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Supporting Information

Nitrogen-rich ion salts of 1-hydroxytetrazole-5-hydrazide: a new series of energetic compounds that combine good stability and high energy performance

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Content

Synthesis of Hydrazine of 1-hydroxy-1H-tetrazole-5-carbohydrazide (2)

Under the condition of the ice-water bath temperature control, hydrazine hydrate (80%) was added to the ethanol solution (10 ml) of compound **1** (0.79 g, 5 mmol) in dropwise until the PH of the mixture is 9, then stir the mixture for another 12 h at room temperature, after that the mixture was filtered, the filter cake was washed with ethanol and dried to obtain a light-yellow product of compound **2** (0.70 g, yield 79.5 %). IR (KBr): 3307, 3239, 3020, 2636, 2161, 1665, 1622, 1562, 1536, 1470, 1426, 1331, 1291, 1207, 1091, 970, 952, 859, 821, 756, 720, 639, 535 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6, δ): 11.09 (s,1H), 7.06 (s,5H), 4.60 (s,2H) ppm; ^{13}C NMR (126 MHz, DMSO-d_6, δ): 156.24, 137.78 ppm; Element analysis, calcd. for $C_2H_8N_8O_2$: C 13.64, H 4.58, N 63.62 %; found C 13.79, H 4.62, N 63.69 %.

Synthesis of 1-hydroxy-1H-tetrazole-5-carbohydrazide (3)

Compound **2** (0.88 g, 5 mmol) was dissolved in 10 ml of deionized water, then 10% HCl solution was slowly added to it until the pH is 2, after which it was extracted with 5 ml*3 ethyl acetate, the organic phase was treated with saturated brine and anhydrous sodium sulfate, and then evaporated to obtain compound **3** (0.65 g, yield 90.9 %) as a light-yellow solid. IR (KBr): 3306, 3160, 3015, 2611, 1660, 1537, 1470, 1428, 1331, 1282, 1206, 1116, 1079, 1015, 970, 953, 860, 748, 638 cm^{-1}; ^{1}H NMR (500MHz, DMSO-d_6, δ): 11.09 (s, 1H), 7.06 (s, 1H), 4.59 (s, 2H) ppm; ^{13}C NMR (126 MHz, DMSO-d_6, δ): 156.27, 137.78 ppm; Element analysis, calcd. for $C_2H_4N_6O_2$: C 16.67, H 2.80, N 58.32 %; found C 16.59, H 2.87, N 58.25 %.

Synthesis of 1-hydroxy-1H-tetrazole-5-carbohydrazide derivatives (4)-(6)

Compound **3** (**CHZTO**) (0.72 g, 5 mmol) was dissolved in 20 ml of deionized water, then silver nitrate (0.85 g, 5 mmol) was added to it, and the mixture was filtered after stirring for 8 hours in a dark environment. After the filter cake was dried, the silver salt of **3** was obtained as off-white solid (1.21 g, yield 97.1 %), then the silver salt (0.502 g, 2.0 mmol) was added to 10 ml of deionized water, after this an equimolar amount of hydrochloride compounds (ammonium chloride, diaminoguanidine hydrochloride and triaminoguanidine hydrochloride) was added to it and react for 6 h at room temperature. Finally, the mixture was filtered and slowly evaporate the filtrate

to obtain compounds **4**, **5** and **6** in the form of crystals.

Compound **4**: 0.30 g, yield 93.2 %. IR (KBr): 3308, 3037, 1672, 1627, 1545, 1465, 1436, 1398, 1310, 1220, 1156, 1113, 1068, 1004, 859, 743, 700, 652 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6, δ): 11.07 (s, 1H), 7.18 (s, 4H), 4.69 (s, 2H) ppm; ^{13}C NMR (126 MHz, DMSO-d_6, δ): 156.22, 137.77 ppm; Element analysis, calcd. for $C_2H_7N_7O_2$: C14.91, H4.38, N 60.85%; found C 14.84, H 4.42, N 60.91 %.

Compound **5**: 0.44 g, yield 94.4 %. IR (KBr): 3390, 3307, 3189, 1660, 1549, 1430, 1287, 1203, 1121, 1078, 1014, 990, 955, 863, 744, 700, 582 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6, δ): 8.59 (s, 1H), 7.16 (s, 3H), 4.29 (br, 6H) ppm; ^{13}C NMR (126 MHz, DMSO-d_6, δ): 159.20, 156.11, 137.75 ppm; Element analysis, calcd. for $C_3H_{11}N_{11}O_2$: C 15.45, H 4.75, N 66.07 %; found C 15.50, H 4.82, N 66.11 %.

Compound **6**: 0.46 g, yield 92.7 %. IR (KBr): 3358, 3333, 3213, 1672, 1652, 1614, 1531, 1453, 1427, 1408, 1374, 1280, 1216, 1134, 968, 793, 750, 720, 704, 650 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6, δ): 11.09 (s, 1H), 8.61 (s, 3H), 4.50 (s, 8H) ppm; ^{13}C NMR (126 MHz, DMSO-d_6, δ): 159.41, 156.25, 137.78 ppm; Element analysis, calcd. for $C_3H_{12}N_{12}O_2$: C 14.52, H 4.87, N 67.72 %; found C 14.60, H 4.79, N 67.80 %.

Table S1. Crystallographic data of compound **2**

Compound	**2**
CCDC number	2107863
Chemical formula	$C_2H_8N_8O_2$
Formula mass	176.16
Crystal system	Monoclinic
Space group	$P2_1/c$
a, b, c [Å]	3.6249(5), 24.182(3), 15.487(2)
α, β, γ [°]	90, 92.123(6), 90
Volume [$Å^3$]	1356.7(3)
Temperature [K]	193
Z	8
μ [mm^{-1}]	0.817
ρ [$g \cdot cm^{-3}$]	1.725
F (000)	736.0
θ range [°]	5.898 to 120.634
Index range	$-3 \le h \le 4$; $-28 \le k \le 30$; $-20 \le l \le 19$
Reflections collected	10727
Independent reflections	3004
Data/restraints/parameters	3004/0/281
R1 / wR2 [all data]	0.0504/0.1207
R1 / wR2 [I > 2σ(I)]	0.0432/0.1146
GOF on F^2	1.064

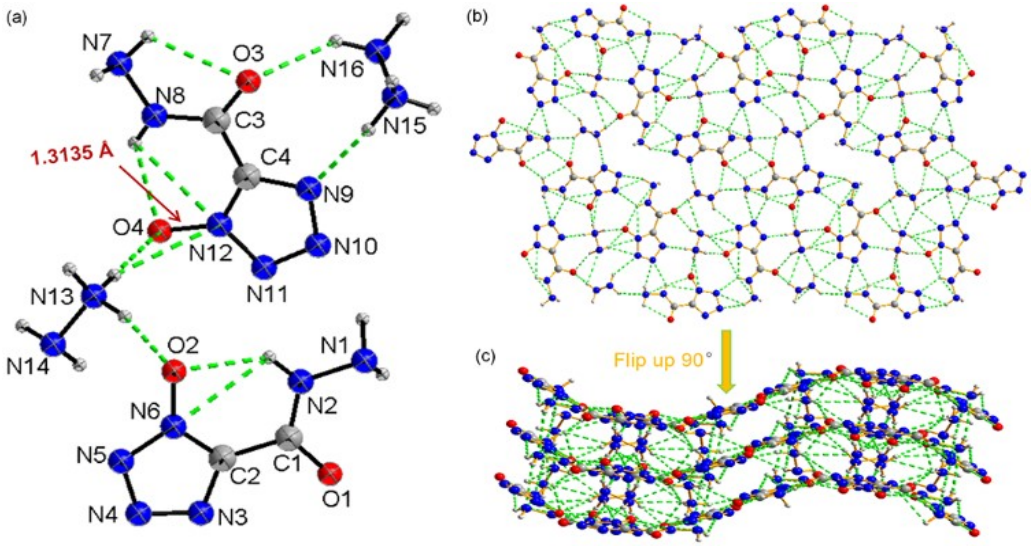


Figure S1. The crystal structure of **2**.

Table S2. Crystallographic data of compound **3**·H_2O

Compound	**3**·H_2O
CCDC number	2115133
Chemical formula	$2C_2H_4N_6O_2·3H_2O$
Formula mass	342.27
Crystal system	Triclinic
Space group	P-1
a, b, c [Å]	8.5771(4), 8.9197(4), 9.7491(5)
α, β, γ [°]	70.6800(10), 71.5520(10), 77.6680(10)
Volume [$Å^3$]	662.73(6)
Temperature [K]	296(2)
Z	2
μ [mm^{-1}]	0.156
ρ [$g·cm^{-3}$]	1.715
F (000)	356
θ range [°]	2.297 to 28.377
Index range	$-11 \le h \le 11$; $-11 \le k \le 11$; $-13 \le l \le 12$
Reflections collected	10488
Independent reflections	3305
Data/restraints/parameters	3305/0/219
R1 / wR2 [all data]	0.0447/0.1074
R1 / wR2 [I > 2σ(I)]	0.0372/0.1020
GOF on F^2	1.014

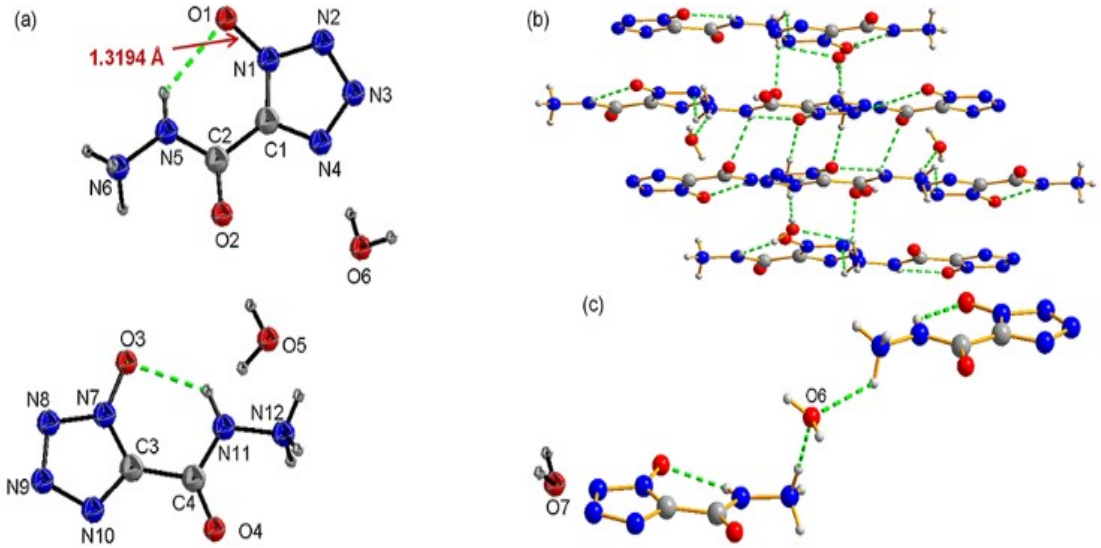


Figure S2. The crystal structure of **3**·H_2O.

Table S3. Crystallographic data of compound **4**

Compound	**4**
CCDC number	2119635
Chemical formula	$C_2H_7N_7O_2$
Formula mass	161.15
Crystal system	Orthorhombic
Space group	$Pca2_1$
a, b, c [Å]	21.016(4), 3.6758(7), 8.0868(15)
α, β, γ [°]	90, 90, 90
Volume [$Å^3$]	624.7(2)
Temperature [K]	296(2)
Z	4
μ [mm^{-1}]	0.147
ρ [$g·cm^{-3}$]	1.713
F (000)	336
θ range [°]	3.179 to 27.398
Index ranges	$-25 \le h \le 27$; $-4 \le k \le 4$; $-10 \le l \le 9$
Reflections collected	5864
Independent reflections	1371
Data/restraints/parameters	1371/22/118
R1 / wR2 [all data]	0.0586/0.1353
R1 / wR2 [$I > 2\sigma(I)$]	0.0542/0.1325
GOF on F^2	1.050

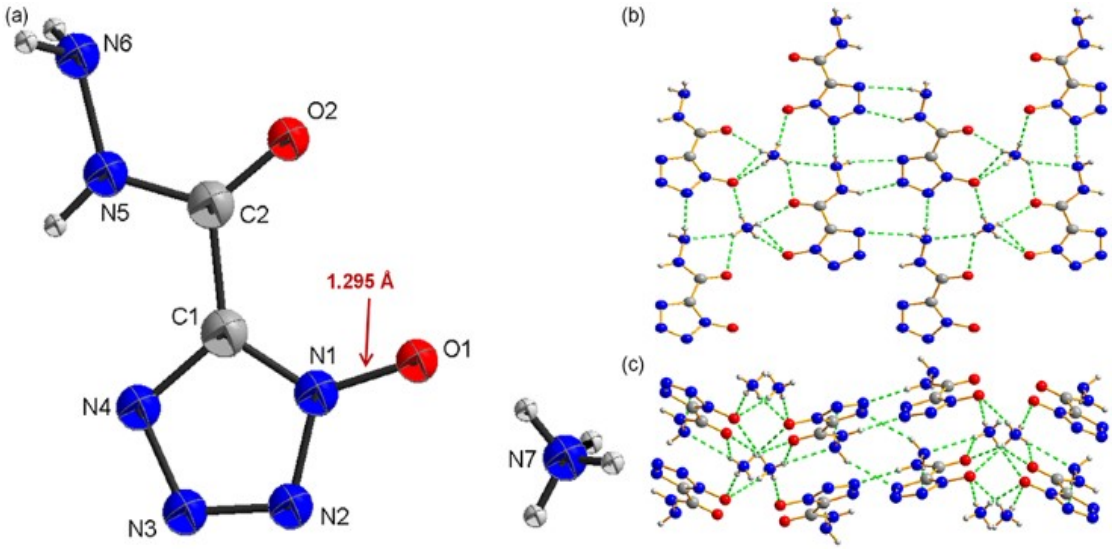


Figure S3. The crystal structure of **4**.

Table S4. Crystallographic data of compound **5**

Compound	**5**
CCDC number	2111832
Chemical formula	$C_3H_{11}N_{11}O_2$
Formula mass	233.23
Crystal system	Monoclinic
Space group	$P2_1/c$
a, b, c [Å]	8.3985(6), 15.6955(12), 7.4981(6)
α, β, γ [°]	90, 105.102(3), 90
Volume [$Å^3$]	954.25(13)
Temperature [K]	296(2)
Z	4
μ [mm^{-1}]	0.135
ρ [$g \cdot cm^{-3}$]	1.623
F (000)	488
θ range [°]	2.512 to 27.528
Index ranges	$-10 \le h \le 10$; $-16 \le k \le 20$; $-9 \le l \le 9$
Reflections collected	9110
Independent reflections	2183
Data/restraints/parameters	2183/0/178
R1 / wR2 [all data]	0.0632/0.1134
R1 / wR2 [$I > 2\sigma(I)$]	0.0420/0.1035
GOF on F^2	1.036

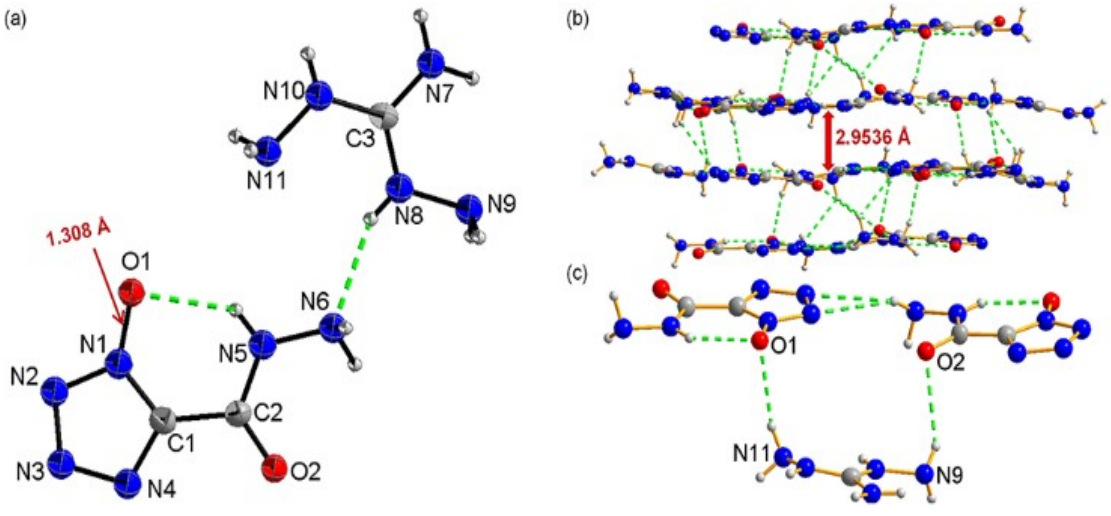


Figure S4. The crystal structure of **5**.

Table S5. Crystallographic data of compound **6**·H_2O

Compound	**6**·H_2O
CCDC number	2119636
Chemical formula	$C_3H_{12}N_{12}O_2 \cdot H_2O$
Formula mass	266.26
Crystal system	Triclinic
Space group	P-1
a, b, c [Å]	7.2673(5), 7.5778(5), 11.4906(7)
α, β, γ [°]	99.301(2), 99.086(2), 113.948(2)
Volume [$Å^3$]	629.95(7)
Temperature [K]	552.91(6)
Z	2
μ [mm^{-1}]	0.136
ρ [$g \cdot cm^{-3}$]	1.599
F (000)	280
θ range [°]	3.038 to 27.585
Index ranges	$-9 \le h \le 9$; $-9 \le k \le 9$; $-14 \le l \le 14$
Reflections collected	8535
Independent reflections	2530
Data/restraints/parameters	2530/0/203
R1 / wR2 [all data]	0.0478 /0.1080
R1 / wR2 [I > 2σ(I)]	0.0389/0.1024
GOF on F^2	1.048

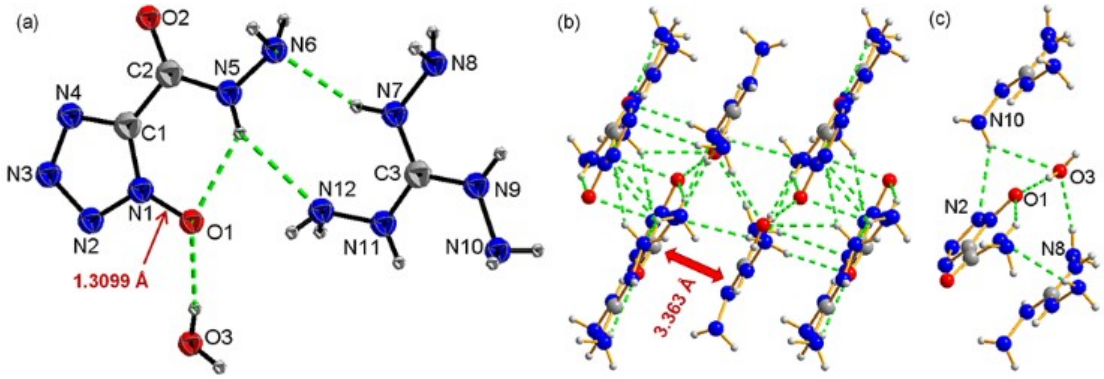


Figure S5. The crystal structure of **6**·H_2O.

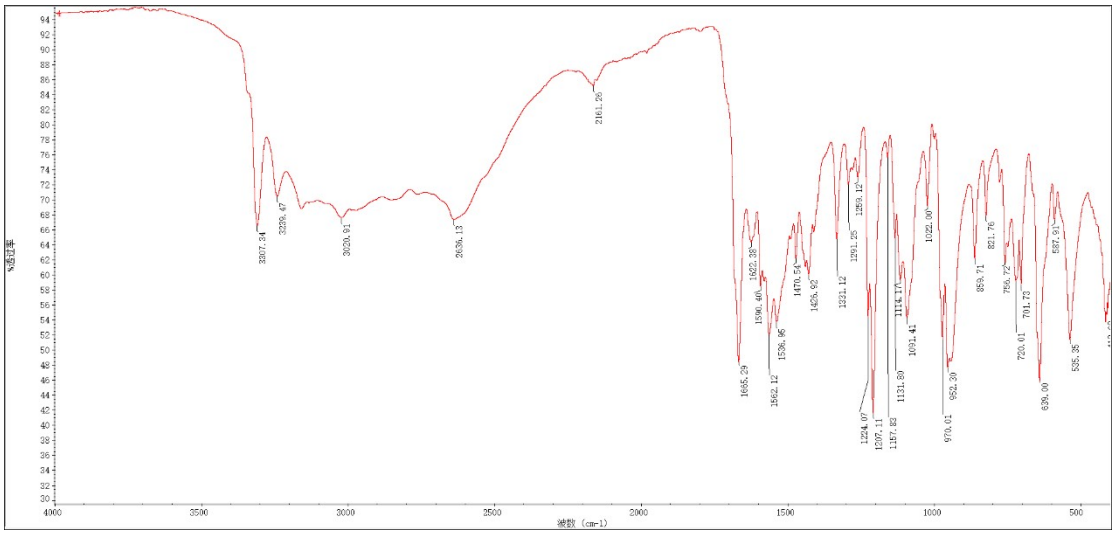


Figure S6 IR spectra of **2**

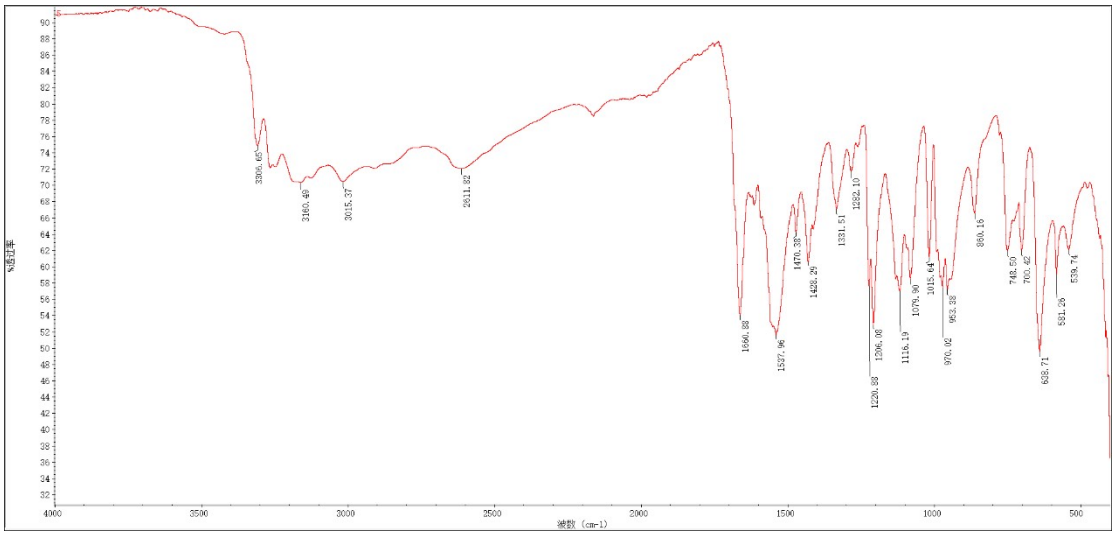


Figure S7 IR spectra of **3**

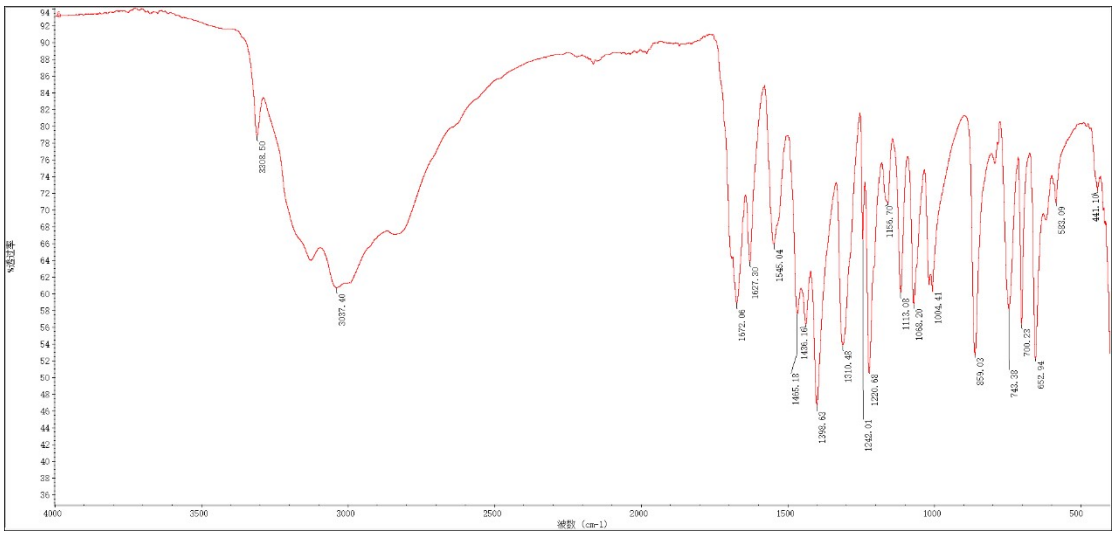


Figure S8 IR spectra of **4**

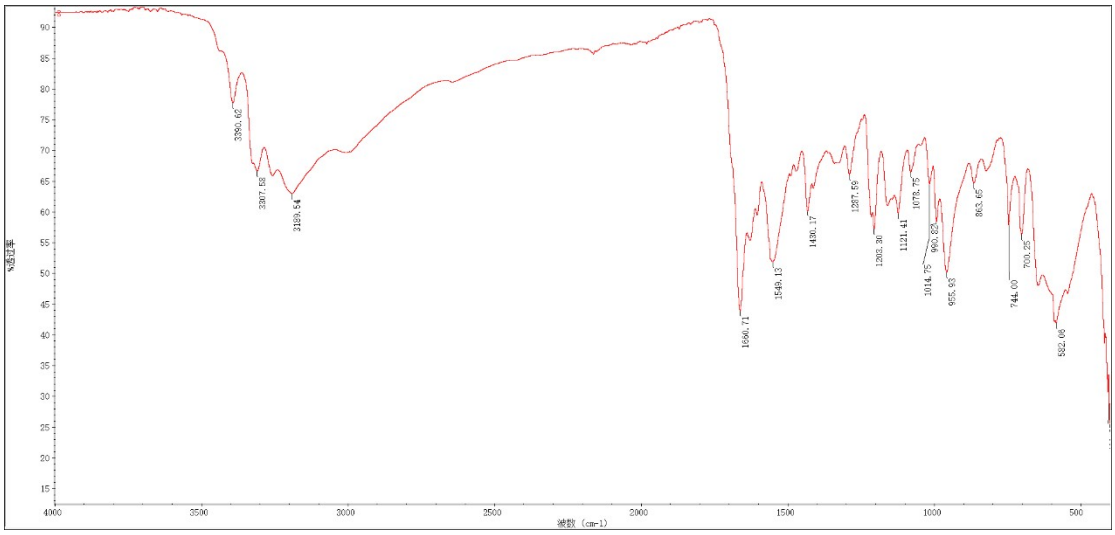


Figure S9 IR spectra of **5**

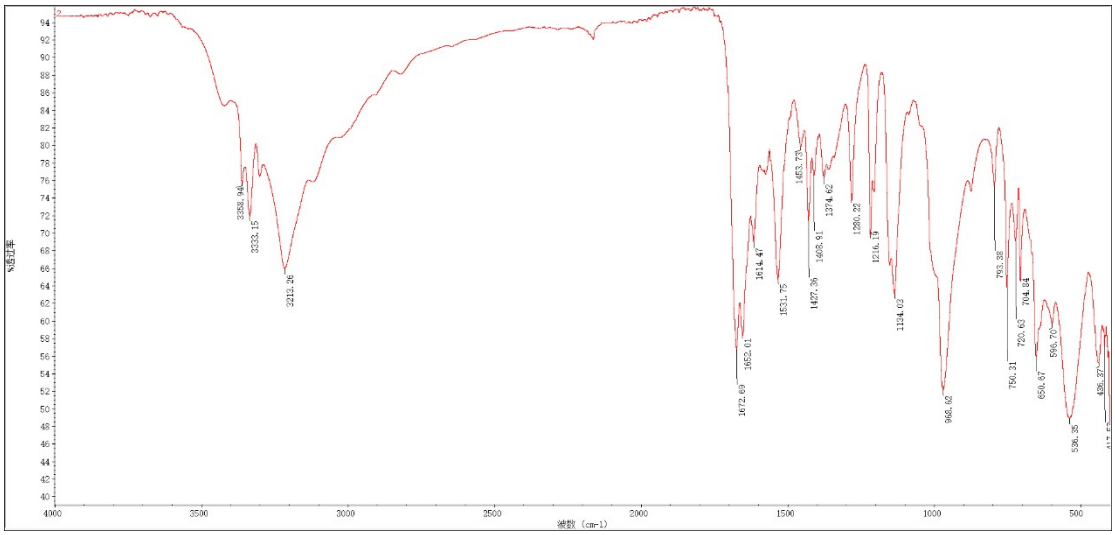


Figure S10 IR spectra of **6**

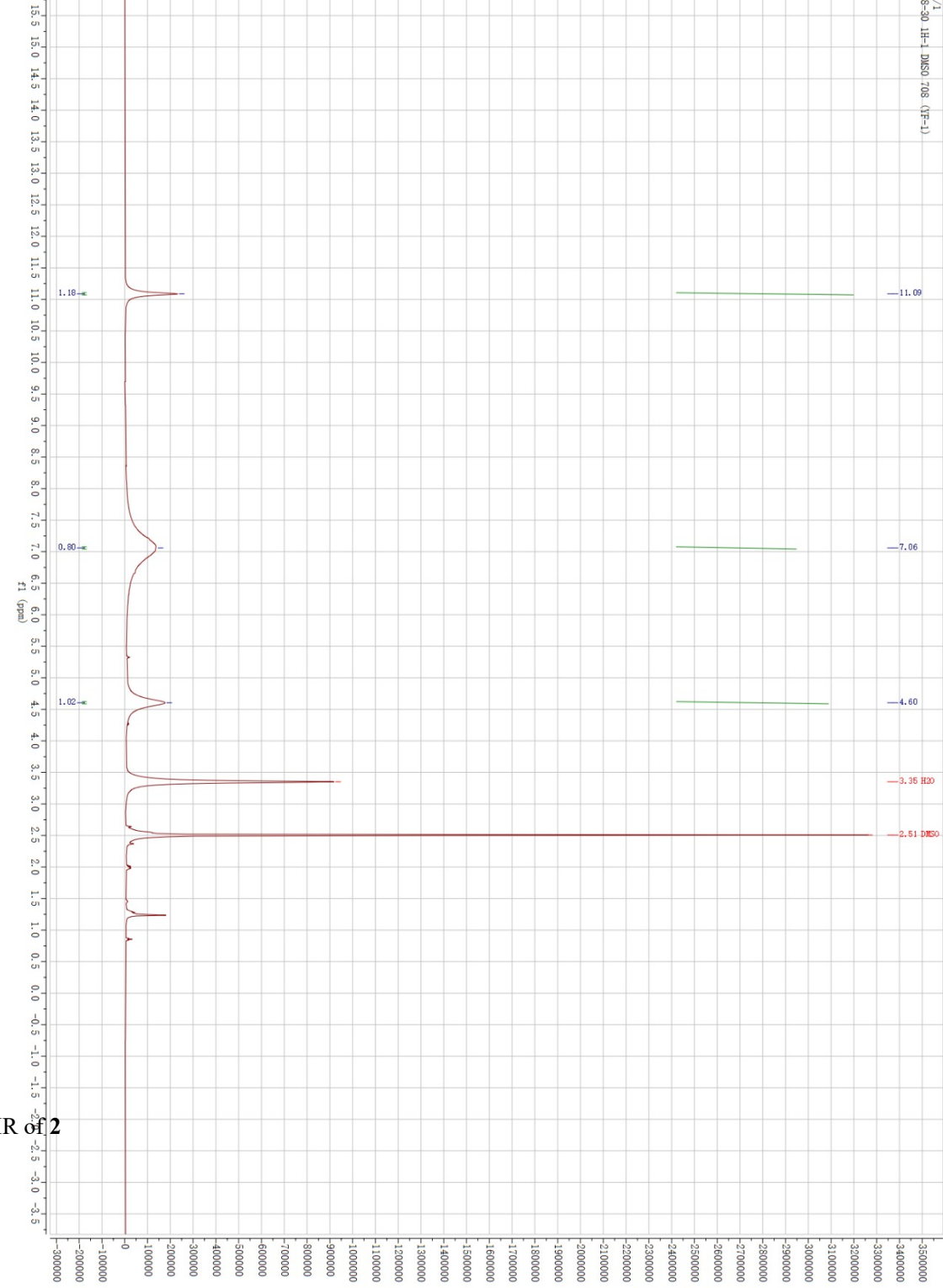


Figure S11 ^{1}H NMR of **2**

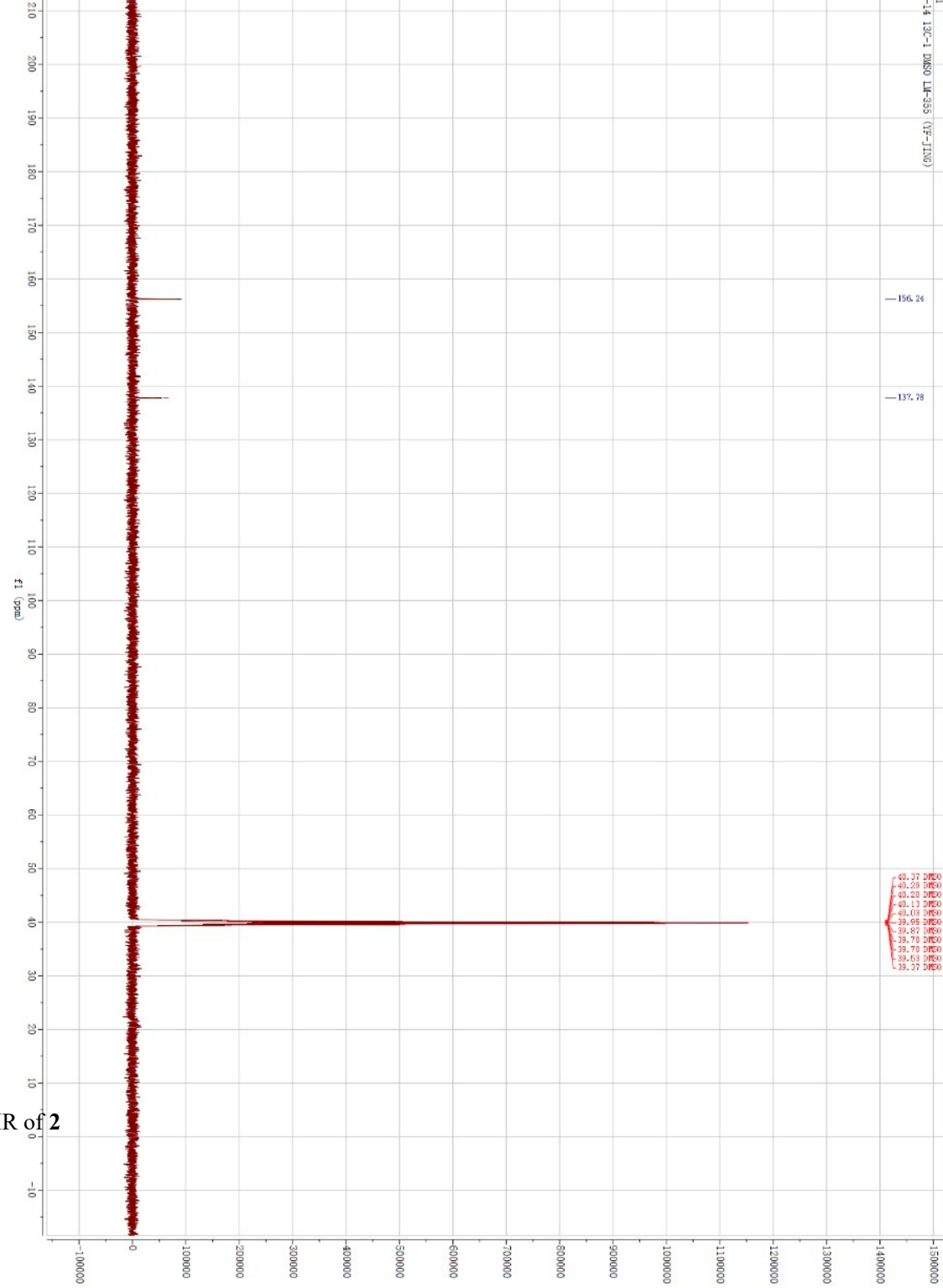


Figure S12 ^{13}C NMR of **2**

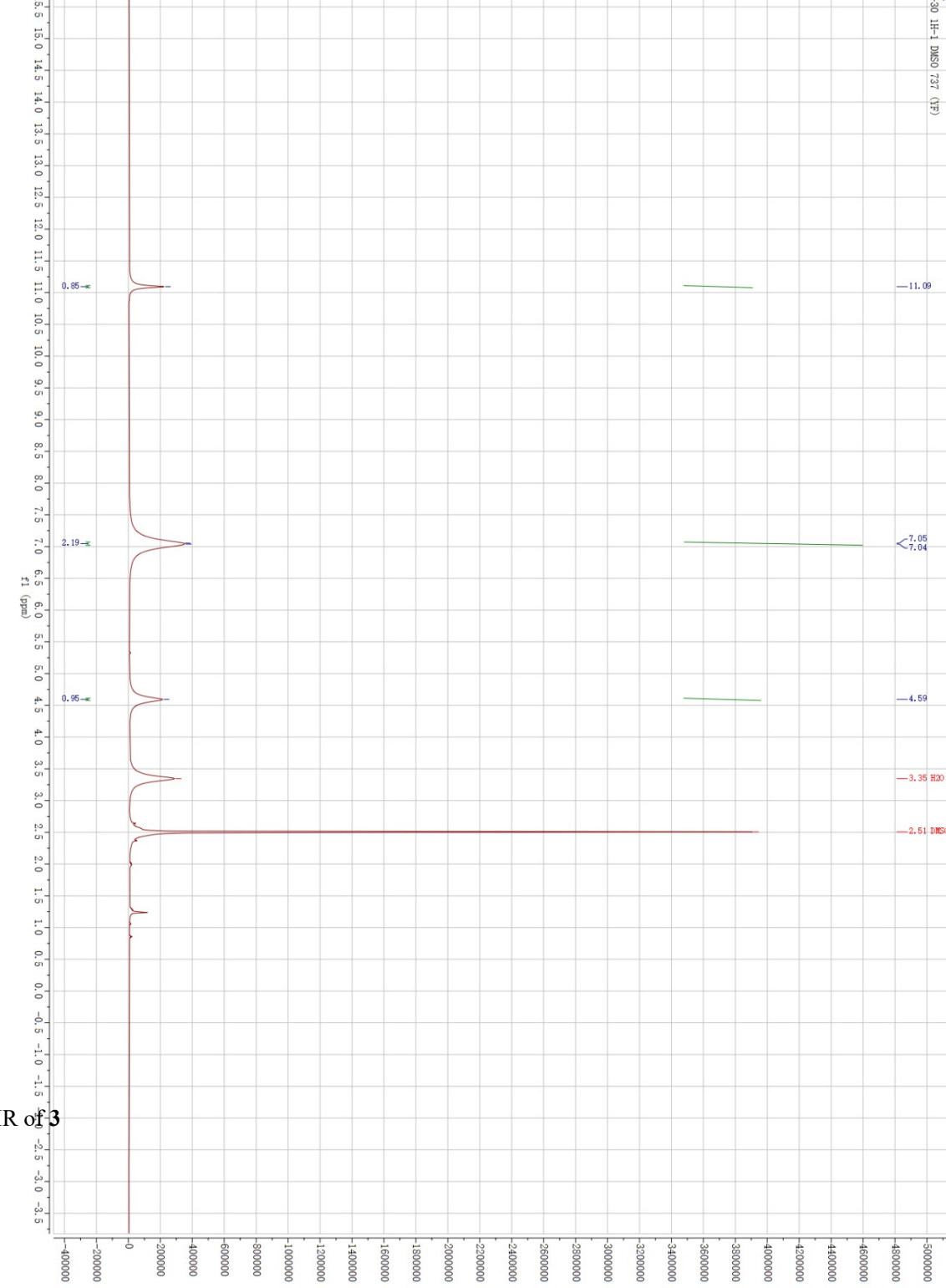


Figure S13 ^{1}H NMR of **3**

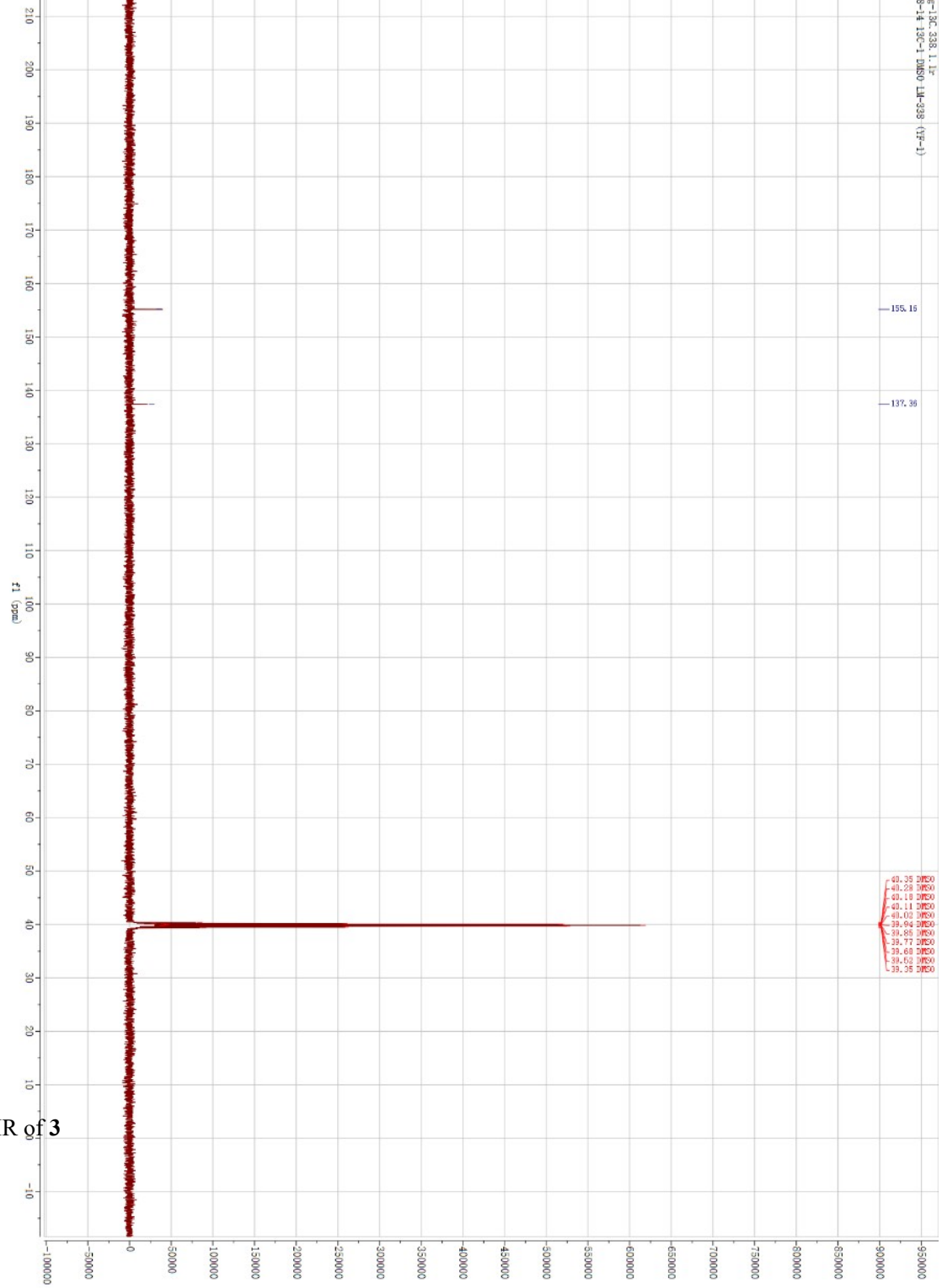


Figure S14 ^{13}C NMR of **3**

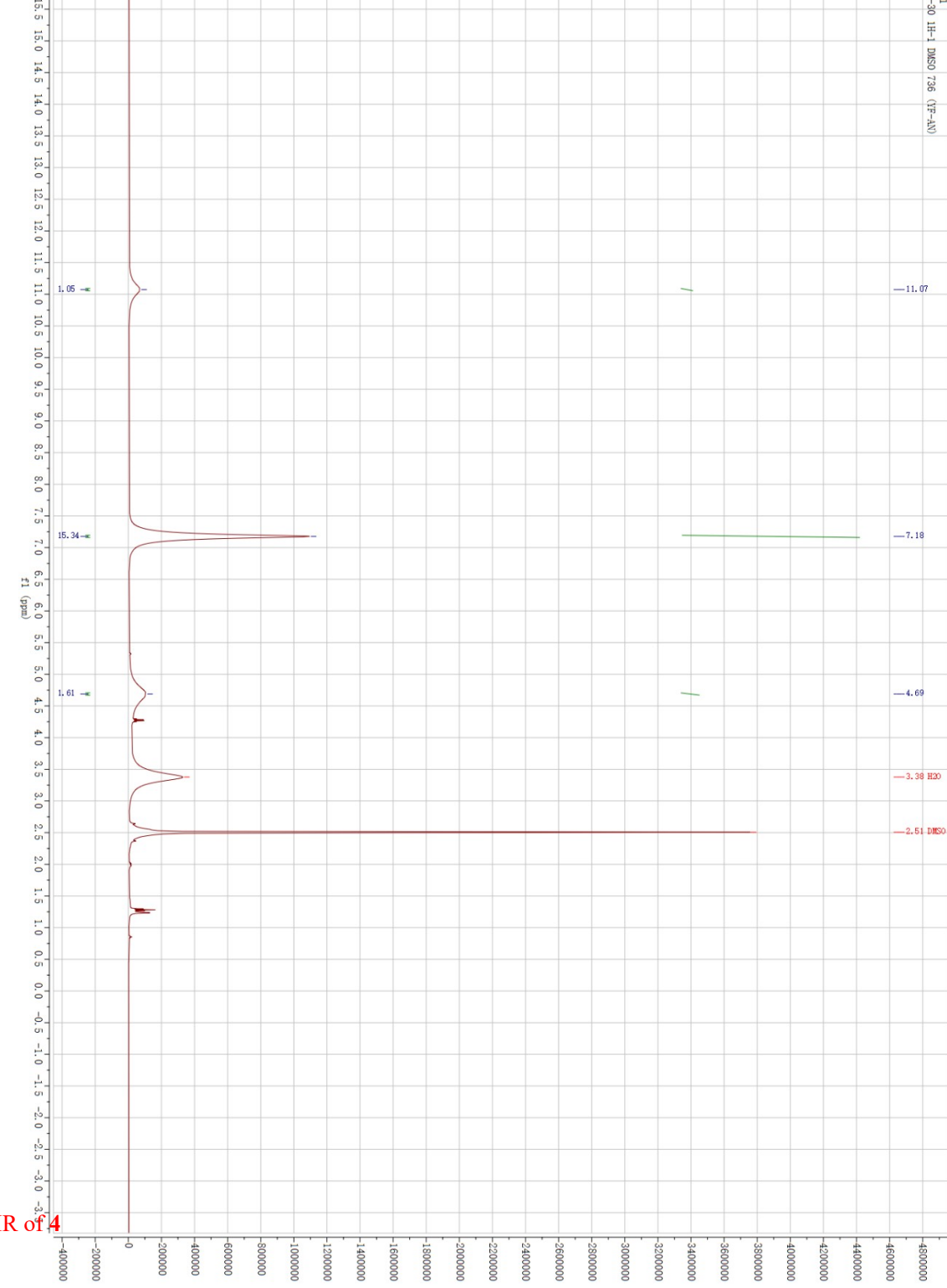


Figure S15 ^{1}H NMR of **4**

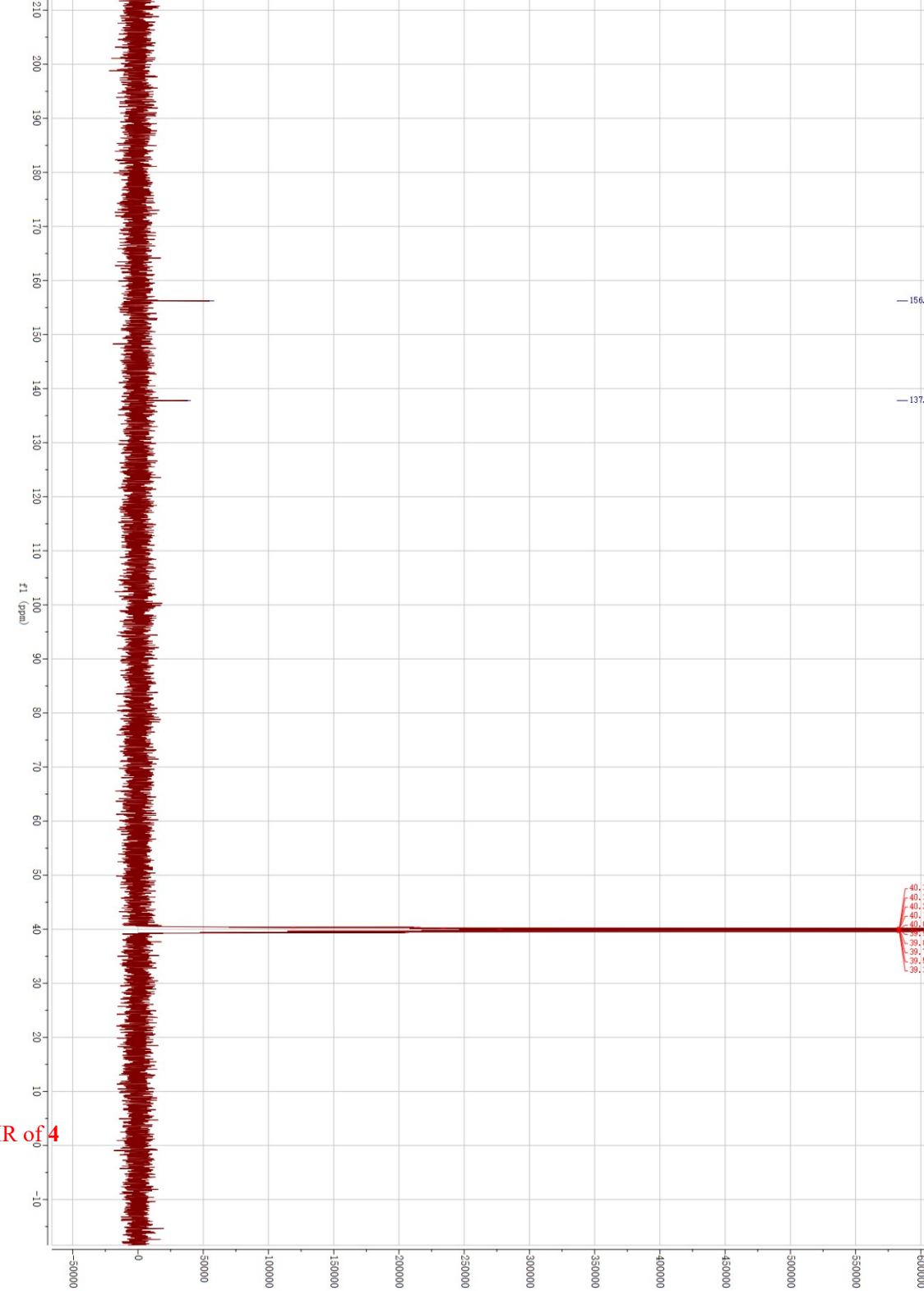


Figure S16 ^{13}C NMR of **4**

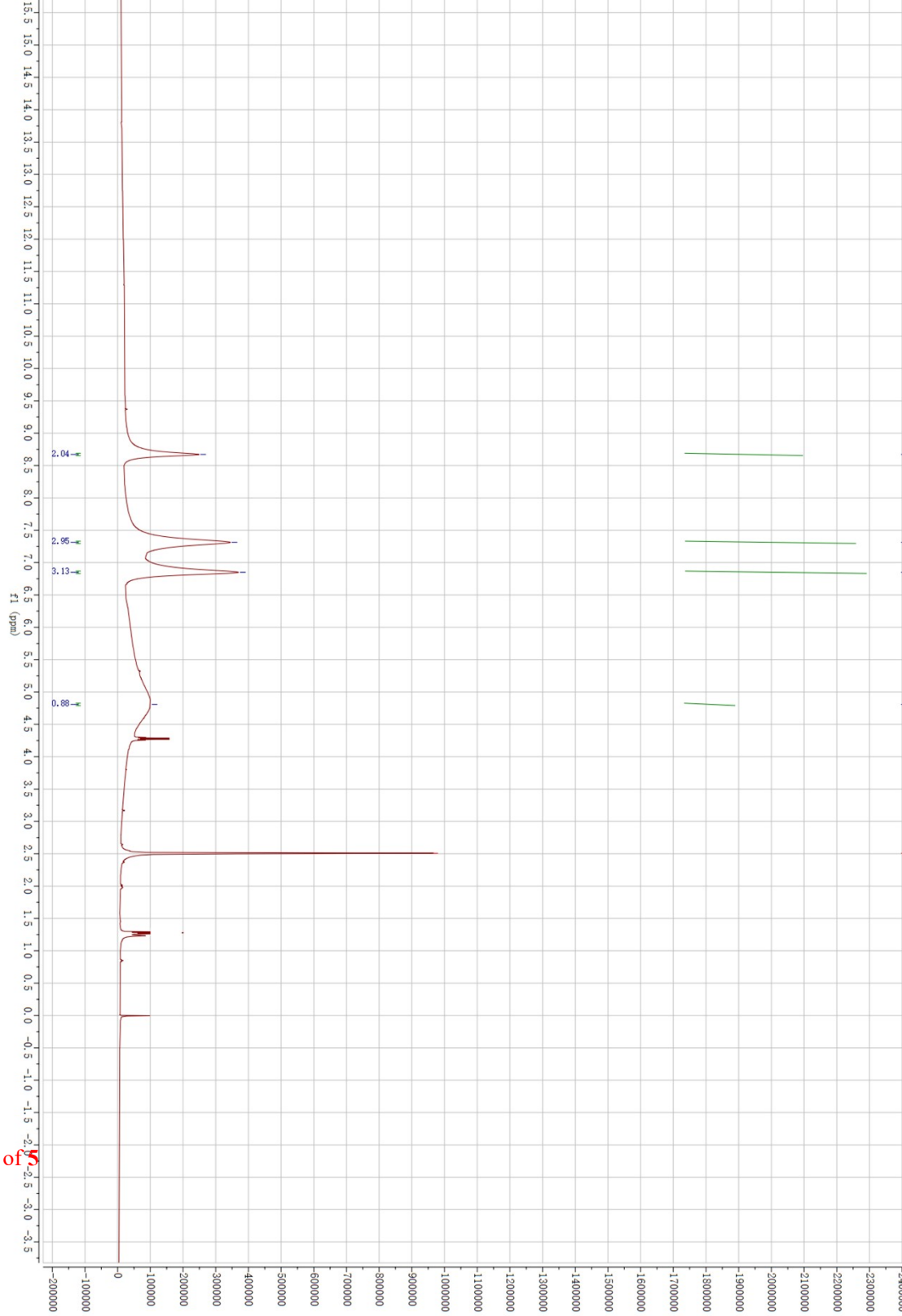


Figure S17 ^{1}H NMR of **5**

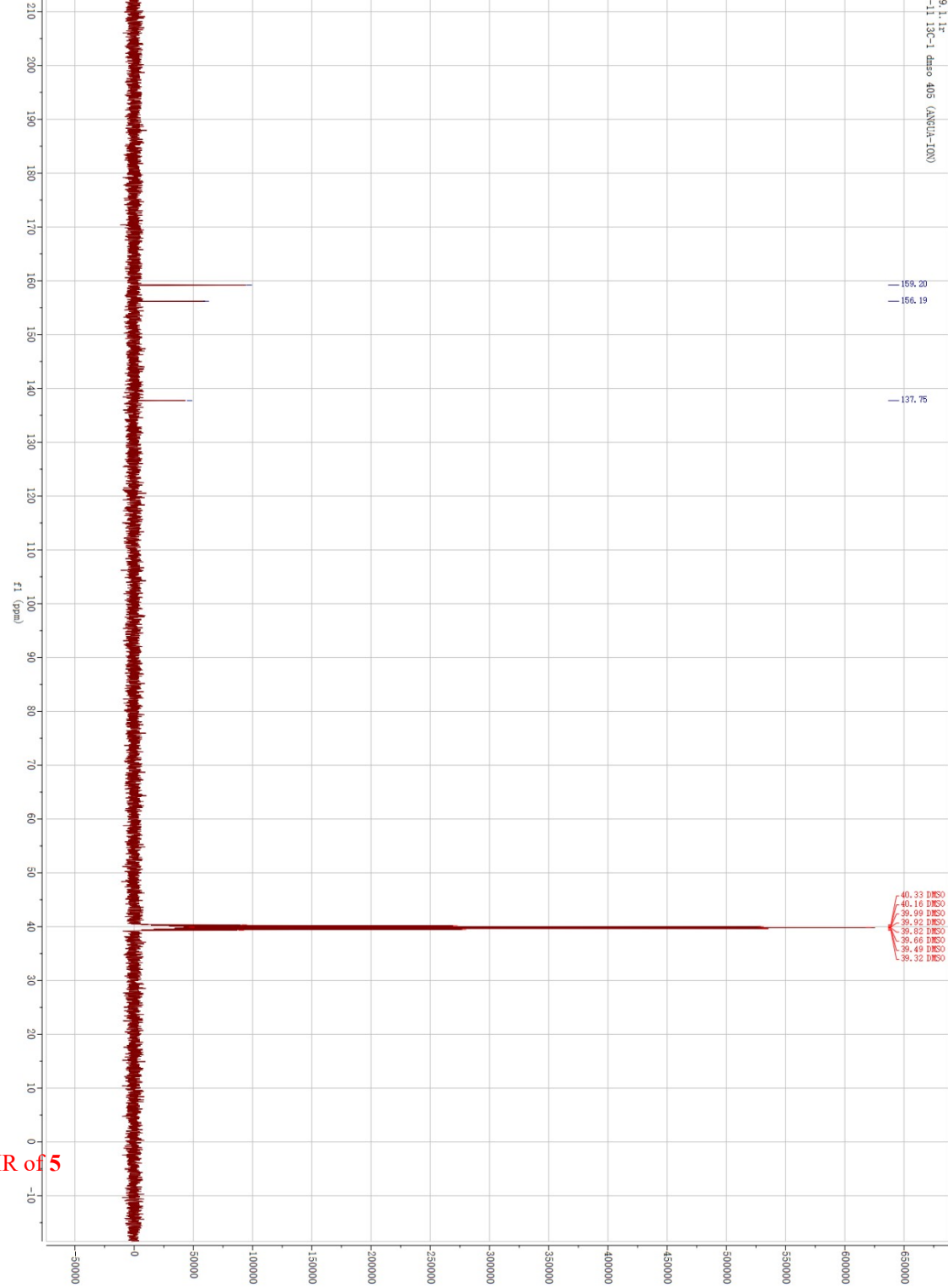


Figure S18 ^{13}C NMR of **5**

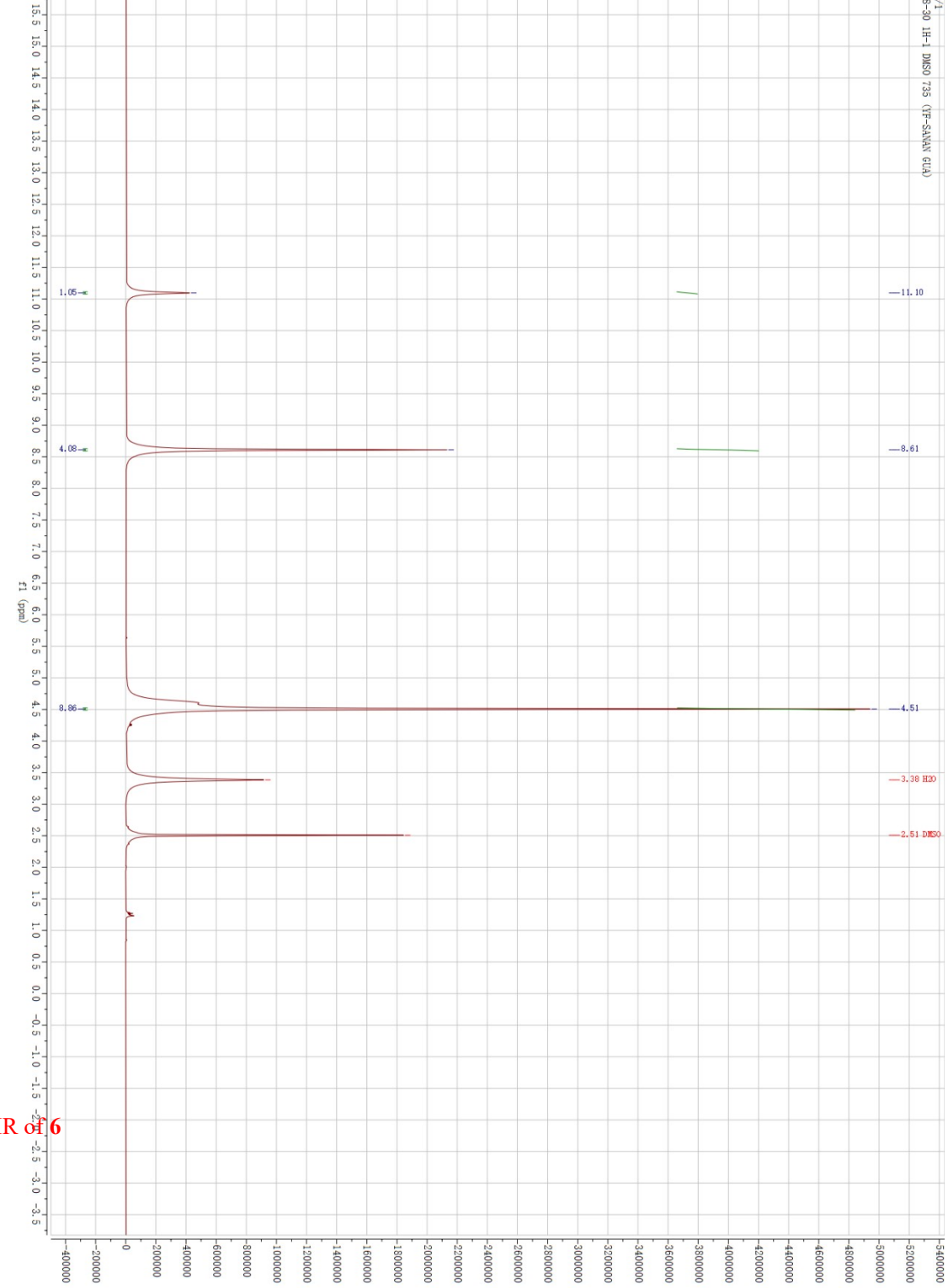


Figure S19 ^{1}H NMR of **6**

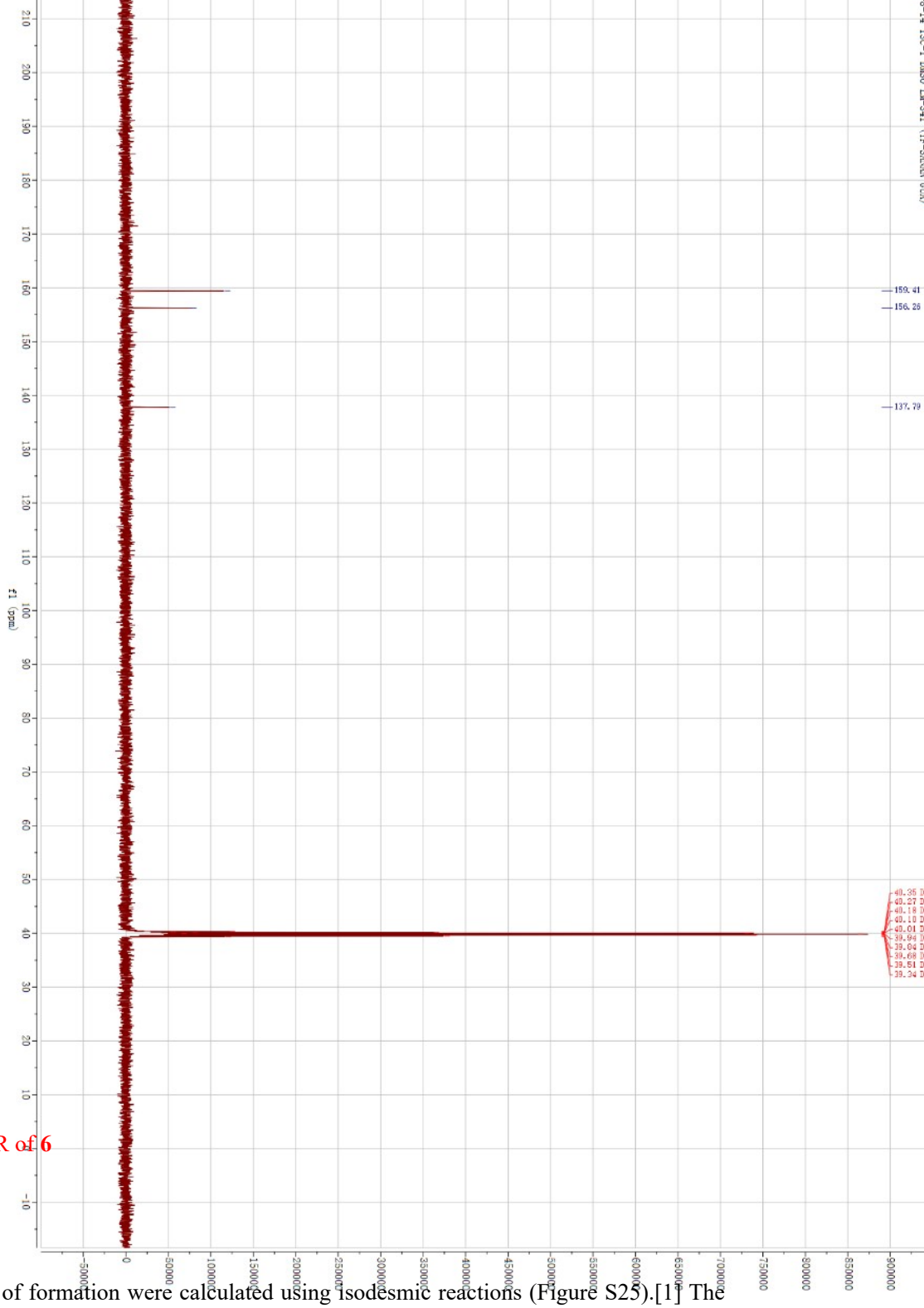


Figure S20 ^{13}C NMR of **6**

The gas phase heats of formation were calculated using isodesmic reactions (Figure S25).[1] The calculations were carried out using Gaussian 09 suite of programs,[2] at the B3LYP/6-31 G* level. And the solid state heats of formation were calculated using the equation 1.[3]

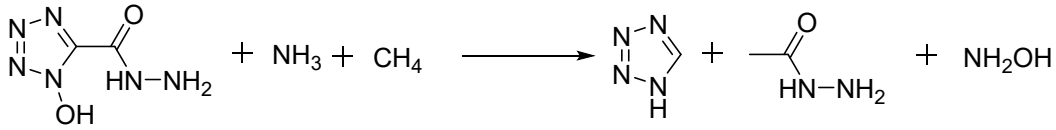


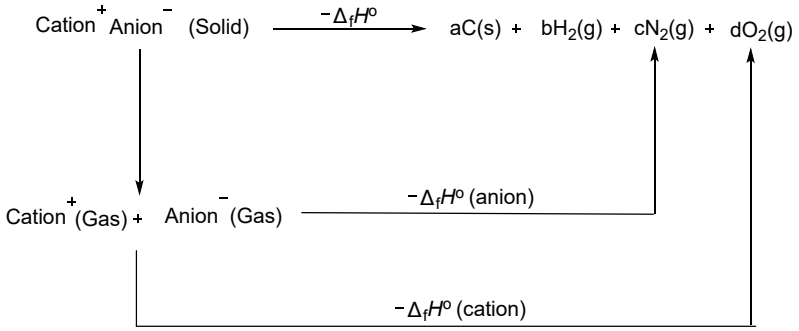
Figure S21 Isodesmic reaction of compound CHZTO.

The enthalpy of sublimation can be represented as eq (1) and on the basis of thepredicted electrostatic potential of a molecule.[4]

$$\Delta H_{sub} = a(SA)^2 + b\sqrt{\upsilon\sigma_{tot}^2} + c \qquad (1)$$

Here SA is the surface area of the 0.001 electrons bohr^{-3} isosurface of the electronic density of the compounds, $\upsilon\sigma_{tot}^2$ is derived from the molecular electrostatic potential calculation, and a, b, c are fitting parameters reported by Politzer et al.[4]

For energetic salts, the solid-phase heats of formation are calculated based on a Born-Haberenergy cycle (Figure S26).[5]



Scheme S1. Born-Haber Cycle for the formation of energetic salts.

$$\Delta Hf^{o}\ (salt, 298\ K) = \Delta Hf^{o}\ (cation, 298K) + \Delta Hf^{o}\ (anion, 298K) - \Delta HL \qquad (2)$$

where ΔHL is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al. [Eq. (3)]

$$\Delta HL = UPOT + [p(nM/2 - 2) + q(nX/2 - 2)]RT \qquad (3)$$

where nM and nX represent the nature of the ions, Mq+and Xp-, and are equal to 3 for monatomic ions, 5 for linear polyatomicions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} is as the follow:

$$U_{POT}\ [kJ\ mol^{-1}] = \gamma(\rho m/Mm)1/3 + \delta \qquad (4)$$

where ρm (g cm^{-3}) is the density of the salt, Mm is the formula mass of the ionic compound, and values for γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.8

Table S6. Calculated total energy (E_0), zero-point energy (*ZPE*), thermal correction to enthalpy (ΔH_T), and heats of formation (*HOF*) in gas state.

Compound	E_0 / a. u.	*ZPE* / kJ mol^{-1}	ΔH_T / a. u.	*HOF*/kJ mol^{-1}
CHZTO	-557.4035255	250.407	0.104526	416.71
CH_4	-40.5240195	118.22	0.048836	-74.60
NH_3	-56.5479476	90.67	0.038336	-45.87
CHZTO$^-$	-556.7936108	230.709	0.095234	464.66
$C_2N_2OH_6$	-264.5186001	237.659	0.097191	-20.80
NH_2OH	-131.7049237	105.77	0.044446	15.02

CN_4H_2	-258.2508991	123.262	0.051376	364.43
$N_2H_5^+$	-112.2045521	179.384	0.072618	808.59
$CN_5H_8^+$	-316.406198	325.075	0.132175	845.52
$CN_6H_9^+$	-371.5225205	399.552	0.157578	1515.09

Reference

(1) J. Zhang, H. D, F. Wang, *et al*. DFT Studies on a High Energy Density Cage Compound 4-Trinitroethyl-2,6,8,10,12-pentanitrohezaazaisowurtzitane. *J. Phys. Chem. A*, 2011, **24**, 6617-6621.

(2) M. J. Frisch, Gaussian 09. Revision a. 02, Gaussian, Inc., Wallingford CT, 2009.

(3) P. W. Atkins, Physical Chemistry. Oxford University Press, Oxford, U. K., 1982.

(4) P. J. Politzer, S. Murray, T. Brinck, P. Lan, Immunoanalysis of agrochemicals. ACS Sympsium Series 586, American Chemical Society, Washington, DC, 1994.

(5) H. D. B. Jenkins, D. Tudela, L. Glasser, Lattice Potential Energy Estimation for Complex Ionic Salts from Density Measurements, *Inorg. Chem.*, 2002, **9**, 2364-2367.