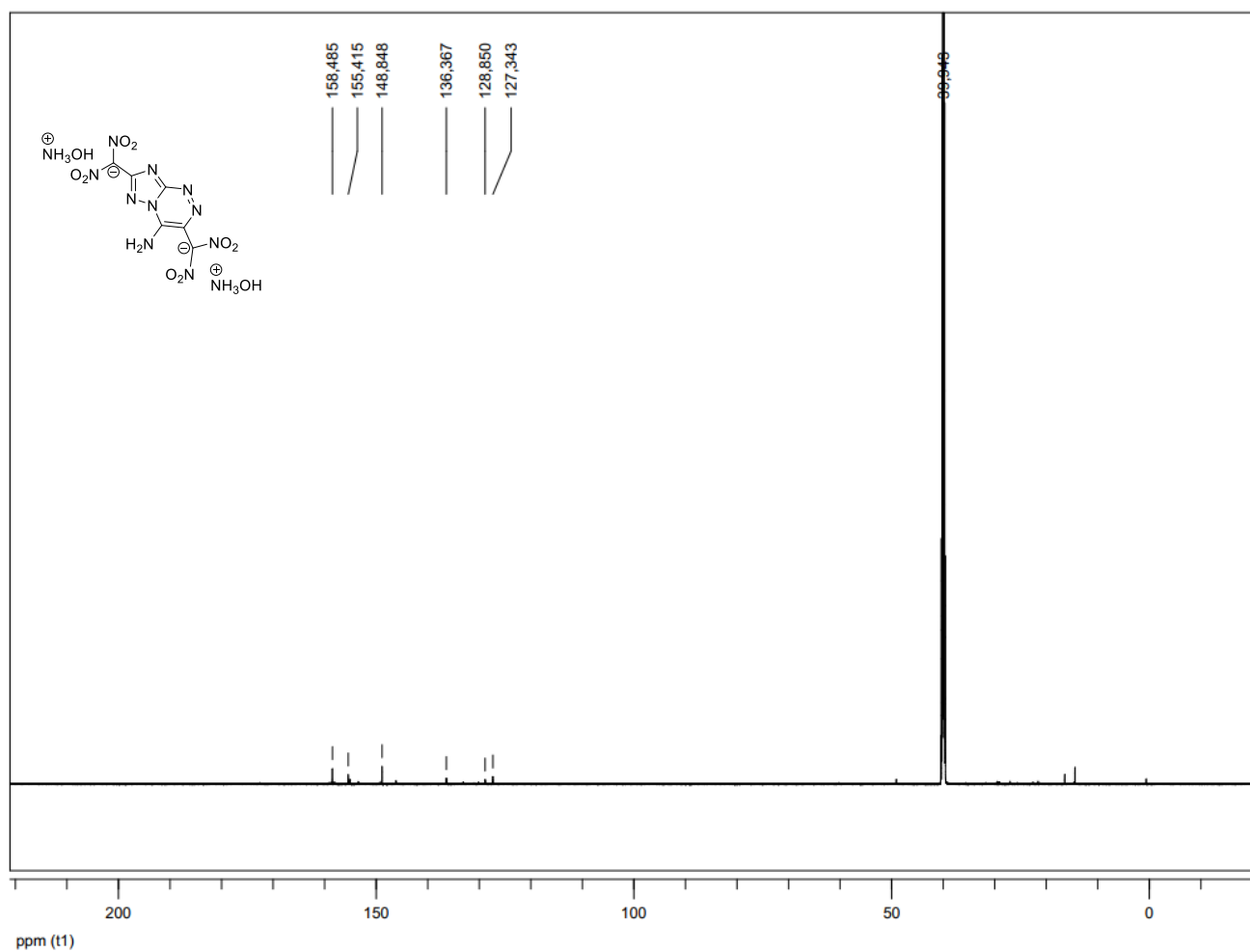


Figure S25 ^{13}C NMR spectrum of 7.

WSQ359 #14 RT: 0.18 AV: 1 NL: 2.21E8
T: FTMS - p ESI Full ms [100.0000-1500.0000]

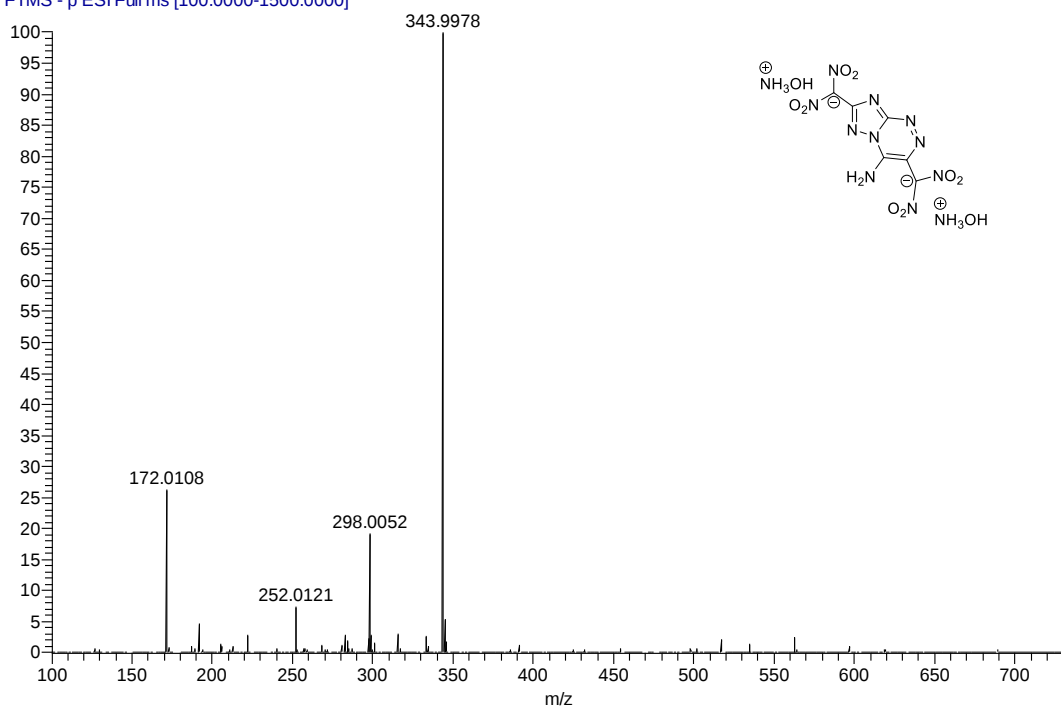


Figure S26 ESI-MS spectrum of 7.

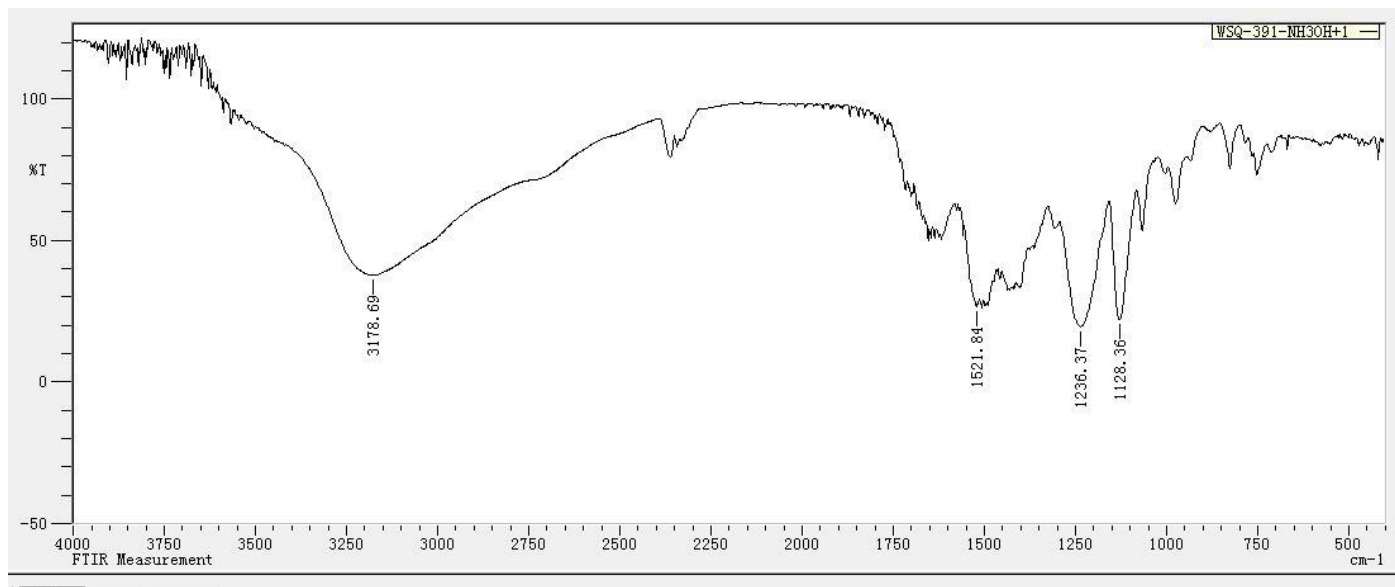


Figure S27 IR spectrum of **7**.

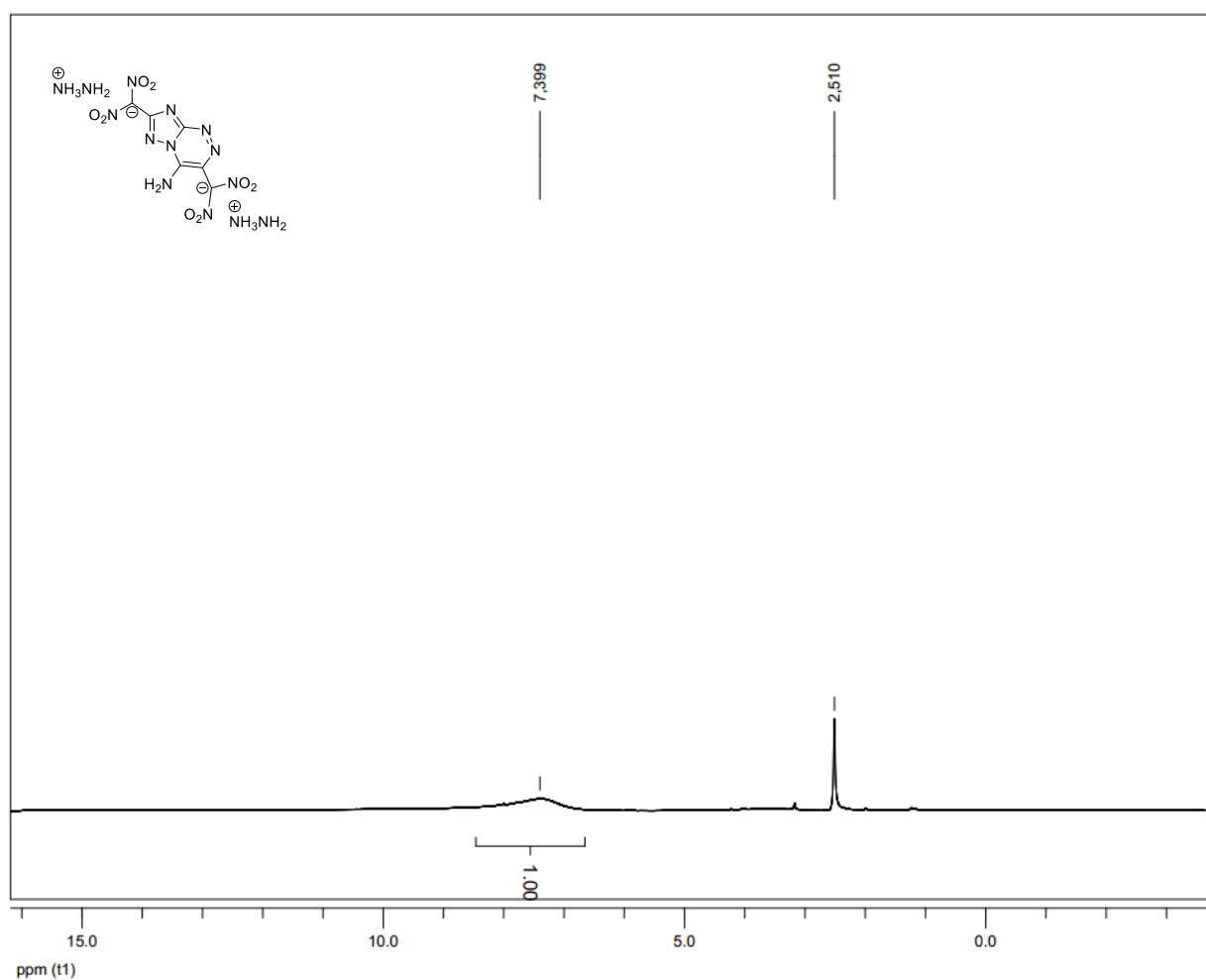


Figure S28 ¹H NMR spectrum of **8**.

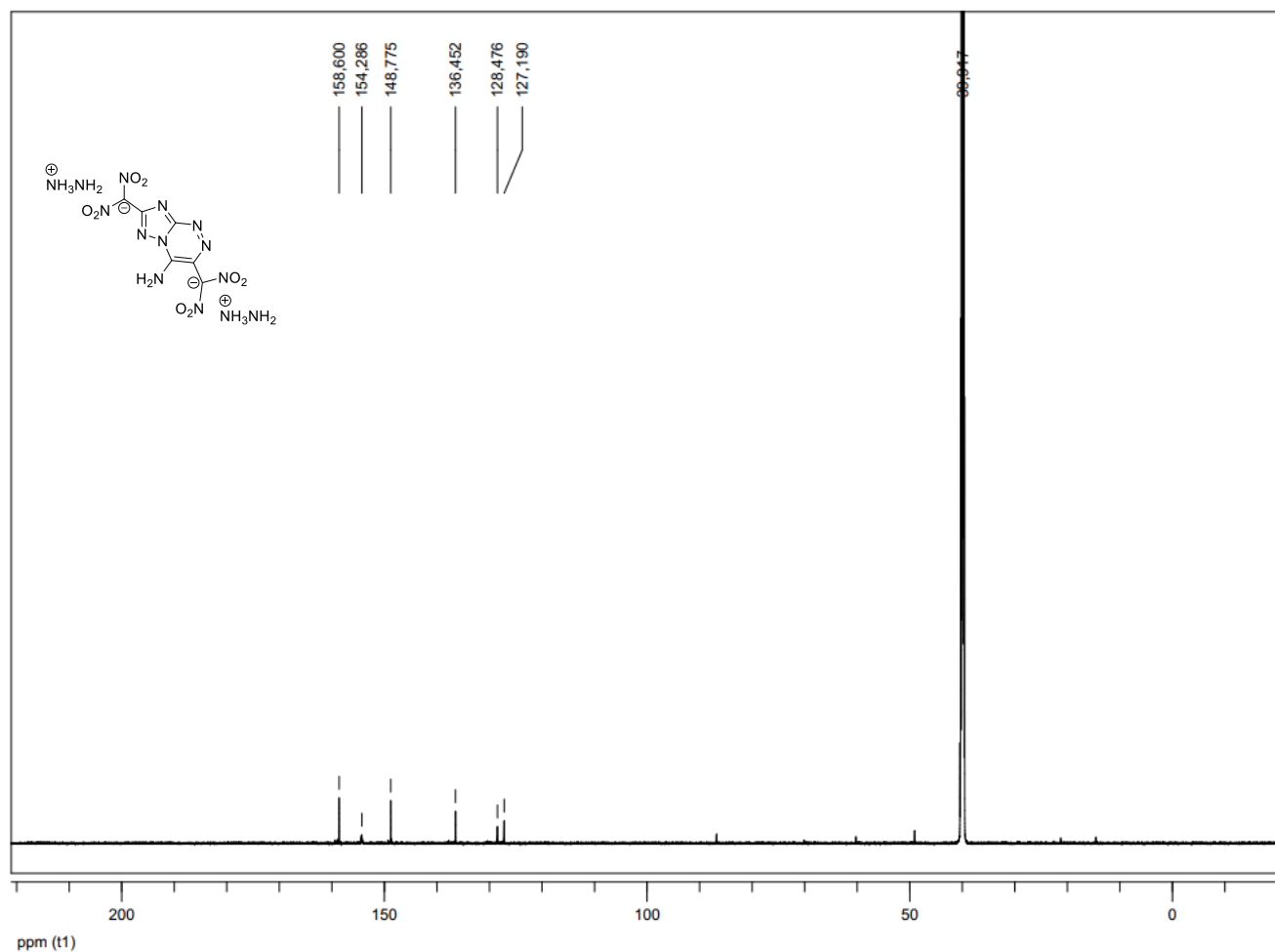


Figure S29 ^{13}C NMR spectrum of **8**.

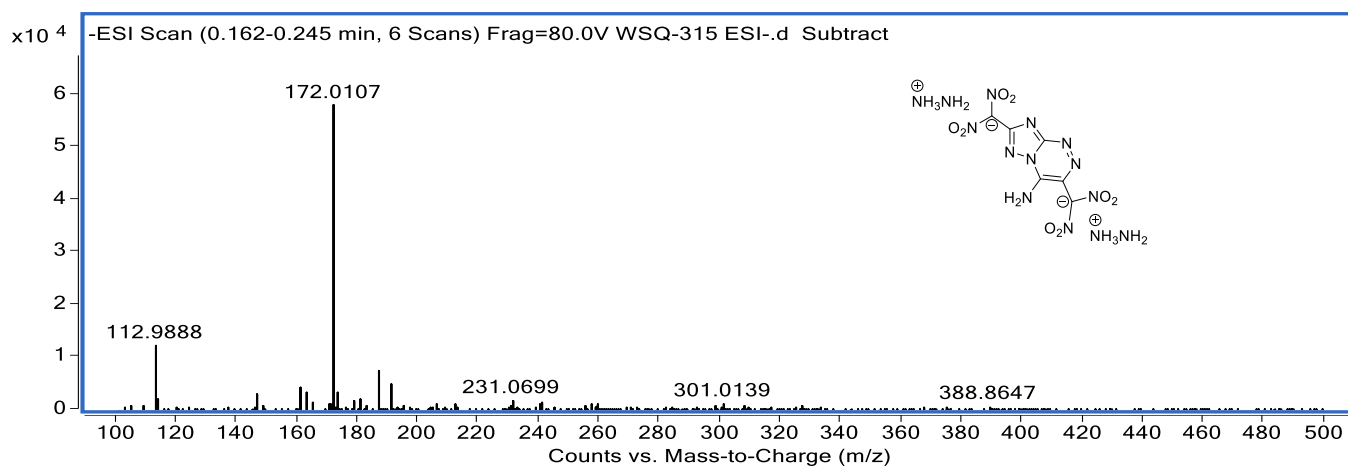


Figure S30 ESI-MS spectrum of **8**.

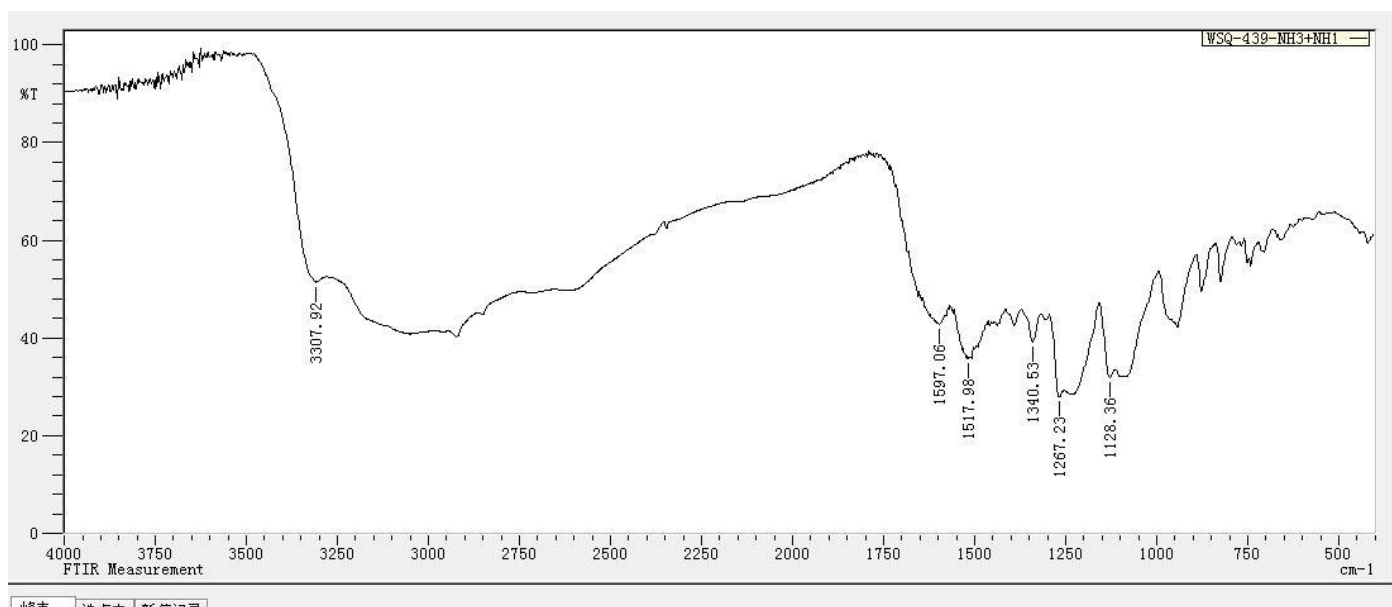


Figure S31 IR spectrum of **8**.

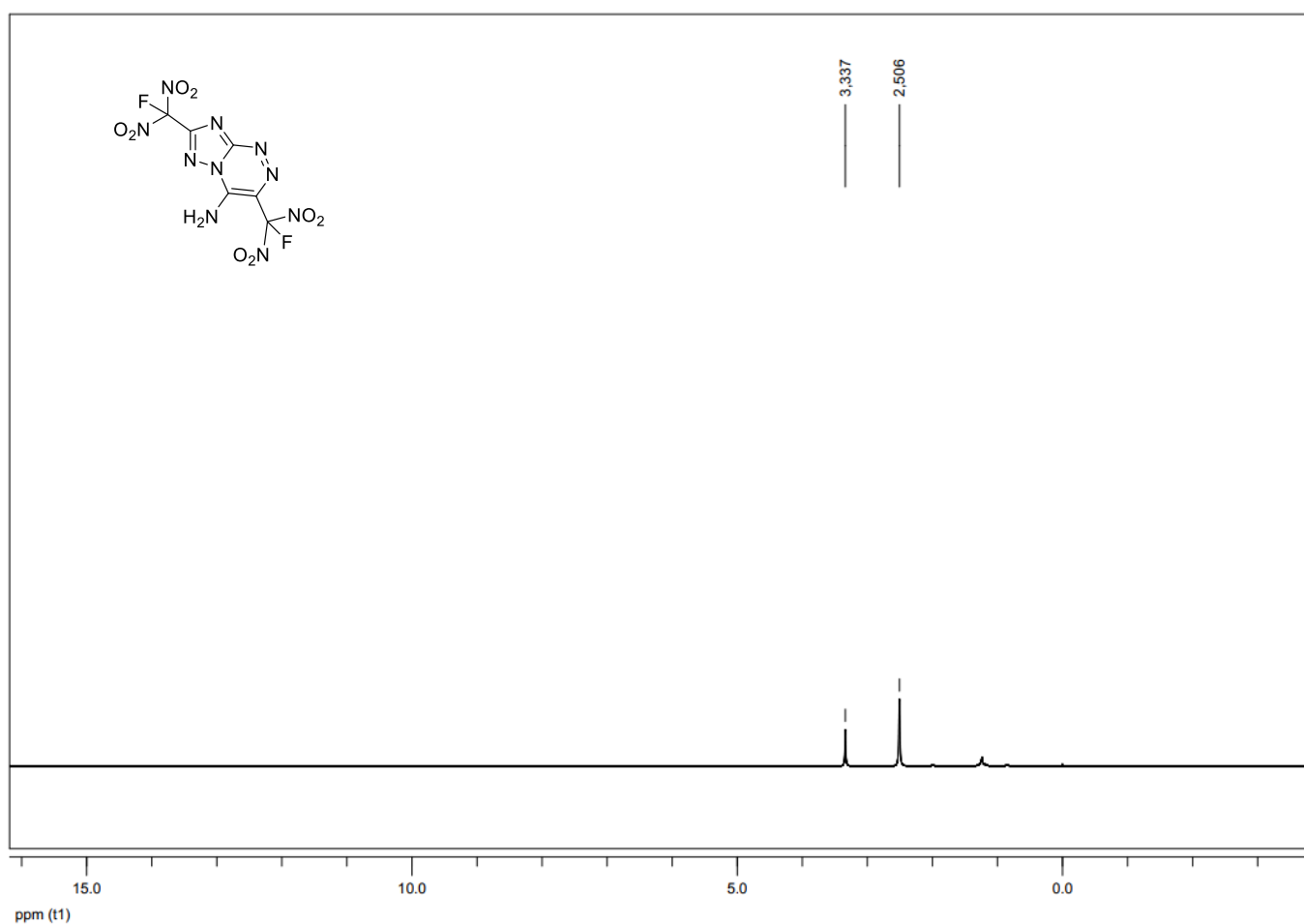


Figure S32 ¹H NMR spectrum of **9**.

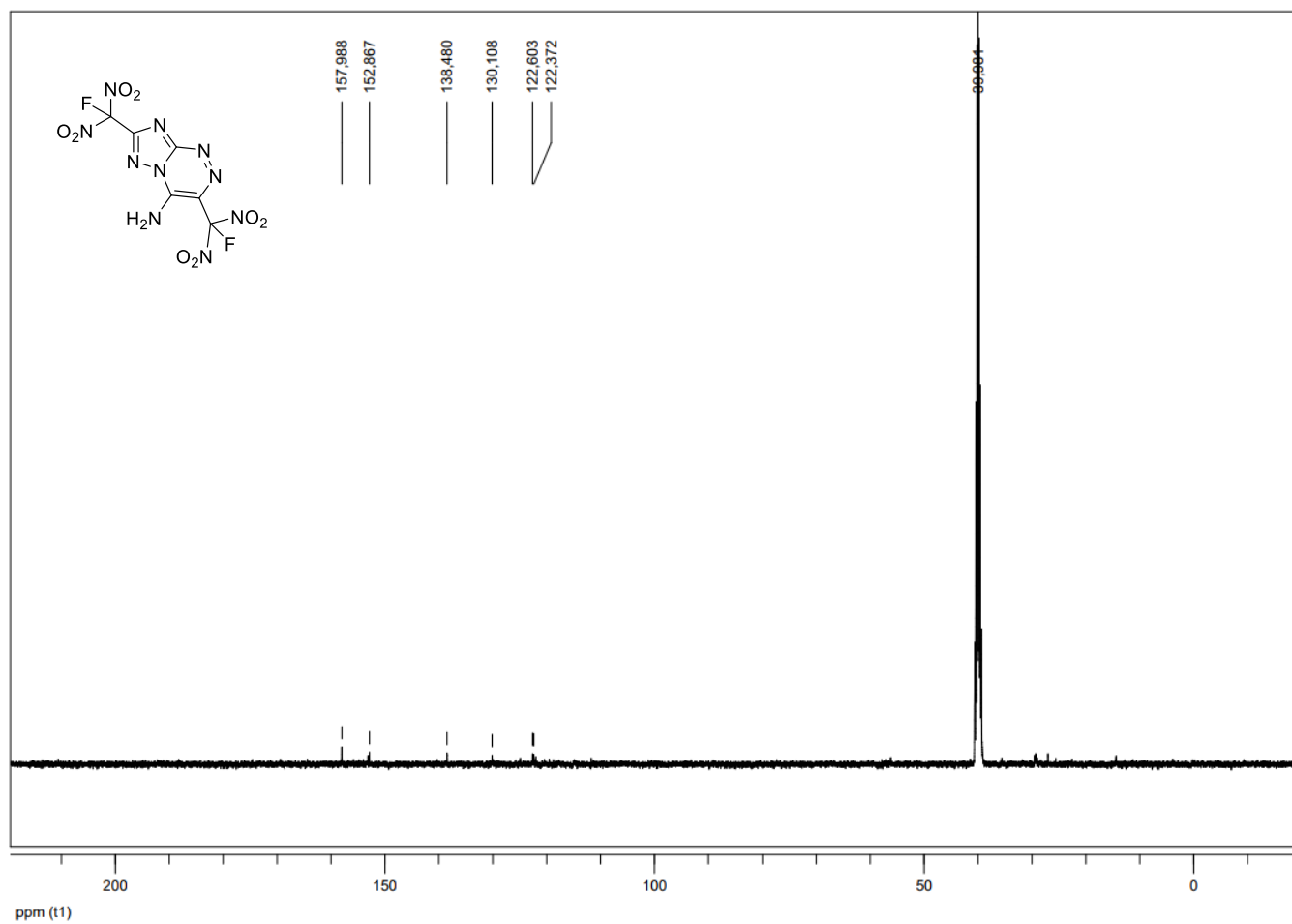


Figure S33 ^{13}C NMR spectrum of **9**.

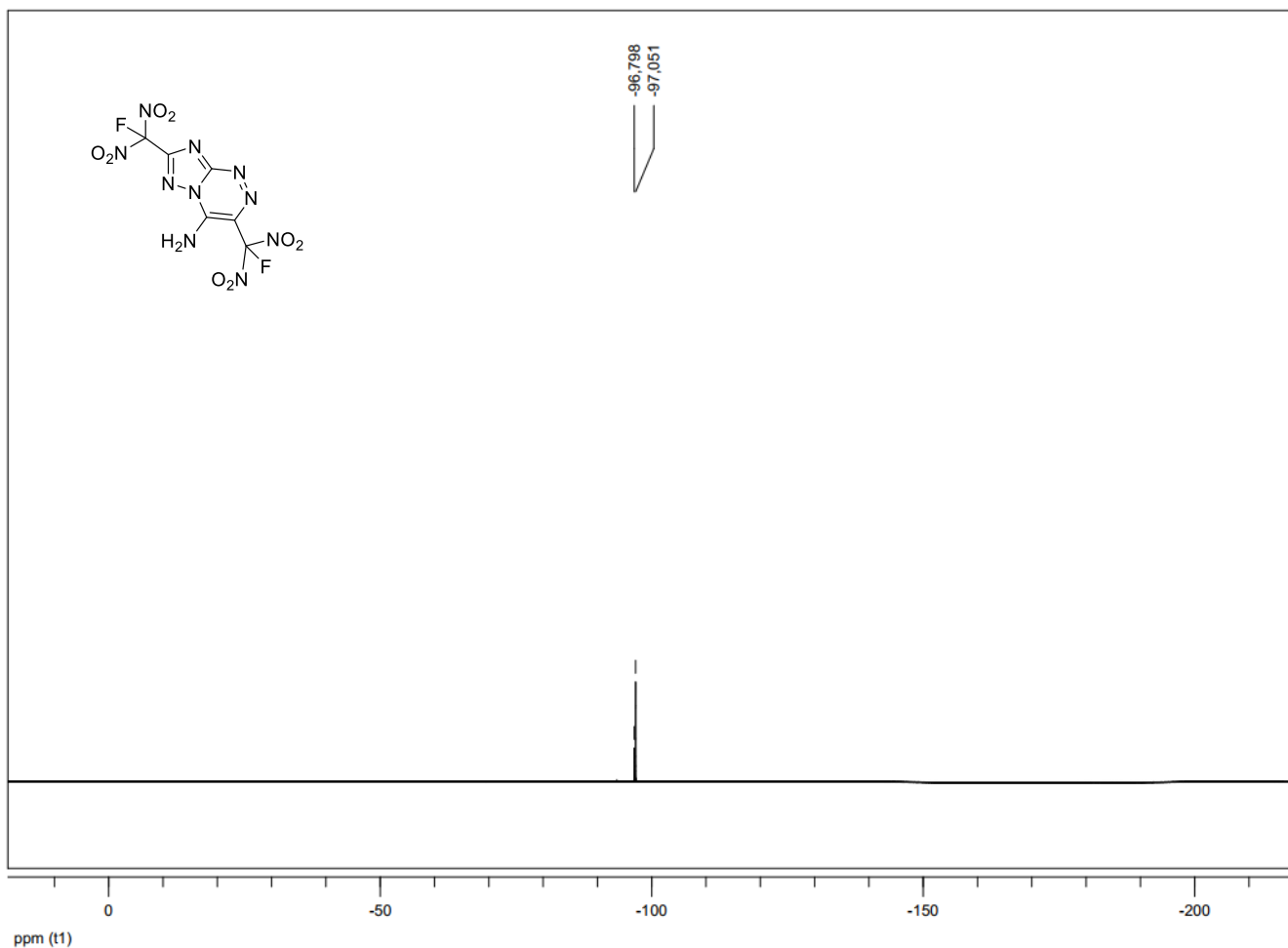


Figure S34 ¹⁹F NMR spectrum of **9**.

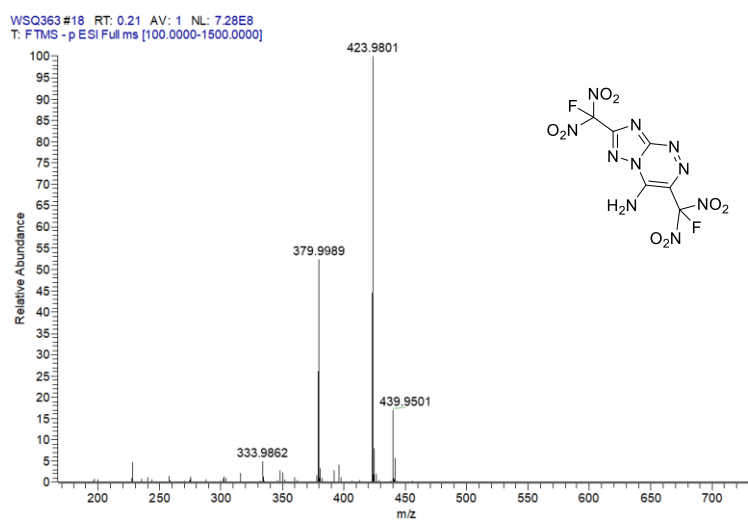


Figure S35 ESI-MS spectrum of **9**.

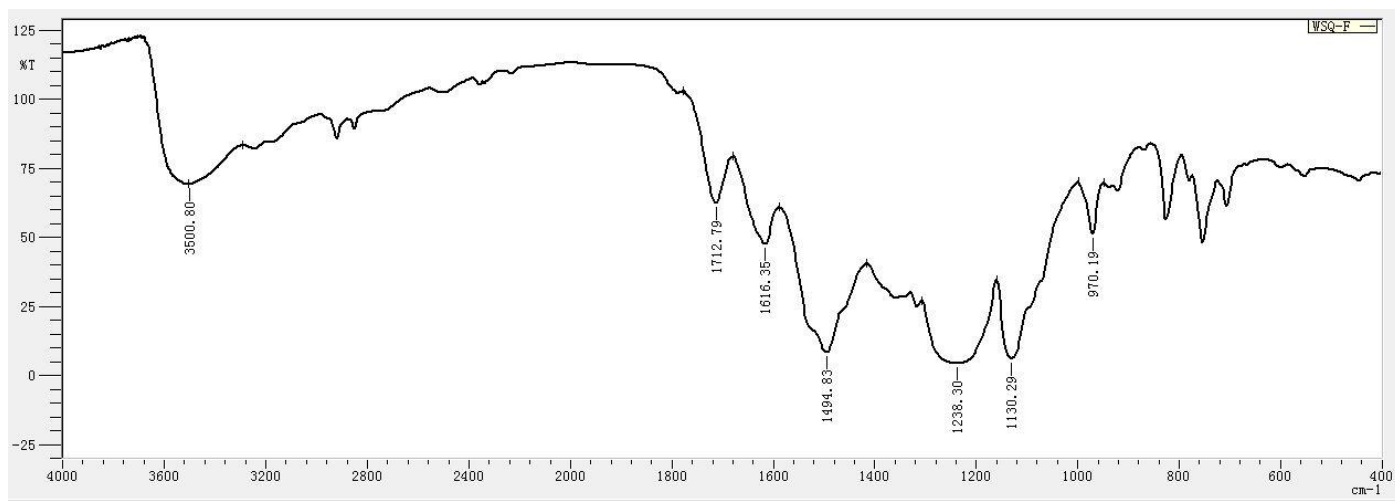


Figure S36 IR spectrum of **9**.

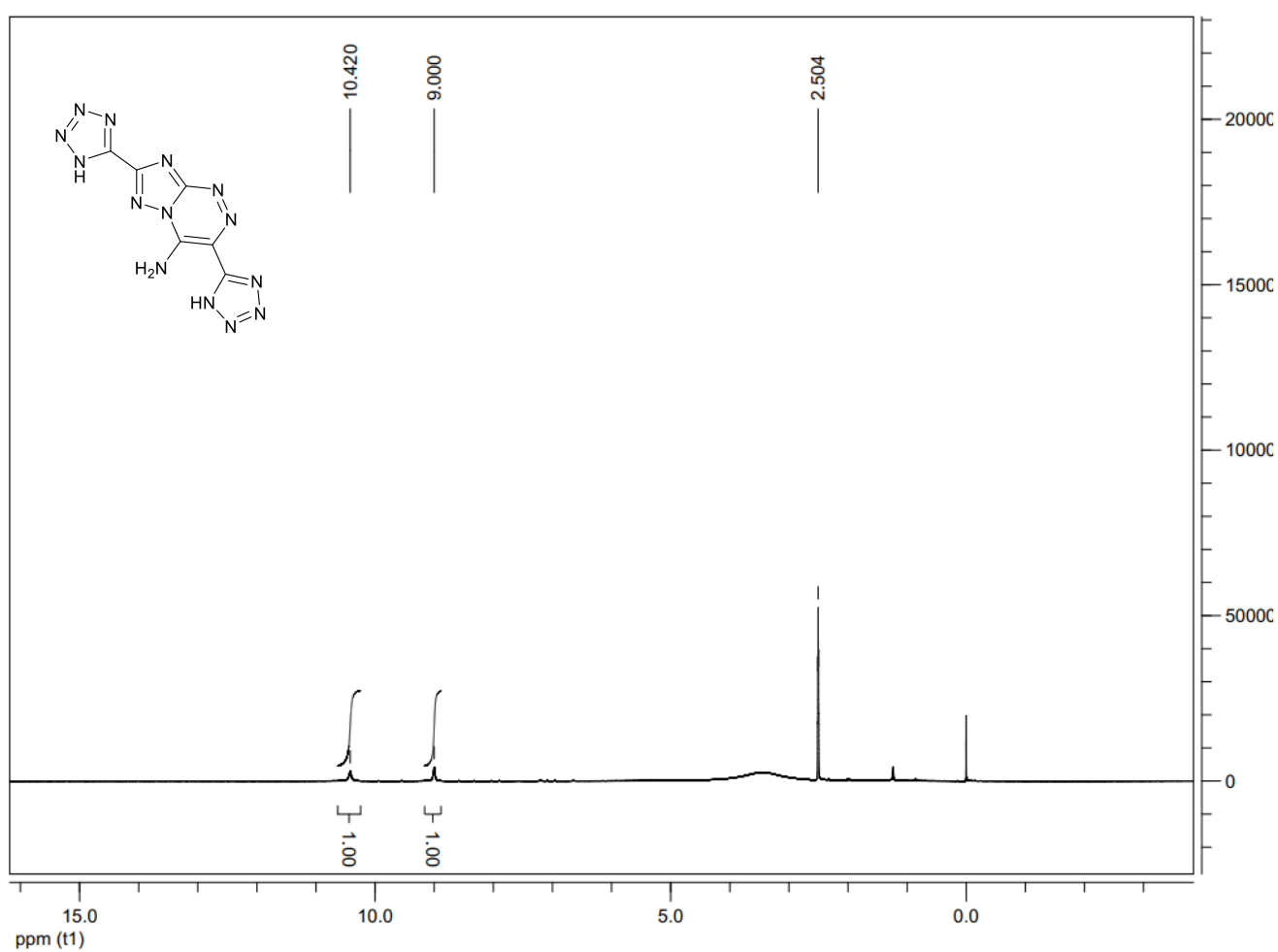


Figure S37 ^1H NMR spectrum of **10**.

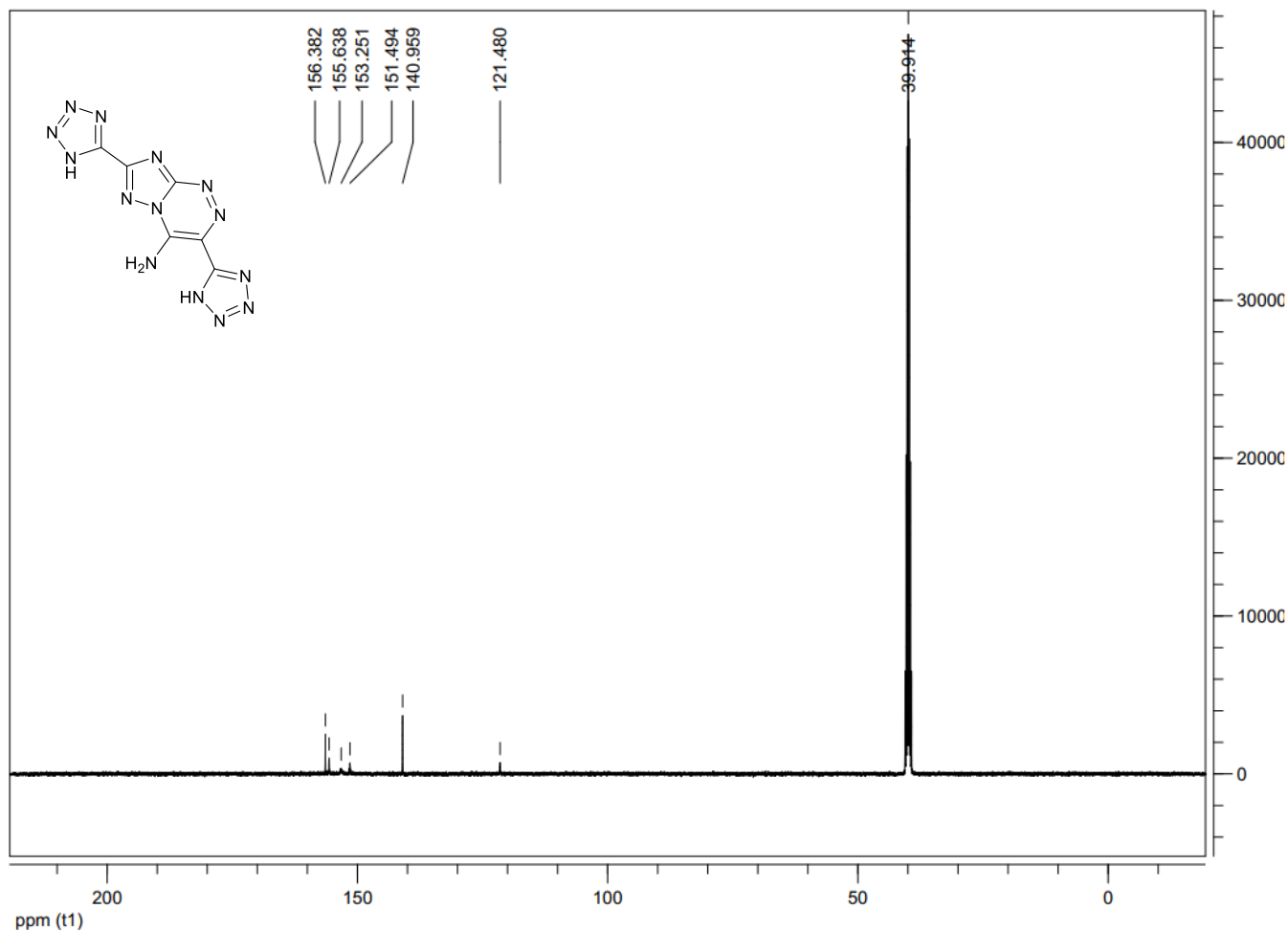


Figure S38 ¹³C NMR spectrum of **10**.

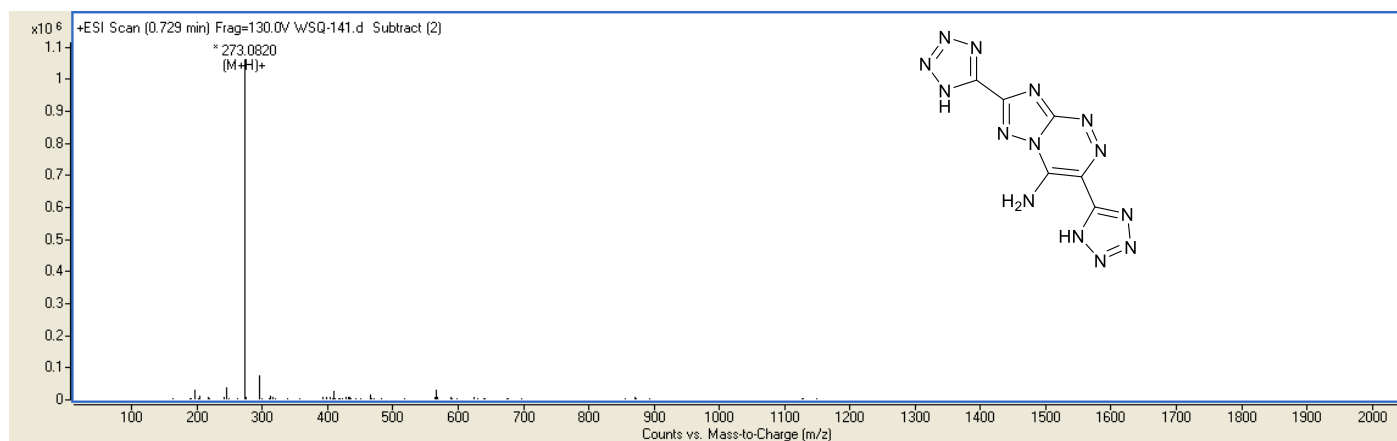


Figure S39 ESI-MS spectrum of **10**.

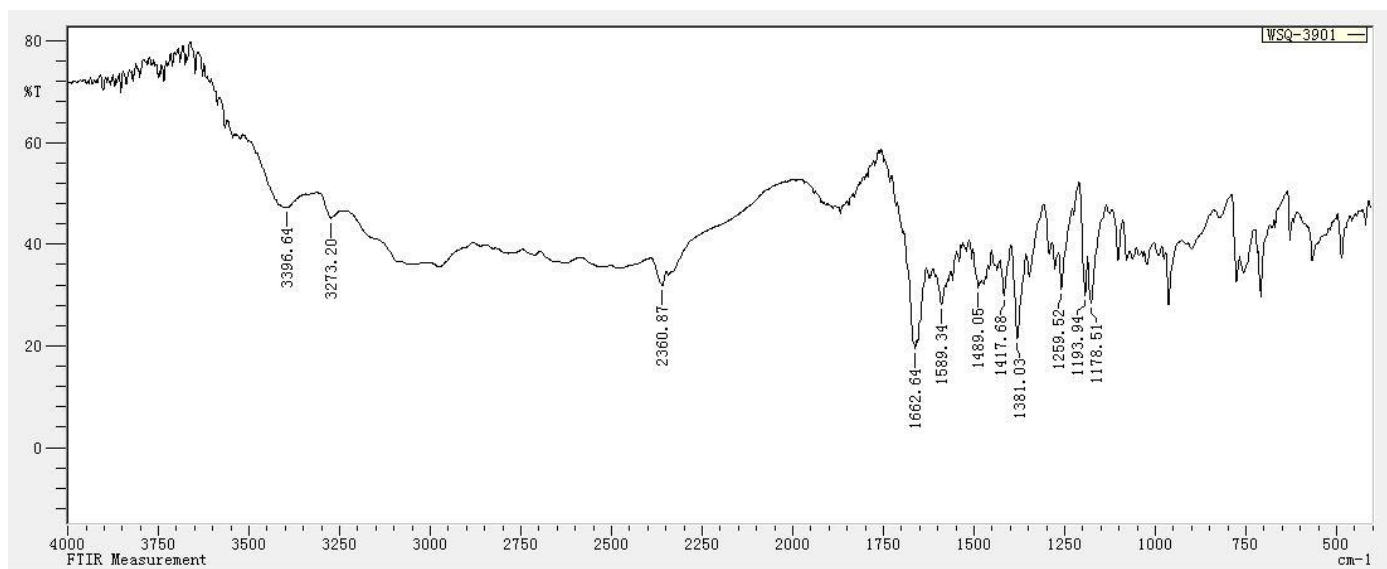


Figure S40 IR spectrum of **10**.