Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Design, synthesis and investigations of a series of energetic salts through the variation of amines and concentration of picrate-anion

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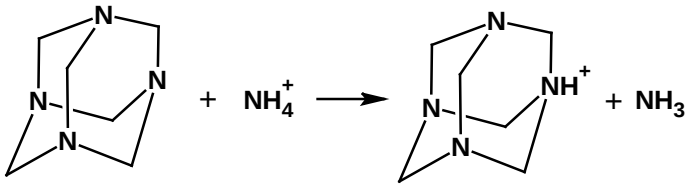
Table of Contents:

1. Computational details

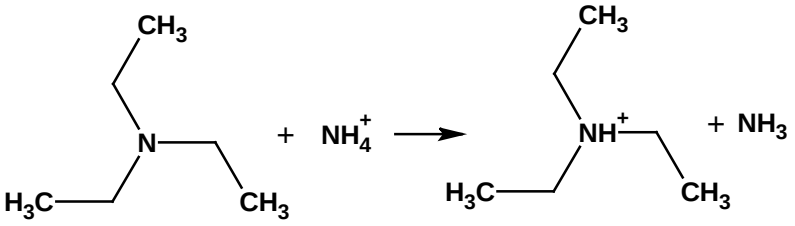
All computations were performed with Gaussian 09 package at B3PW91 method with 6-31G(d,p) basis set [1]. The structural parameters were allowed to be optimized and no constraints were imposed on molecular structure during optimization process. All optimized structures were characterized to the true local energy minima on potential energy surfaces without imaginary frequencies. The oxygen balance (OB) is used to indicate the degree to which an explosive can be oxidized and oxygen is needed in a molecule to oxidize it completely into their gaseous reaction products. OB is used in prediction of detonation velocity, detonation pressure, chemical energy of detonation, and decomposition products. The molecule is said to have a positive (negative) oxygen balance if it contains more (less) oxygen than is needed for complete combustion. OB (%) for an explosive containing the general formula $C_aH_bN_cO_d$ with molecular mass *M* can be calculated as,

$$\mathrm{OB}(\%) = \frac{(d - 2a - 0.5b)}{M} \mathrm{X}\, 1600 \qquad (1)$$

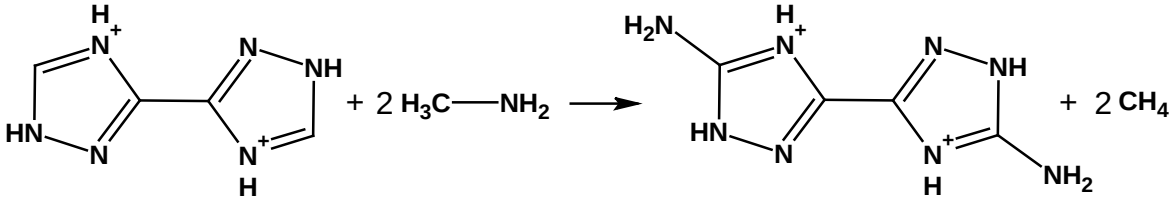
In previous studies, isodesmic reactions have been successfully employed to estimate the heats of formation (HOFs) from the total energies obtained from *ab initio* calculations [2-5]. Therefore, isodesmic reactions are designed in which the basic structural units were retained to minimize errors. The isodesmic reactions used for the prediction of HOF of cations are shown in Figure 1.



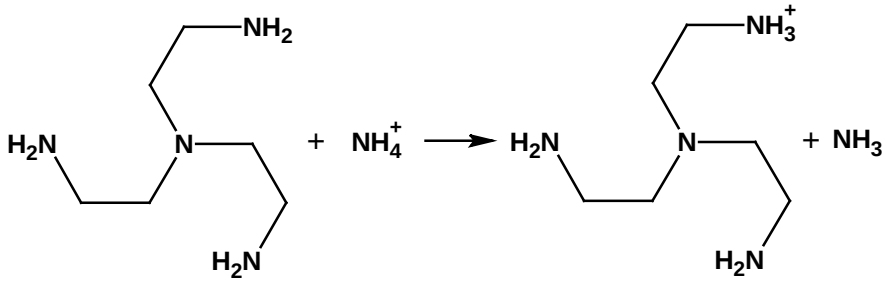
(a) 1,3,5,7-tetraazatricyclo[3.3.1.13,7]decan-1-ium (in salt 1)



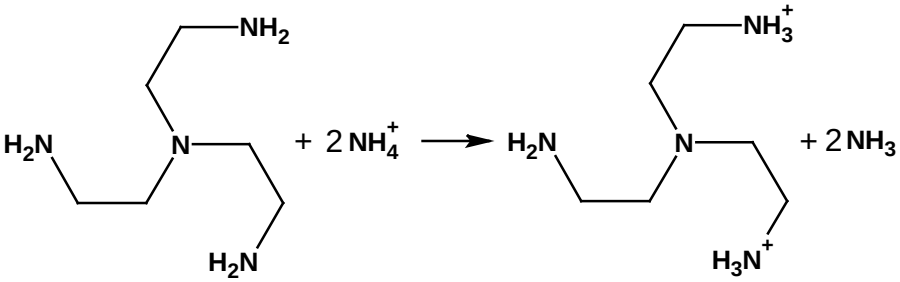
(b) N,N-diethylethanaminium (in salt 2)



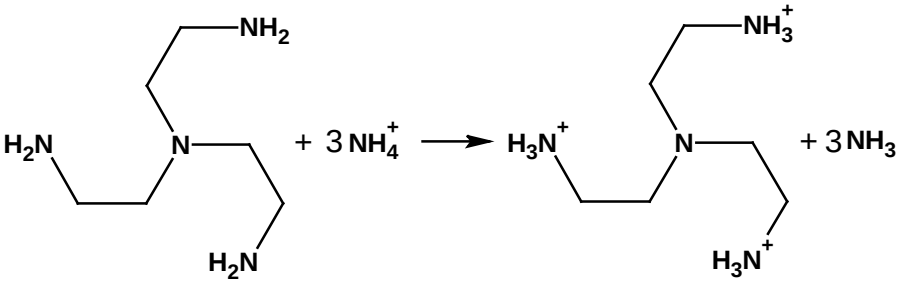
(c) 5,5'-diamino-1H,1'H-3,3'-bi-1,2,4-triazol-4-ium (in salt 4)



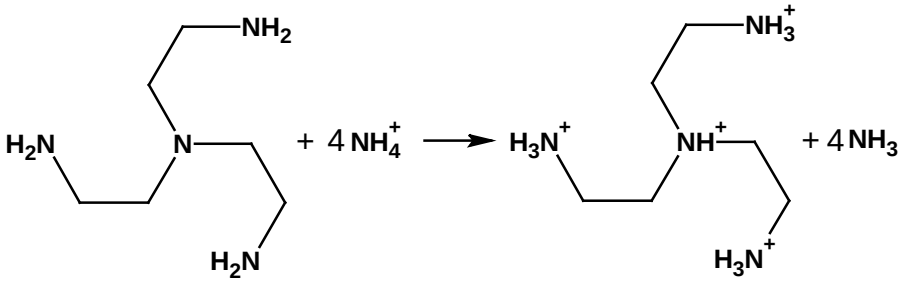
(d) 2-[bis(2-aminoethyl)amino]ethan-1-aminium (in salt 5)



(e) 2,2'-[(2-aminoethyl)azanediyl]di(ethan-1-aminium) (in salt 6)



(f) 2,2',2''-nitrilotri(ethan-1-aminium) (in salt 7)



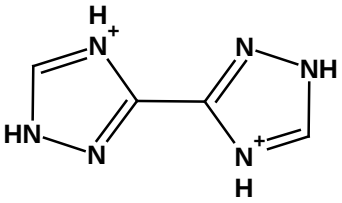
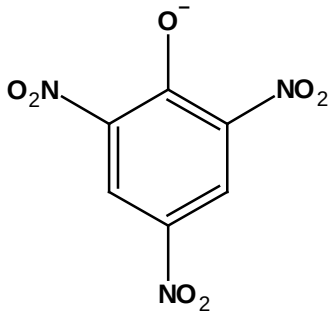
(g) N1,N1-bis(2-azaniumylethyl)ethane-1,2-bis(aminium) (in salt 8)

Figure 1. Isodesmic reactions (a-g) designed for the prediction of HOF of cations.

The total energy (E_0), zero point energy (ZPE), and thermal corrections (ΔH_T) for reference compounds selected in isodesmic reactions and for ionic species are listed in Table S1. Surface area, degree of balance between the positive and negative surface potentials and variability of the electrostatic potential are calculated using Multiwfn program [6].

Table S1. Total energy (E_0) at 298K for the cations and anions at the B3PW91/6-31G(d,p) level.

Cation	**E_0 (au)**	**ZPE (au)**	**H_T (au)**
1,3,5,7-tetraazatricyclo[3.3.1.13,7]decan-1-ium (in salt 1)	-454.840601	0.2126	0.0075
N,N-diethylethanaminium (in salt 2)	-292.489620	0.2219	0.0105
5,5'-diamino-1H,1'H-3,3'-bi-1,2,4-triazol-4-ium (in salt 4)	-594.307856	0.1605	0.0114
2-[bis(2-	-458.388656	0.2743	0.0145

aminoethyl)amino]ethan-1-aminium (in salt 5)			
2,2'-[(2-aminoethyl)azanediyl]di(ethan-1-aminium) (in salt 6)	-458.56677	0.2896	0.0145
2,2',2''-nitrilotri(ethan-1-aminium) (in salt 7)	-458.828012	0.3049	0.0145
N1,N1-bis(2-azaniumylethyl)ethane-1,2-bis(aminium) (in salt 8)	-458.961147	0.3168	0.0147
	-593.681372	0.1345	0.0111
NH_4^+	-56.833905	0.0499	0.0038
	-919.994191	0.1001	0.0137

Based on the Born–Haber cycle (shown in Figure 2), the heat of formation of an ionic compound can be simplified by subtracting the lattice energy of the salt (H_L) from the total heat of formation of salt *i.e.* sum of the heats of formation of the cation and anion as shown in equation (2).

HOF (salt, 298 K) = HOF (cation, 298 K) + HOF (anion, 298 K) - H_L (2)

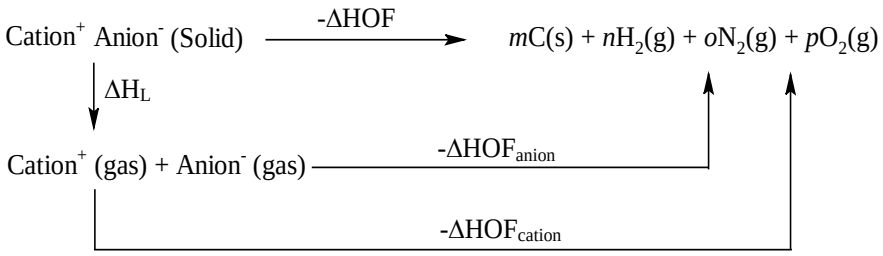


Figure 2. Born-Haber cycle for the formation of energetic salts.

Lattice potential energy is the energy associated with the process in which a crystalline solid lattice, M_pX_q is converted into its constituent gaseous ions, ${}_pM^{q+}$ (g) and ${}_qX^{p-}$ (g). The lattice energy can be predicted with reasonable accuracy by using Jenkins' equation (3) [7].

$$H_L = U_{POT} + [p(\frac{n_M}{2} - 2) + q(\frac{n_X}{2} - 2)]RT \quad (3)$$

where *nM* and *nX* depend on the nature of the ions M_p^+ and X_q^-, respectively, and are equal to 3 for monoatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. When lattice potential energy (U_{POT}), is incorporated and made part of a Born–Haber cycle, it needs to be converted into a lattice enthalpy term. This lattice enthalpy (H_L), involves correction of the U_{POT} term by an appropriate number of RT terms. The U_{POT} (kJ mol^{-1}) can be predicted from four different equations (4-7) as suggested by Jenkins et al. [8-10] using following equations,

$$U_{POT} = AI(\frac{2I}{V})^{1/3} \quad (4)$$

$$U_{POT} = B(I^4 \frac{\rho}{M})^{1/3} \quad (5)$$

$$U_{POT} = \gamma(\frac{\rho}{M})^{1/3} + \delta \quad (6)$$

$$U_{POT} = 2I[\alpha(V)^{-1/3} + \beta] \quad (7)$$

In above equations (4-7), I is the ionic strength factor, where $I = {}^{1}/_{2}\Sigma n_i z_i^2$. Here n_i is the number of ions in the formula unit having a charge z_i. For the salts with 3:1 charge ratio (cation:anion) listed in this work, the ionic strength, I=6. ρ is the density (g cm^{-3}), V is the estimated volume of ionic material (nm^3), and M is the chemical formula mass of the ionic material (g mol^{-1}). The coefficients A (121.4 kJ mol^{-1}), B (1291.7 kJ mol^{-1}), γ (2342.6·I kJ mol^{-1}.cm), δ (55.2·I kJ mol^{-1}) and g*eneralised parameters* α and β for salts (*3*:*1*) are 138.7 kJ mol^{-1}.nm and 27.6 kJ mol^{-1}, respectively. Equation (4) is normally employed for salts likely to have lattice energy greater than 5000 kJ mol^{-1} but it seems to work quite well in this case and for these materials. Calculated lattice potential energies and lattice enthalpies are summarized in Table S2.

Table S2. Energetic properties of salts (1-8).

Salt	HOF_c [a]	HOF_a [b]	U_{Pot} [c]	H_L [d]	Q [e]
1	797	-458	426	431	1051
2	435	-458	425	430	963
3	2084	-458	1413	1425	1328
4	1818	-458	1328	1340	991
5	619	-458	418	423	1012
6	1477	-458	1306	1319	1004
7	2589	-458	1930	1942	1151
8	3802	-458	3262	3274	1098

[a]Heat of formation of cation (kJ mol^{-1}). [b]Heat of formation of anion (kJ mol^{-1}). [c]Lattice potential energy (kJ mol^{-1}). [d]Lattice energy (kJ mol^{-1}). [e]Chemical energy of detonation (cal g^{-1}).

Previously, Hofmann [11] reported the average atom volume of various elements including the thermal expansion and similar had been used in the equation (8) for the prediction of densities.

$$Density\ (\rho) = \frac{MW_{explosive}}{(aV_C + bV_H + cV_N + dV_O)} X\ 0.00164 \qquad (8)$$

Where a, b, c, and d are the number of carbon, hydrogen, nitrogen and oxygen atoms in the molecular structure of explosive, respectively. While, V_C, V_H, V_N, and V_O represent the volumes of corresponding atoms and summarized in Table S3. Density estimation for compounds having strong H–bonding, van der Waals or electrostatic interactions is more complex and challenging. The presence of two or more $–NH_2$ or $–NH_3^+$ groups in explosive compound improves the density of the corresponding compound. Hence, along with elemental composition, the contribution from these functional groups in equation (8) is to be accounted [12] and can be optimized as:

$$Density\ (\rho) = \frac{MW_{explosive}}{(aV_C + bV_H + cV_N + dV_O)} X\ 0.00175 \qquad (9)$$

Table S3. The volume of C, H, N, and O elements at 298 K.

Element	**Volume (nm^3)**
C	0.01387
H	0.00508
N	0.0118
O	0.01139

The empirical Kamlet-Jacobs [13-15] equations were employed to estimate the values of detonation velocity (*D*) and detonation pressure (*P*) for the high energy materials containing C, H, O and N as following equations:

$$D = 1.01(NM^{0.5}Q^{0.5})^{0.5}(1+1.30\rho) \quad (10)$$

$$P = 1.55\rho^2 NM^{0.5}Q^{0.5} \quad (11)$$

where in above equations D is detonation velocity (km/s), P is detonation pressure (GPa), N is moles of gaseous detonation products per gram of explosives, M is average molecular weights of gaseous products, Q is chemical energy of detonation (cal/g) defined as the difference of the HOFs between products and reactants, and ρ is the density of explosive (g/cm^3).

2. The electrostatic potential

Politzer et al.[16-19] found that the heats of sublimation can correlate well with the molecular surface area and electrostatic interaction index $v\sigma^2_{tot}$ of energetic compounds. The electrostatic potential V(r) that is produced in the surrounding space around a molecule by its nuclei and electrons is given by equation (12):

$$V(\mathrm{r}) = \sum_{\mathrm{A}} \frac{\mathrm{Z_A}}{|\mathrm{R_A} - \mathrm{r}|} - \int \frac{\rho(\mathrm{r}')\mathrm{dr}'}{|\mathrm{r}' - \mathrm{r}|} \quad (12)$$

In above equation, Z_A is the charge on nucleus A, located at R_A, and ρ(r) is the electronic density. V(r) is a physical observable, which can be determined experimentally by diffraction methods [20, 21] as well as computationally. The sign and magnitude of V(r) at any point **r** are the net result of the positive and negative contributions of the nuclei and the electrons, respectively. V(r) is commonly computed on an appropriate outer surface of the molecule and following the suggestion of Bader et al., [22] the 0.001 au (electrons/bohr^3) contour of the molecule's electronic density is frequently taken to be the surface. The positive and negative extrema are just two of several quantities that help to characterize the detailed features of the electrostatic potential on a molecular surface. The calculated electrostatic potential on this

surface is characterized in terms of its average deviation *Π* and its total variances σ^2_{tot}; these are defined by equations (13) and (14):

$$\Pi = \frac{1}{t}\sum_{i=1}^{t} | V_s(r_i) - \overline{V}_s | \tag{13}$$

$$\sigma^2_{tot} = \sigma^2_+ + \sigma^2_- = \frac{1}{m}\sum_{j=1}^{m}[V_s^+(r_j) - \overline{V}_s^+]^2 + \frac{1}{n}\sum_{k=1}^{n}[V_s^-(r_k) - \overline{V}_s^-]^2 \tag{14}$$

$V(r_i)$ is the value of V(r) at any point $\mathbf{r}_i$ on the surface, and $\overline{V}_s$ is the average over the entire surface. The variances σ^2_+, σ^2_-, and σ^2_{tot} reflect the strengths and variabilities of the positive, negative and overall surface potentials [23]. Due to the terms being squared, they emphasize particularly the local extrema, the V_S,max and V_S,min (there may be several of each). Finally, the parameter *ν* is a measure of the degree of balance between the positive and negative potentials; when $\sigma^2_+ = \sigma^2_-$, *ν* has its maximum value of 0.25. In these summations, t is the total number of points on the surface grid and m and n are the numbers of points at which $V_S(r)$ is positive, $V_s^+(r_j)$ and negative, $V_s^-(r_k)$, respectively. $\overline{V}_s$, $\overline{V}_s^+$, $\overline{V}_s^-$, and *ν* (electrostatic balance parameter) are computed by appropriate summations over a finely spaced grid covering the entire molecular surface and defined in equations (15-18):

$$\overline{V}_s = \frac{1}{t}\sum_{i=1}^{t} V_s(r_i) \tag{15}$$

$$\overline{V}_s^+ = \frac{1}{m}\sum_{j=1}^{m} V_s^+(r_j) \tag{16}$$

$$\overline{V}_s^- = \frac{1}{n}\sum_{k=1}^{n} V_s^-(r_k) \tag{17}$$

$$\nu = \frac{\sigma^2_+\sigma^2_-}{(\sigma^2_+ + \sigma^2_-)^2} \tag{18}$$

3. X-ray crystallography

Suitable single crystals of all six compounds were carefully picked under a polarizing microscope and glued to a very thin glass fiber with the help of cyanoacrylate (superglue) adhesive. The single-crystal X-ray data collection was carried out at Bruker D8 Quest PHOTON II diffractometer with monochromatic Mo $K\alpha$ radiation (λ = 0.71073 Å) at 296(2) K operating at 50 kV voltage and 20 mA current by using ω and ϕ scan. The resulted data was reduced with the help of APEX3 while SAINTPLUS [24] program was used for integration of diffraction profiles. The absorption correction (multiscan) was carried out through SADABS program [25]. The crystal structure was initially solved by SIR 92 [26] and refined thoroughly by full matrix least square method on F^2 using SHELXL-1997 [27] existing in the WinGx suit package of programs (Version 1.63.04a) [28]. All the non-hydrogen atoms were positioned successfully from Fourier maps and refined with anisotropic displacement parameters at the final cycles. The hydrogen atoms were fixed at calculated positions and included in the refinement process using riding model associated with isotropic thermal parameters. The highly disordered solvent molecules were treated with SQUEEZE routine of PLATON multipurpose crystallographic software was used to remove their diffraction contributions [29]. The amine-moiety is distorted in the salt of 5, which shows few extra alerts in the time of CIF checking. The detailed explanations of data collection, refined crystal structure and parameters for all six compounds are summarized in Table 1. The various types of hydrogen bonds are displayed in Table S1-S6. The supplementary crystallographic files are deposited with the CCDC numbers 1972972-1972977 for the Salts 1a, 1b, 2, 5, 7a and 7b, respectively by free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

Table S4: Selected Hydrogen-Bond Lengths (A˚) and Angles (°) for Salt 1a.

Sl. No.	Donor --- H....Acceptor	D – H (A˚)	H... A (A˚)	D.... A (A˚)	D -- H.... A (°)
1.	N(11) --H(11) ..O(4)$^{\#1}$	0.90(4)	2.15(4)	2.873(4)	137(4)
2.	N(11) --H(11) ..O(7)$^{\#1}$	0.90(4)	1.93(4)	2.666(3)	137(4)
3.	C(9) --H(9A) ..O(1)$^{\#2}$	0.97	2.42	3.363(5)	164
4.	C(9) --H(9B) ..O(4)$^{\#3}$	0.97	2.46	3.411(5)	168
5.	C(11) --H(11A) ..O(3)$^{\#3}$	0.97	2.53	3.480(5)	165
6.	C(12) --H(12B) ..O(6)$^{\#4}$	0.97	2.53	3.481(5)	166
$^{\#}$Symmetry codes: (1): 1-x,-1/2+y,1-z; (2): -x,1/2+y,-z; (3): 1-x,1/2+y,1-z; (4): x,-1+y,z					

Table S5: Selected Hydrogen-Bond Lengths (A˚) and Angles (°) for Salt 1b.

Sl. No.	Donor --- H....Acceptor	D – H (A˚)	H... A (A˚)	D.... A (A˚)	D -- H.... A (°)
1.	N(4) --H(4) ..O(6)$^{\#1}$	0.91	2.30	2.896(4)	122
2.	N(4) --H(4) ..O(7)$^{\#1}$	0.91	1.83	2.665(3)	152
3.	C(12) --H(12A) ..O(6)$^{\#2}$	0.97	2.51	3.400(4)	152
4.	C(12) --H(12B) ..O(3)$^{\#3}$	0.97	2.42	3.375(5)	168
$^{\#}$Symmetry codes: (1): 1-x,1/2+y,1/2-z; (2): 1-x,-1/2+y,1/2-z; (3): -x,-1/2+y,1/2-z					

Table S6: Selected Hydrogen-Bond Lengths (A˚) and Angles (°) for Salt 2.

Sl. No.	Donor --- H....Acceptor	D – H (A˚)	H... A (A˚)	D.... A (A˚)	D -- H.... A (°)
1.	N(1) --H(1) ..O(1)$^{\#1}$	0.91	1.89	2.787(6)	167
2.	N(8) --H(8) ..O(8)$^{\#2}$	0.91	1.86	2.770(6)	175
3.	C(3) --H(3B) ..O(1)$^{\#1}$	0.96	2.60	3.301(14)	131
4.	C(3) --H(3B) ..O(2)$^{\#1}$	0.96	2.58	3.477(19)	154
5.	C(5) --H(5B) ..O(10)$^{\#3}$	0.96	2.59	3.512(13)	162
6.	C(6) --H(6B) ..O(12)$^{\#1}$	0.97	2.59	3.269(12)	128
7.	C(19) --H(19A) ..O(14)$^{\#2}$	0.96	2.53	3.477(10)	169
8.	C(20) --H(20B) ..O(4)$^{\#2}$	0.97	2.43	3.333(8)	154

9.	C(22) --H(22A) ..O(4)[#4]	0.97	2.58	3.424(9)	145
10.	C(23) --H(23B) ..O(12)[#5]	0.96	2.58	3.491(9)	159
[#]Symmetry codes: (1): 1/2-x,y,-1/2+z; (2): 1/2+x,1-y,z; (3): -x,2-y,-1/2+z; (4): 1/2+x,-y,z; (5): x,-1+y,z					

Table S7: Selected Hydrogen-Bond Lengths (A˚) and Angles (°) for Salt 5.

Sl. No.	**Donor --- H....Acceptor**	**D – H (A˚)**	**H... A (A˚)**	**D.... A (A˚)**	**D -- H.... A (°)**
1.	N(4) --H(4C) ..N(5)	0.89	2.45	3.142(9)	135
2.	N(5) --H(5A) ..N(4)	0.86	2.44	3.142(9)	140
3.	N(5) --H(5A) ..N(7)	0.86	2.45	2.739(8)	100
4.	N(5) --H(5B) ..O(1)[#1]	0.86	2.35	2.976(8)	130
5.	N(5) --H(5B) ..N(6)[#2]	0.86	2.28	2.850(9)	124
6.	N(6) --H(6B) ..N(5)[#3]	0.86	2.04	2.850(9)	156
7.	C(7) --H(7B) ..O(3)[#4]	0.97	2.28	3.246(11)	173
[#]Symmetry codes: (1): -1/2+x,1/2-y,-z; (2): -x,1/2+y,1/2-z; (3): -x,-1/2+y,1/2-z; (4): 1-x,1/2+y,1/2-z					

Table S8: Selected Hydrogen-Bond Lengths (A˚) and Angles (°) for Salt 7a.

Sl. No.	**Donor --- H....Acceptor**	**D – H (A˚)**	**H... A (A˚)**	**D.... A (A˚)**	**D -- H.... A (°)**
1.	N(11) --H(11) ..O(9)[#1]	0.89	2.45	2.886(4)	111
2.	N(11) --H(11A) ..O(14)[#1]	0.89	2.02	2.898(4)	167
3.	N(11) --H(11B) ..O(11)[#2]	0.89	2.17	3.040(4)	166
4.	N(11) --H(11C) ..O(1)[#3]	0.89	2.28	2.854(6)	122
5.	N(11) --H(11C) ..O(7)[#3]	0.89	2.12	2.983(4)	164
6.	N(12) --H(12A) ..O(5)[#3]	0.89	2.30	2.792(4)	114
7.	N(12) --H(12A) ..O(7)[#3]	0.89	2.02	2.895(4)	167
8.	N(12) --H(12B) ..O(2)[#4]	0.89	2.19	2.978(4)	148
9.	N(12) --H(12C) ..O(10)[#1]	0.89	2.39	2.761(4)	105
10.	N(12) --H(12C) ..O(14)[#1]	0.89	1.96	2.849(3)	177
11.	N(13) --H(13B) ..O(22)	0.89	2.50	3.107(6)	126
12.	N(13) --H(13B) ..O(21)[#5]	0.89	2.19	2.931(5)	140
13.	N(13) --H(13C) ..O(22)[#5]	0.89	1.89	2.765(5)	167

14.	N(13) --H(13D) ..O(20)[#6]	0.89	2.12	2.979(6)	162
15.	O(22) --H(22) ..O(21)[#5]	0.82	1.86	2.628(5)	155
16.	C(22) --H(22A) ..O(9)[#1]	0.97	2.55	3.156(5)	121
17.	C(23) --H(23A) ..O(5)[#3]	0.97	2.60	3.214(5)	122
18.	C(23) --H(23B) ..O(13)[#3]	0.97	2.59	3.240(5)	125
[#]Symmetry codes: (1): 1-x,-y,1-z; (2): 2-x,-y,1-z; (3): 1-x,1-y,1-z; (4): -x,1-y,1-z; (5): 1-x,1-y,-z; (6): 2-x,1-y,-z					

Table S9: Selected Hydrogen-Bond Lengths (A˚) and Angles (°) for Salt 7b.

Sl. No.	**Donor --- H....Acceptor**	**D – H (A˚)**	**H... A (A˚)**	**D.... A (A˚)**	**D -- H.... A (°)**
1.	N(10) --H(10A) ..O(15)[#1]	0.89	2.09	2.844(3)	142
2.	N(10) --H(10A) ..O(20)[#1]	0.89	2.13	2.859(3)	139
3.	N(10) --H(10B) ..O(1)[#1]	0.89	2.13	2.986(3)	160
4.	N(10) --H(10B) ..O(23)[#1]	0.89	2.57	3.139(3)	123
5.	N(10) --H(10C) ..O(23)	0.89	1.88	2.768(3)	172
6.	N(10) --H(10C) ..O(2)[#1]	0.89	2.59	3.011(3)	110
7.	N(11) --H(11A) ..O(22)[#2]	0.89	2.23	2.952(3)	138
8.	N(11) --H(11A) ..O(13)[#3]	0.89	2.31	3.025(3)	137
9.	N(11) --H(11B) ..O(15)[#2]	0.89	2.05	2.890(3)	156
10.	N(11) --H(11C) ..O(1)[#2]	0.89	2.28	2.867(3)	123
11.	N(11) --H(11C) ..O(6)[#2]	0.89	2.42	3.000(3)	123
12.	N(11) --H(11C) ..O(9)	0.89	2.40	2.979(3)	123
13.	N(12) --H(12A) ..O(8)[#4]	0.89	2.13	3.018(3)	175
14.	N(12) --H(12B) ..O(17)	0.89	2.55	3.057(3)	117
15.	N(12) --H(12B) ..N(13)	0.89	2.49	2.835(3)	103
16.	N(12) --H(12C) ..O(22)[#3]	0.89	1.96	2.802(3)	157
17.	O(23) --H(23A) ..O(1)	1.09(6)	1.84(7)	2.759(3)	140(5)
18.	O(23) --H(23A) ..O(6)	1.09(6)	2.20(6)	3.097(3)	138(5)
19.	O(23) --H(23A) ..N(3)	1.09(6)	2.55(7)	3.393(3)	134(5)
20.	O(23) --H(23B) ..O(15)	0.78(4)	2.55(4)	3.123(3)	132(4)
21.	O(23) --H(23B) ..O(16)	0.78(4)	2.50(4)	3.110(4)	136(4)
22.	O(23) --H(23B) ..O(2)[#1]	0.78(4)	2.44(4)	2.837(3)	113(4)

23.	C(042) --H(04A) ..O(12)[#5]	0.97	2.60	3.441(4)	145
24.	C(19) --H(19A) ..O(11)[#5]	0.97	2.48	3.152(3)	126
[#]Symmetry codes: (1): 3/2-x,1/2+y,1/2-z; (2): x,1+y,z; (3): 1/2-x,1/2+y,1/2-z; (4): 1/2-x,-1/2+y,1/2-z; (5): 1/2+x,3/2-y,1/2+z					

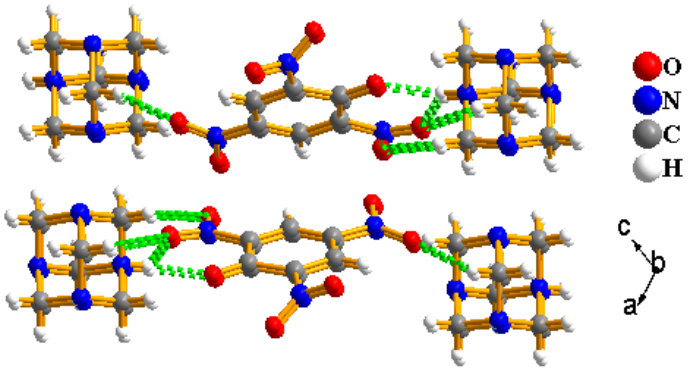


Figure S3. Representation of hydrogen bonding interactions (green doted lines) in **1a.**

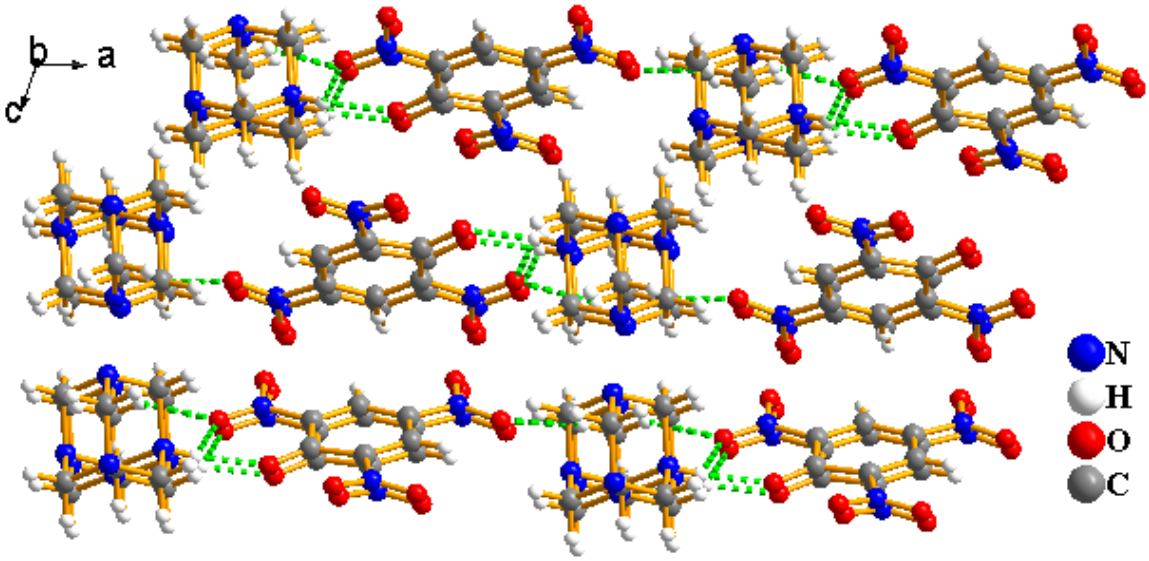


Figure S4. Illustration of various hydrogen bonding interactions (green doted lines) in **1b**.

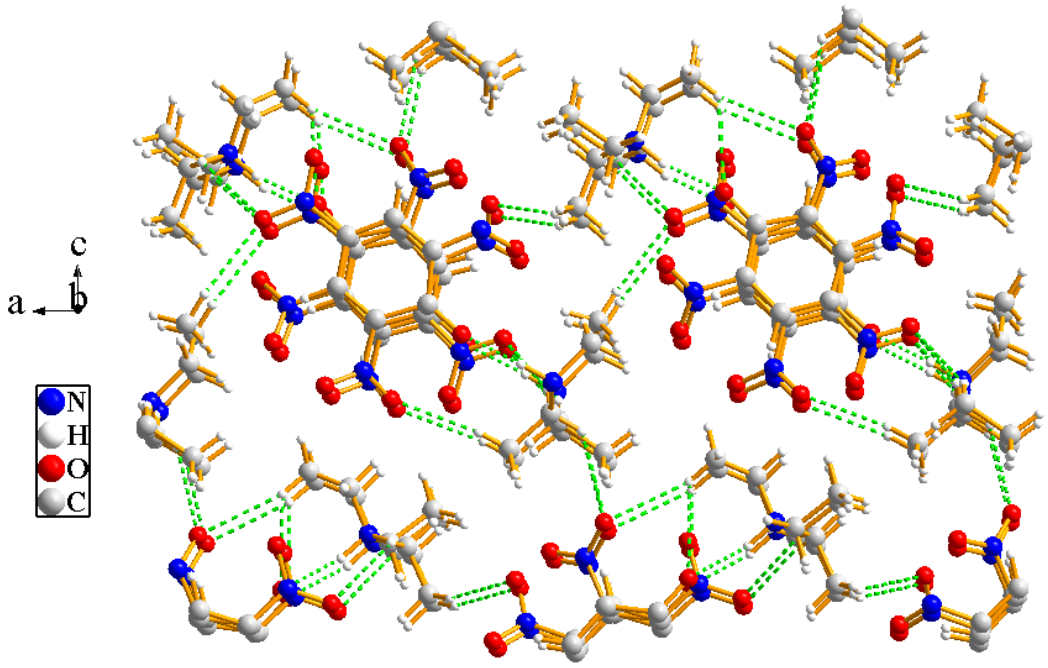


Figure S5. Hydrogen bonding interactions (green dotted line) present in **2**.

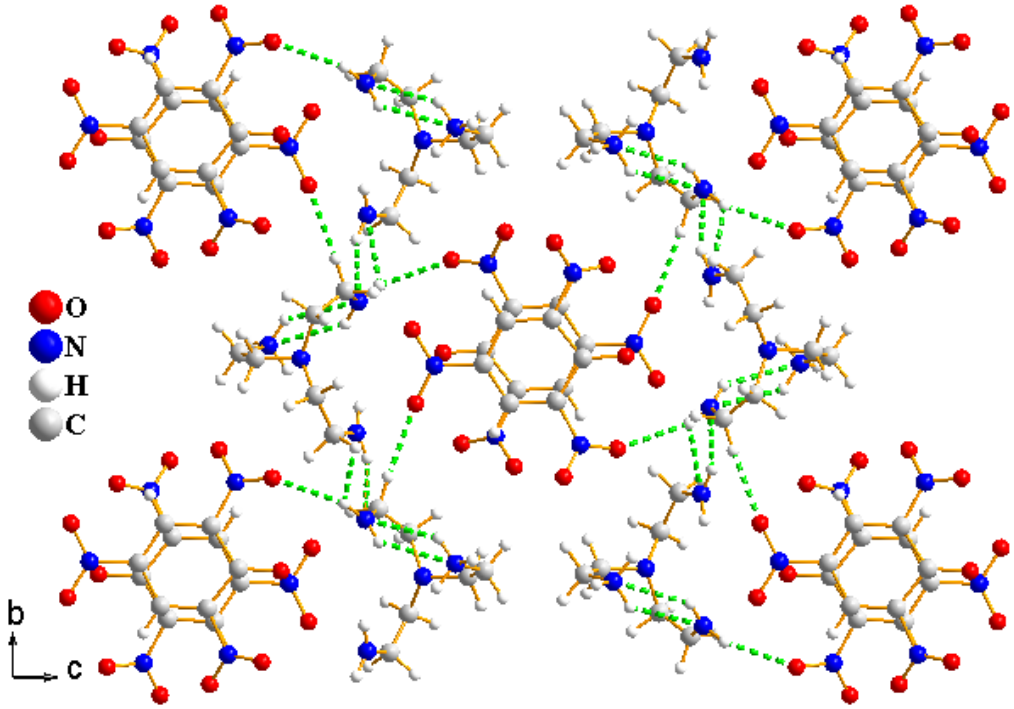


Figure S6. Various types of strong hydrogen bonds (green dotted lines) in **5**.

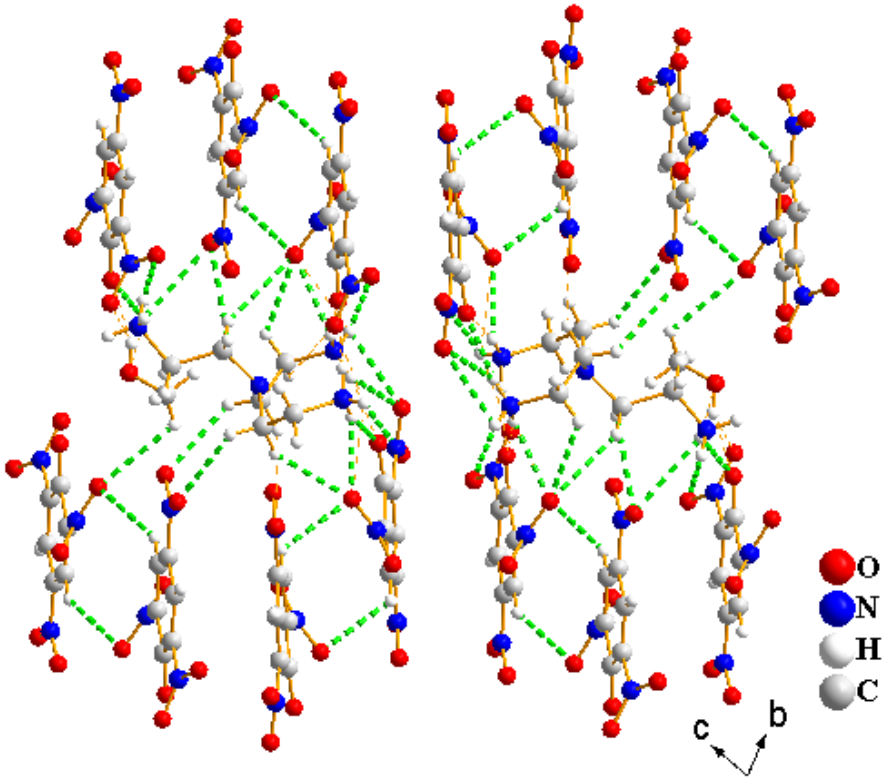


Figure S7. Hydrogen bonding interactions present (green doted lines) in **7a**.

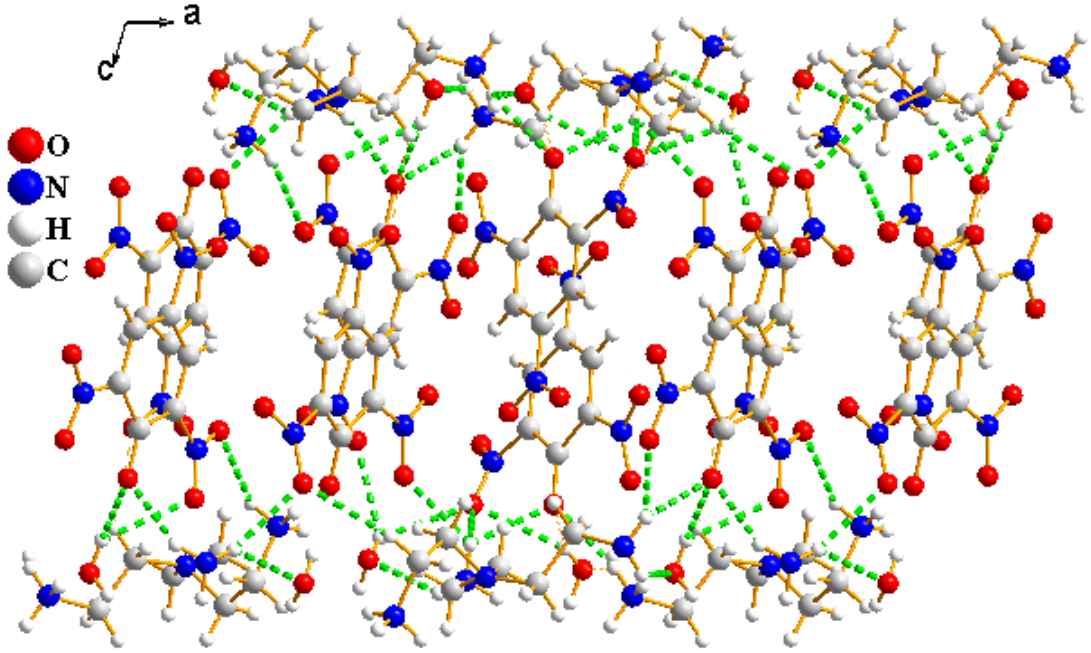


Figure S8. Various types of hydrogen bonding interactions (green doted lines) present in **7b**.

4. Hirshfeld surface analysis

To acquire some important relationship between structural behavior and physical properties, Hirshfeld surface maps and 2D fingerprint plots for all the salts are also analyzed using the Crystal Explorer [30-32]. We can find the percentage contribution of various intermolecular interactions in the crystals due to close contacts of the atoms as the similar studies are also performed with picrate salts [33]. The comparative % contributions to the Hirshfeld surface maps for different close intermolecular contacts in salts 1a, 1b, 2, 5, 7a, and 7b are given in Figure S9. The hydrogen bond characteristic can be seen in all salts as a pair of spikes at the bottom left of the fingerprint plot. In salt 1a and 1b, contacts are linked with O···H interactions of 43.5 and 38.7 %, respectively (Figures S10-S13). The interactions involving hydrogen atoms are H···C [12% in 1a; 8.4% in 1b], H···H [18.1% in 1a; 21% in 1b] and H···N [9.5% in 1a; 10.7% in 1b]. In salt 2, 54.1% contacts in the total Hirshfeld surface area are associated with O···H interactions, while 34.2% contacts are linked with H···H interactions (Figures S14, S15). Similarly, salt 5 shows 49.3 % contacts with O···H interactions and 33.2 % contacts with H···H interactions in the total Hirshfeld surface area (Figures S16, S17). The O···H interactions show a major contribution in crystals 7a and 7b showing 60.5 and 55.5 % intermolecular contacts, respectively. In 7a, H···H and O···O contacts comprise 9 and 10.9 % of the Hirshfeld surface area (Figures S18, S19), whereas the contacts are 9.3 and 10.4 % in the salt 7b (Figures S20, S21).

Table S10. Relative % contributions to the Hirshfeld surface area for the various close intermolecular contacts in salts 1a, 1b, 2, 5, 7a, and 7b.

Salt	Intermolecular contacts (%)									
	C···H or H···C	H···H	H···O or O···H	H···N or N···H	O···O	C···N or N···C	C···C	C···O or O···C	O···N or N···O	N···N
1a	12	18.1	43.5	9.5	7.5	0.8	0	4.2	3.8	0.7
1b	8.4	21	38.7	10.7	7	0	0	9.1	5.2	0
2	0.4	34.2	54.1	1.5	2.3	0.2	4.4	0.8	2.2	0
5	0.6	33.2	49.3	2.2	2.5	0.2	6.6	1.2	4.1	0
7a	2.8	9	60.5	0.9	10.9	1.8	2.8	5.9	5.4	0
7b	4.9	9.3	55.5	1.3	10.4	0	0	11.2	7.3	0.1

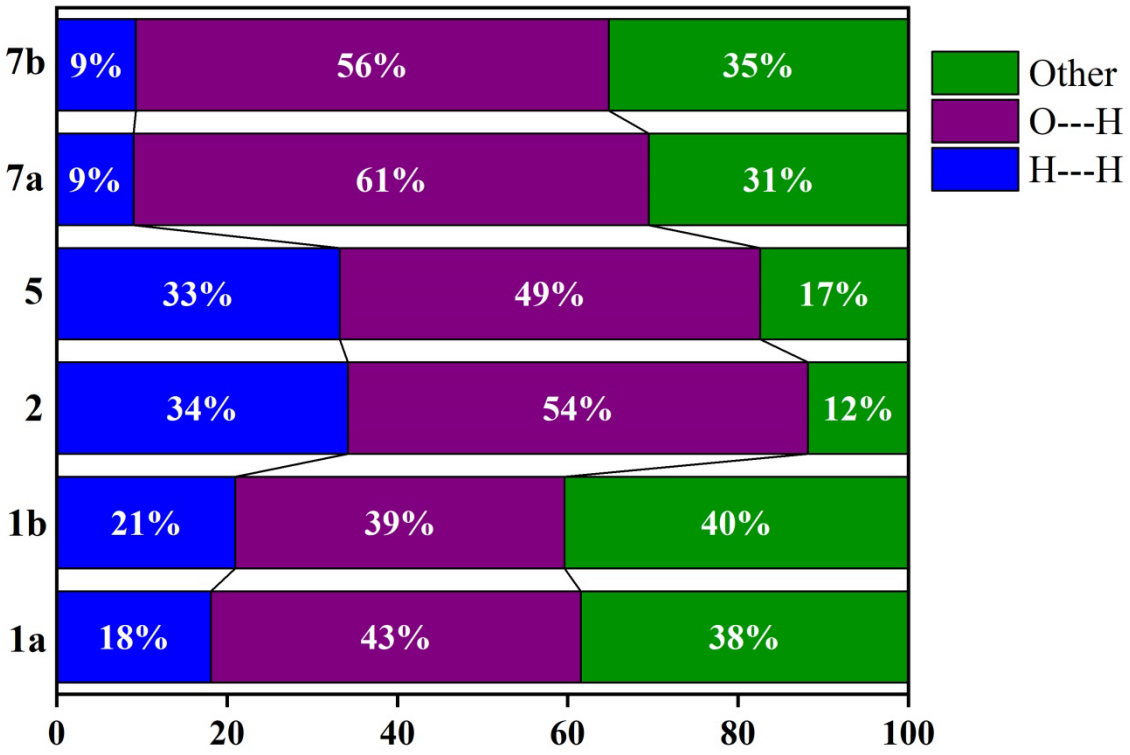


Figure S9. Relative % contribution to the Hirshfeld surface maps for various close intermolecular interactions in salts 1a, 1b, 2, 5, 7a, and 7b, respectively.

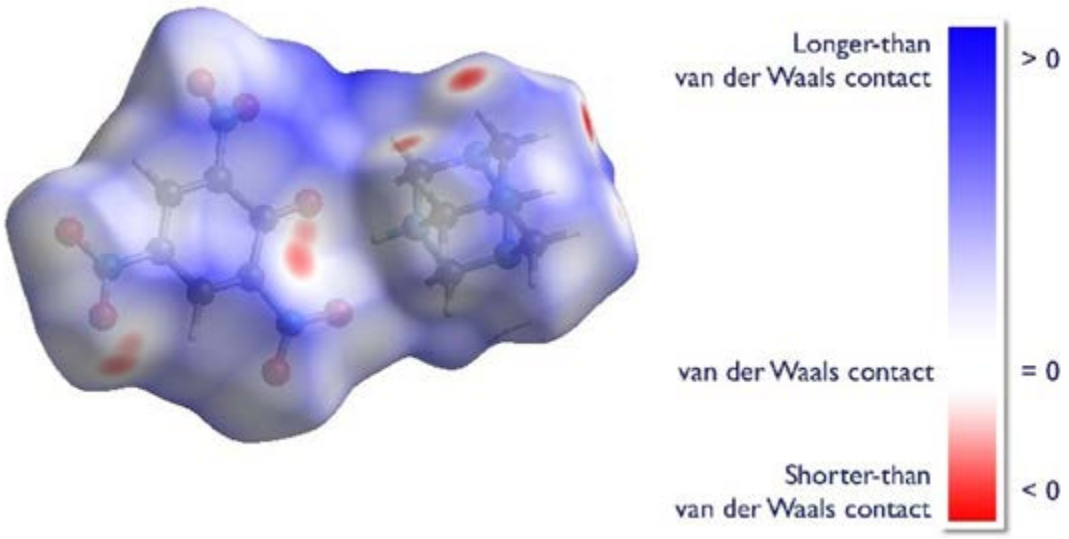


Figure S10. Hirshfeld surface of 1a.

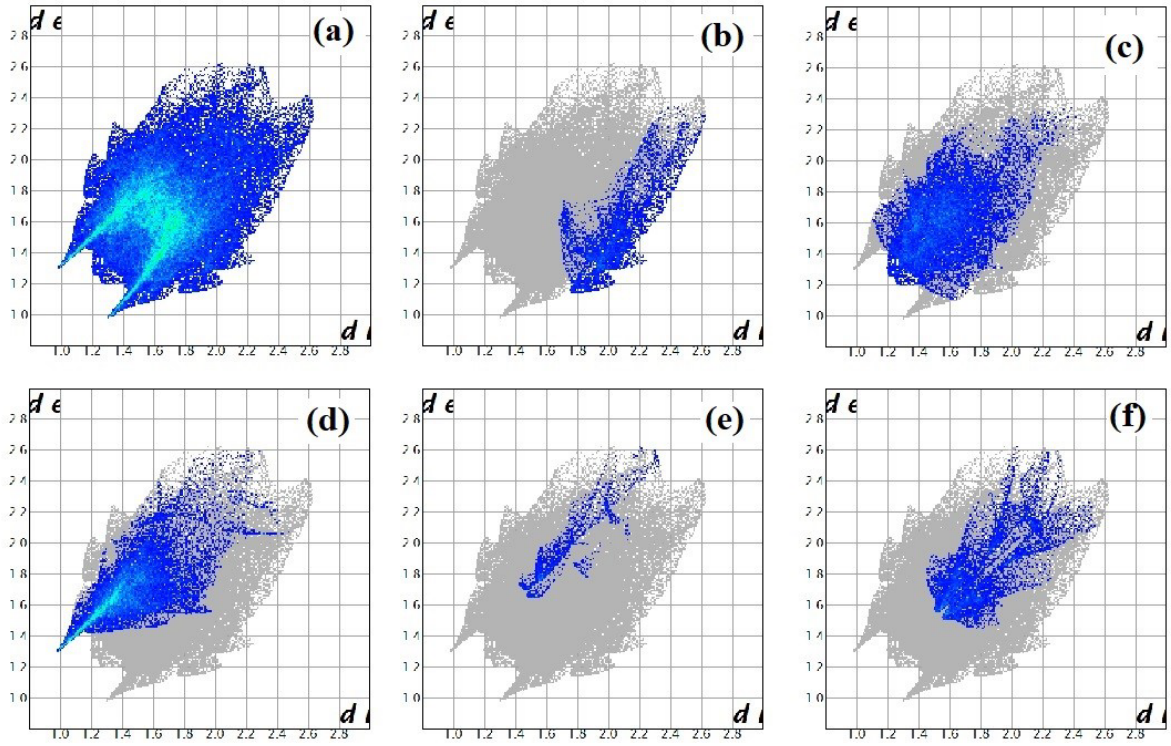


Figure S11. Fingerprint plots for 1a (a) resolved into C···H (b), H···H (c), H···O (d), O···N (e), and O···O (f) contacts.

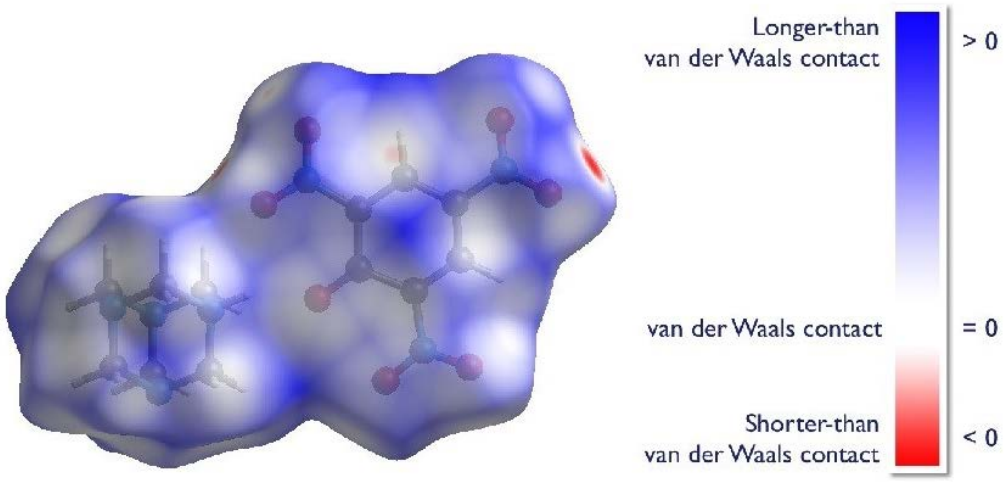


Figure S12. Hirshfeld surface of 1b.

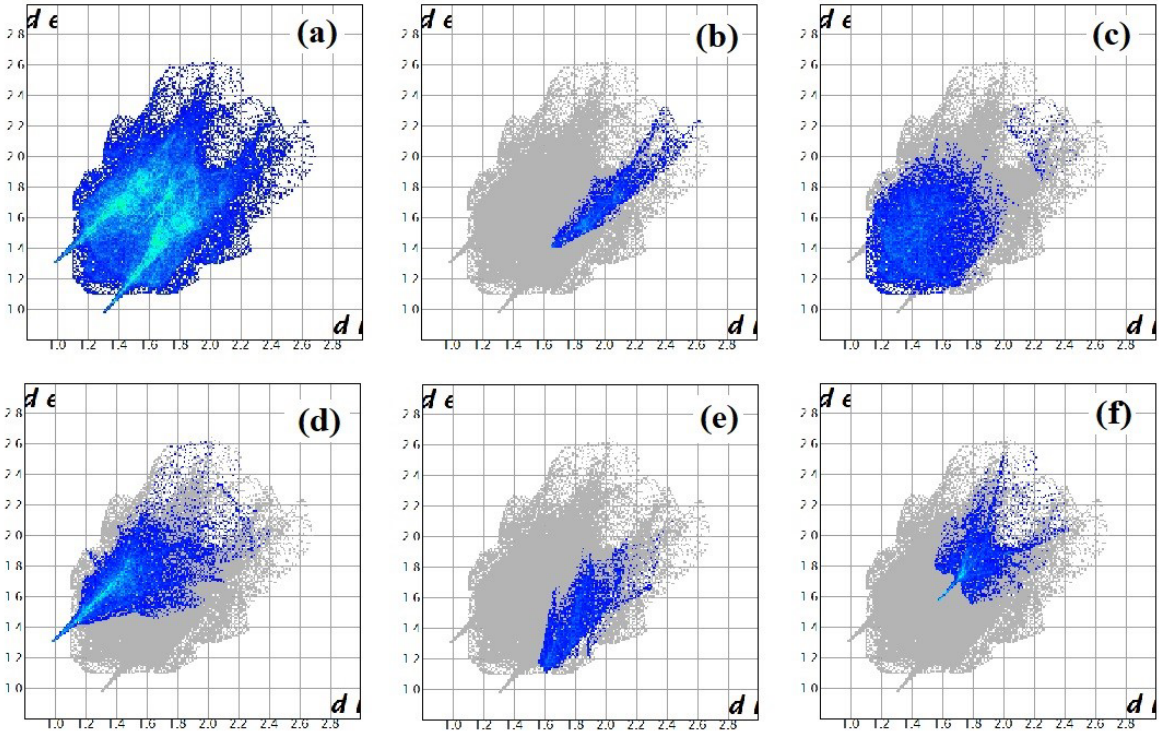


Figure S13. Fingerprint plots for 1b (a) resolved into C···O (b), H···H (c), H···O (d), N···H (e), and O···O (f) contacts.

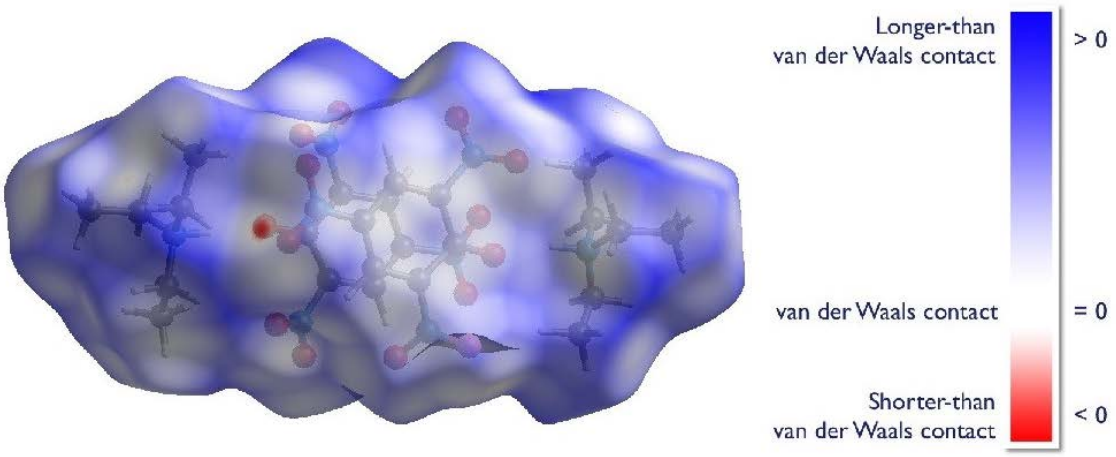


Figure S14. Hirshfeld surface of 2.

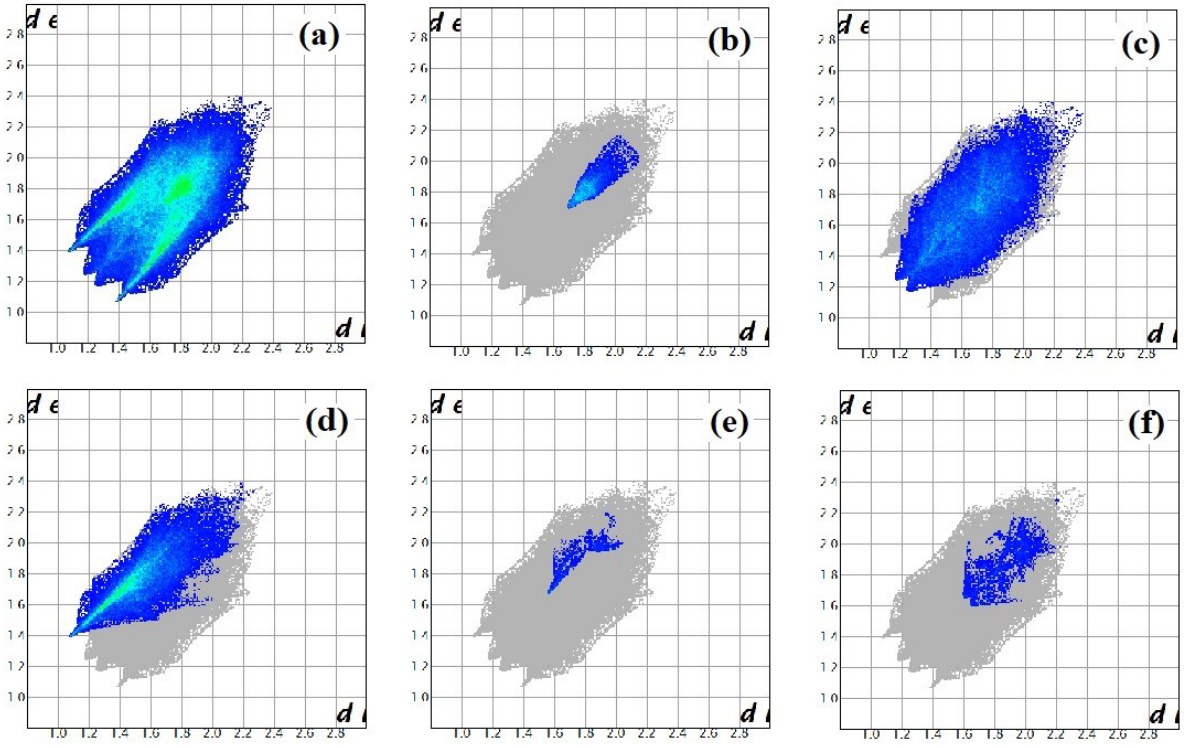


Figure S15. Fingerprint plots for 2 (a) resolved into C···C (b), H···H (c), H···O (d), O···N (e), and O···O (f) contacts.

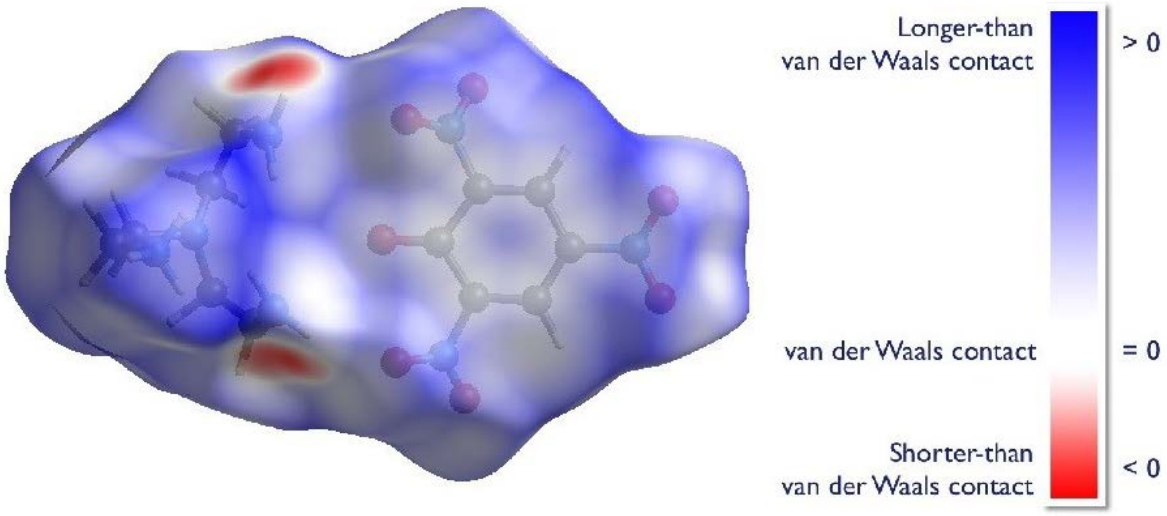


Figure S16. Hirshfeld surface of 5.

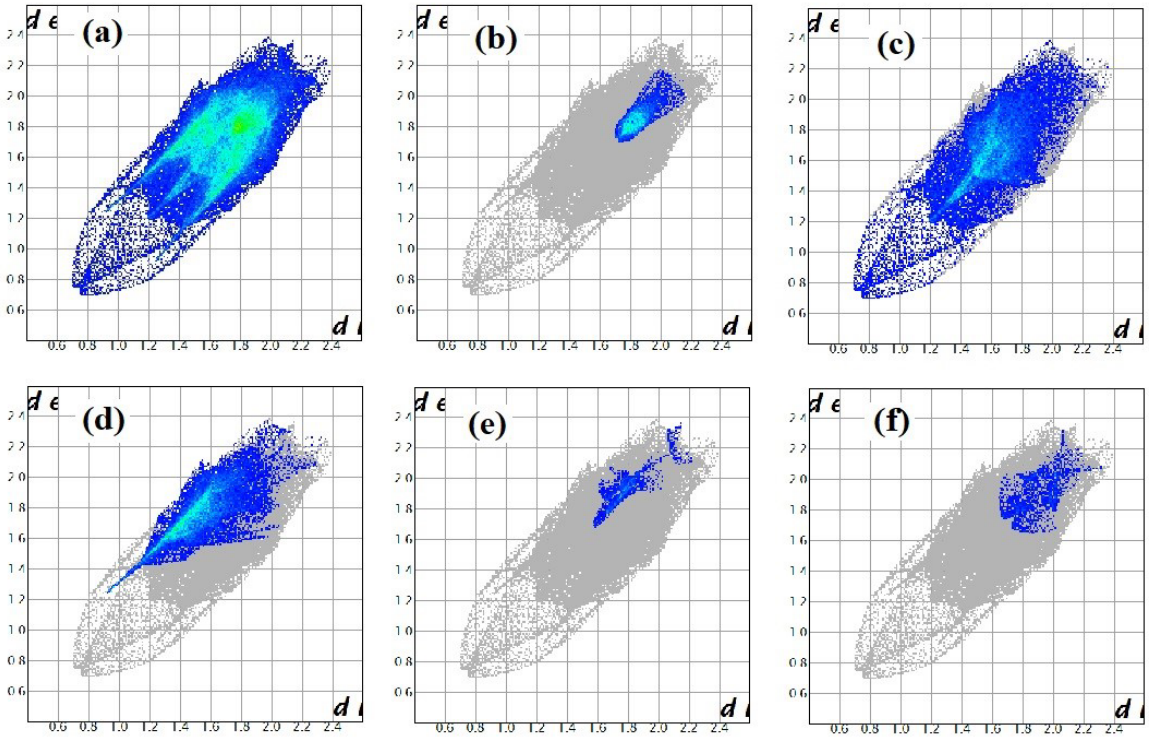


Figure S17. Fingerprint plots for 5 (a) resolved into C···C (b), H···H (c), H···O (d), O···N (e), and O···O (f) contacts.

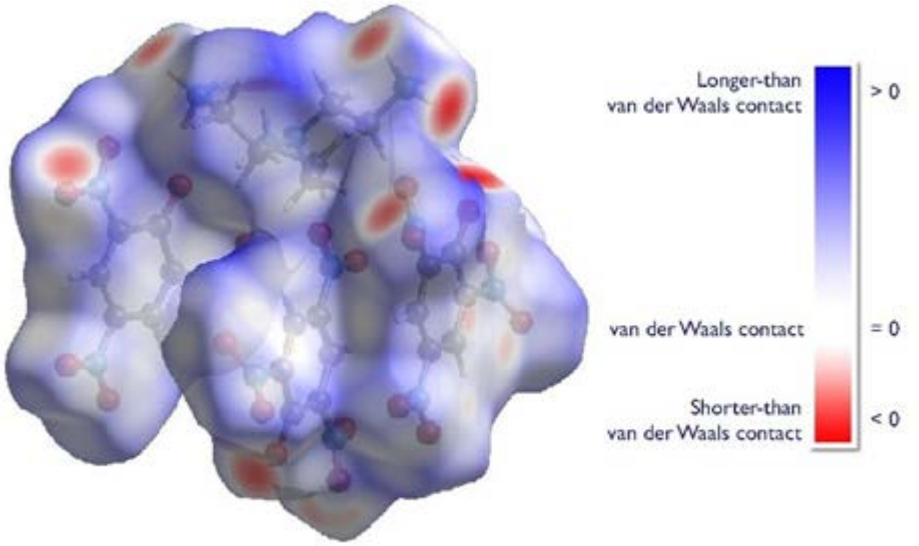


Figure S18. Hirshfeld surface of 7a.

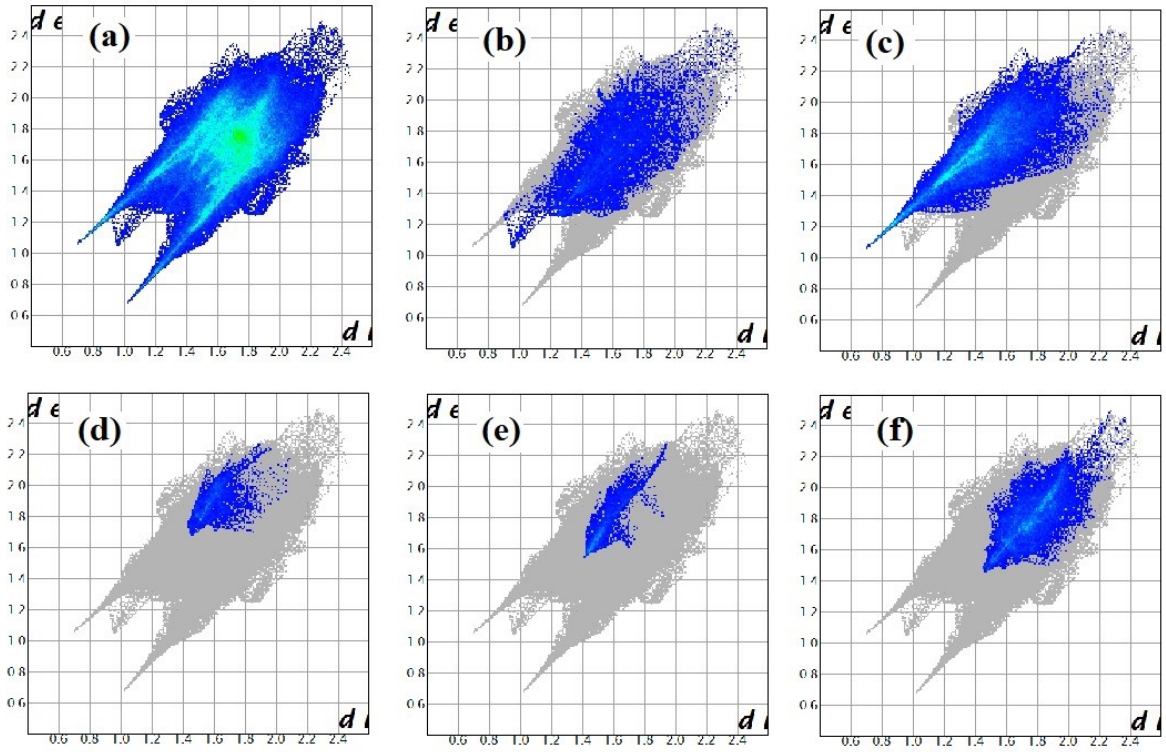


Figure S19. Fingerprint plots for 7a (a) resolved into H···H (b), H···O (c), O···C (d), O···N (e), and O···O (f) contacts.

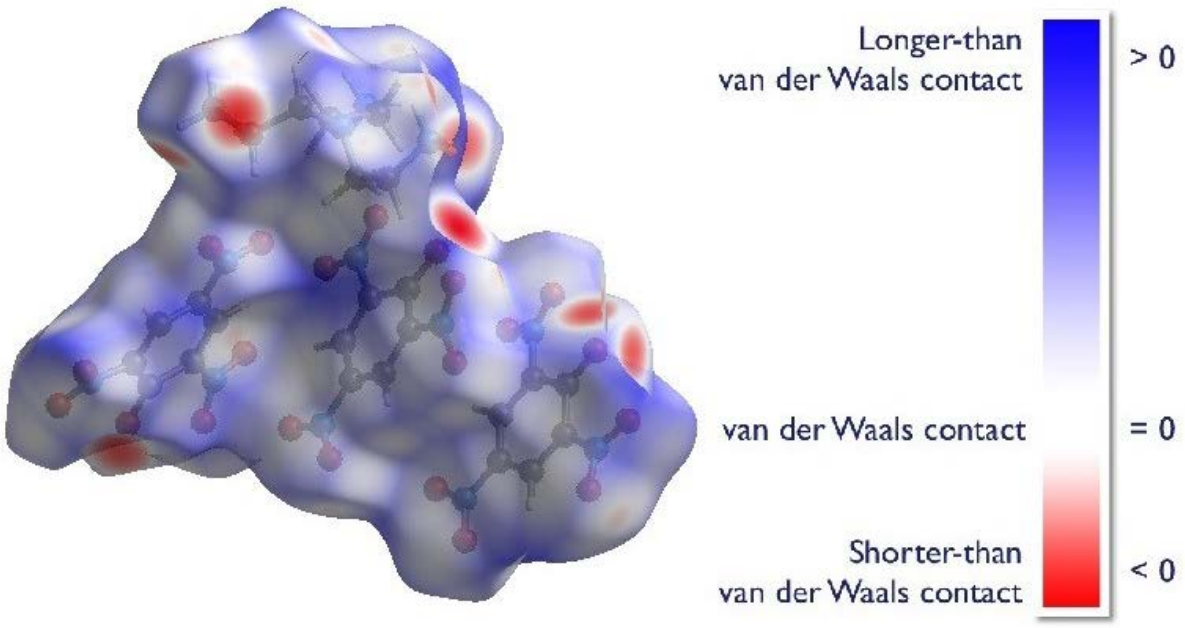


Figure S20. Hirshfeld surface of 7b.

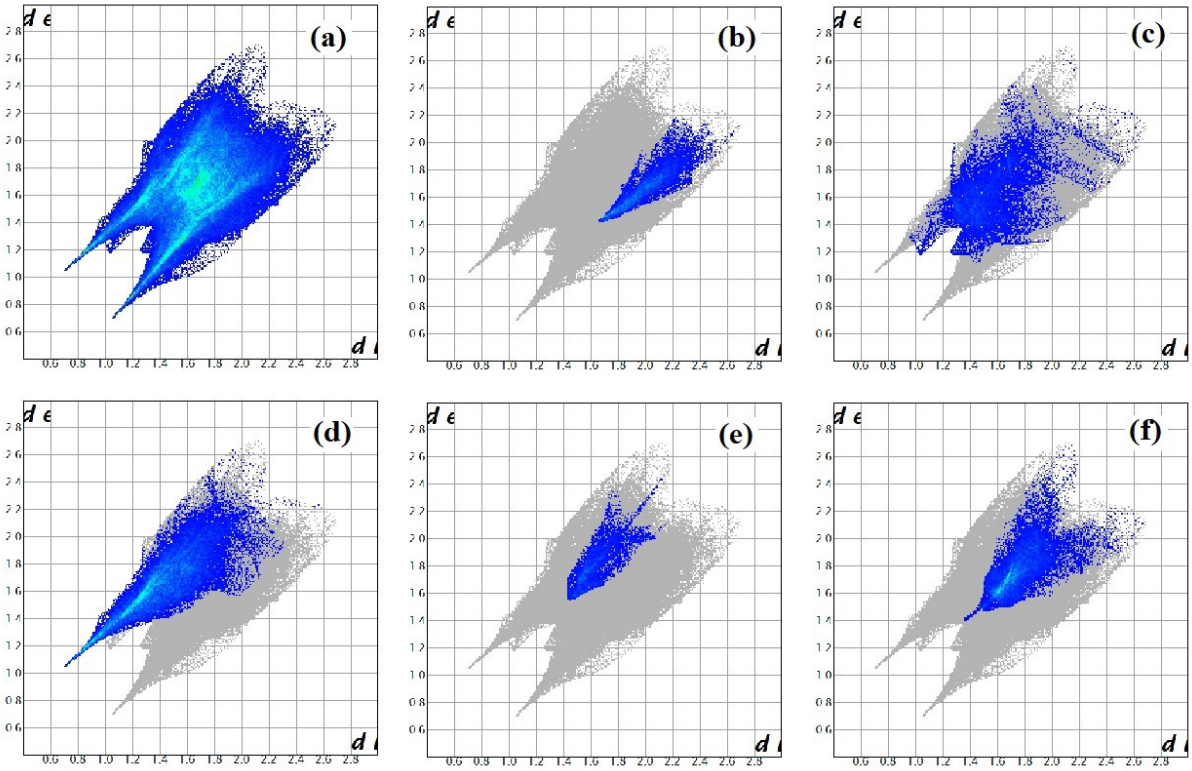


Figure S21. Fingerprint plots for 7b (a) resolved into C···O (b), H···H (c), H···O (d), O···N (e), and O···O (f) contacts.

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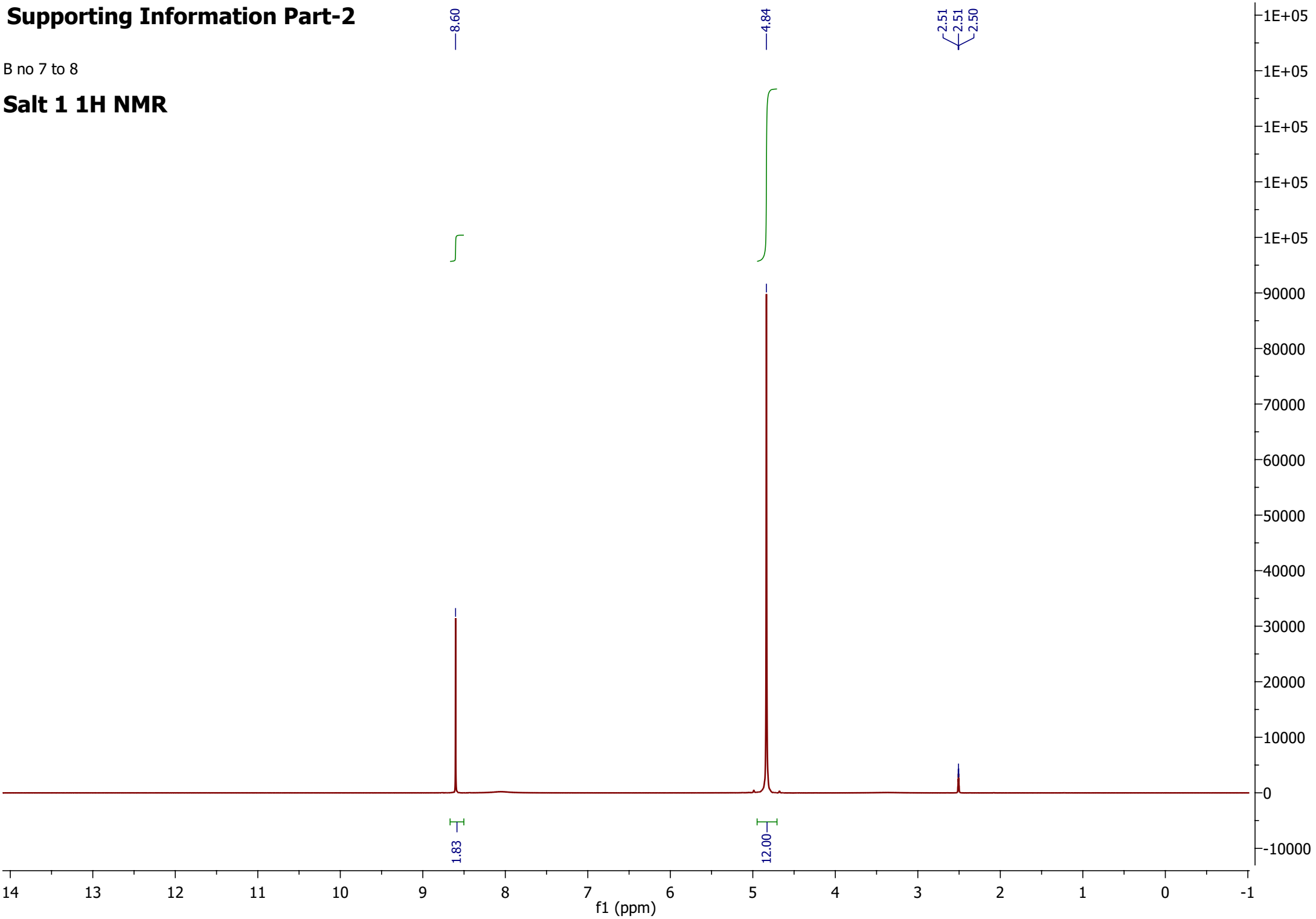
Supporting Information Part-2

B no 7 to 8

Salt 1 1H NMR



B no 7 to 8

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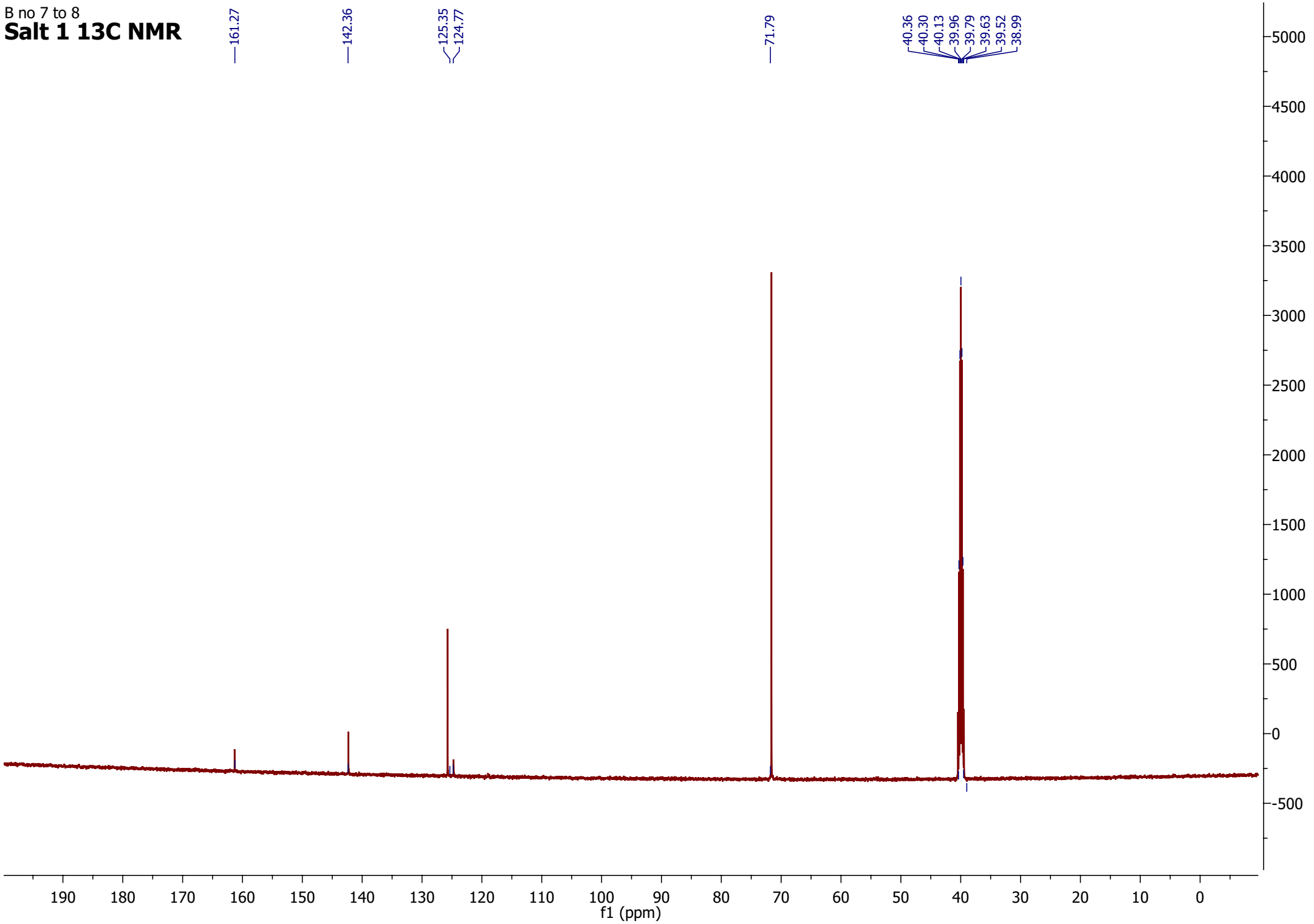

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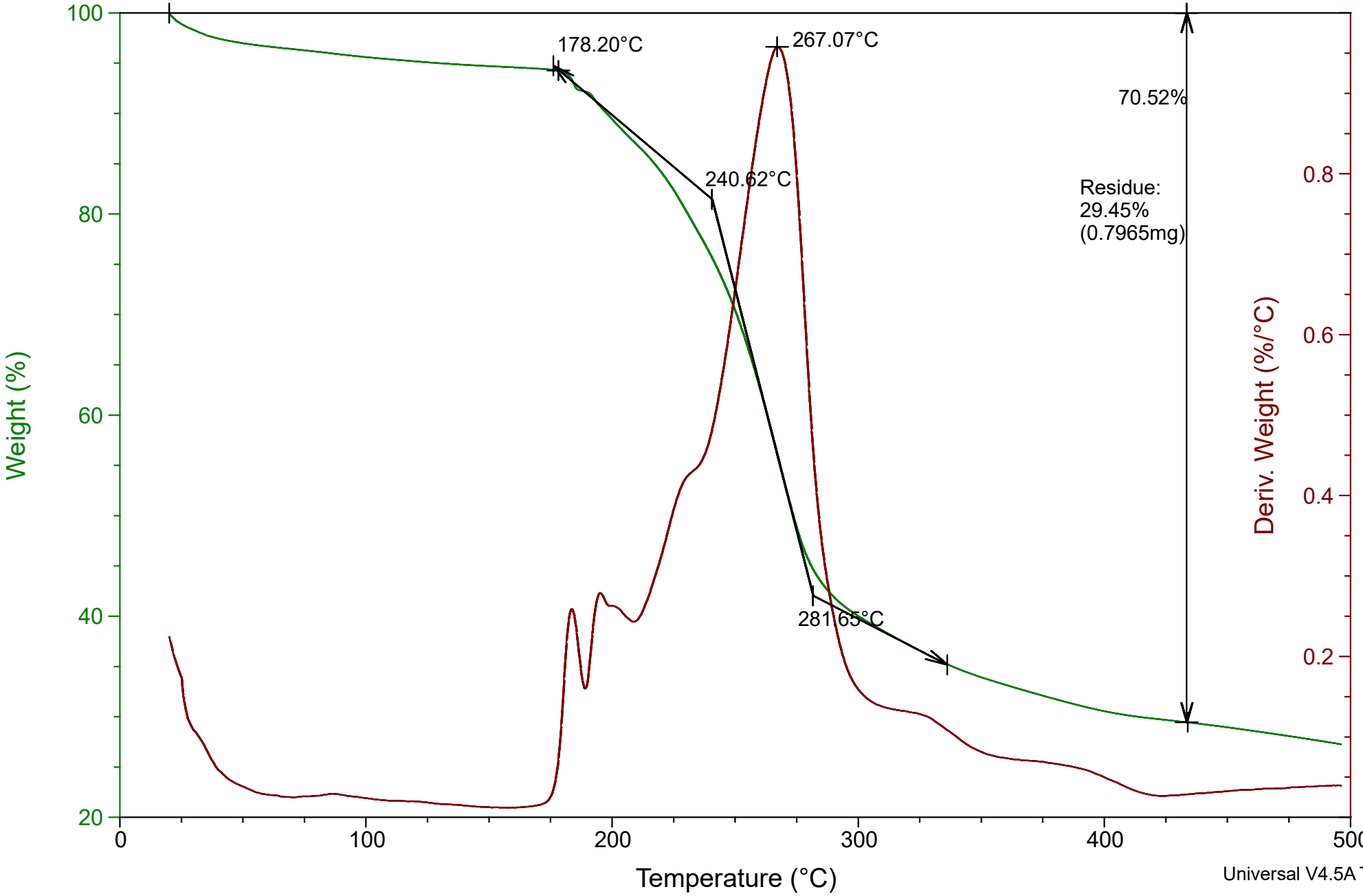

Universal V4.5A TA Instruments

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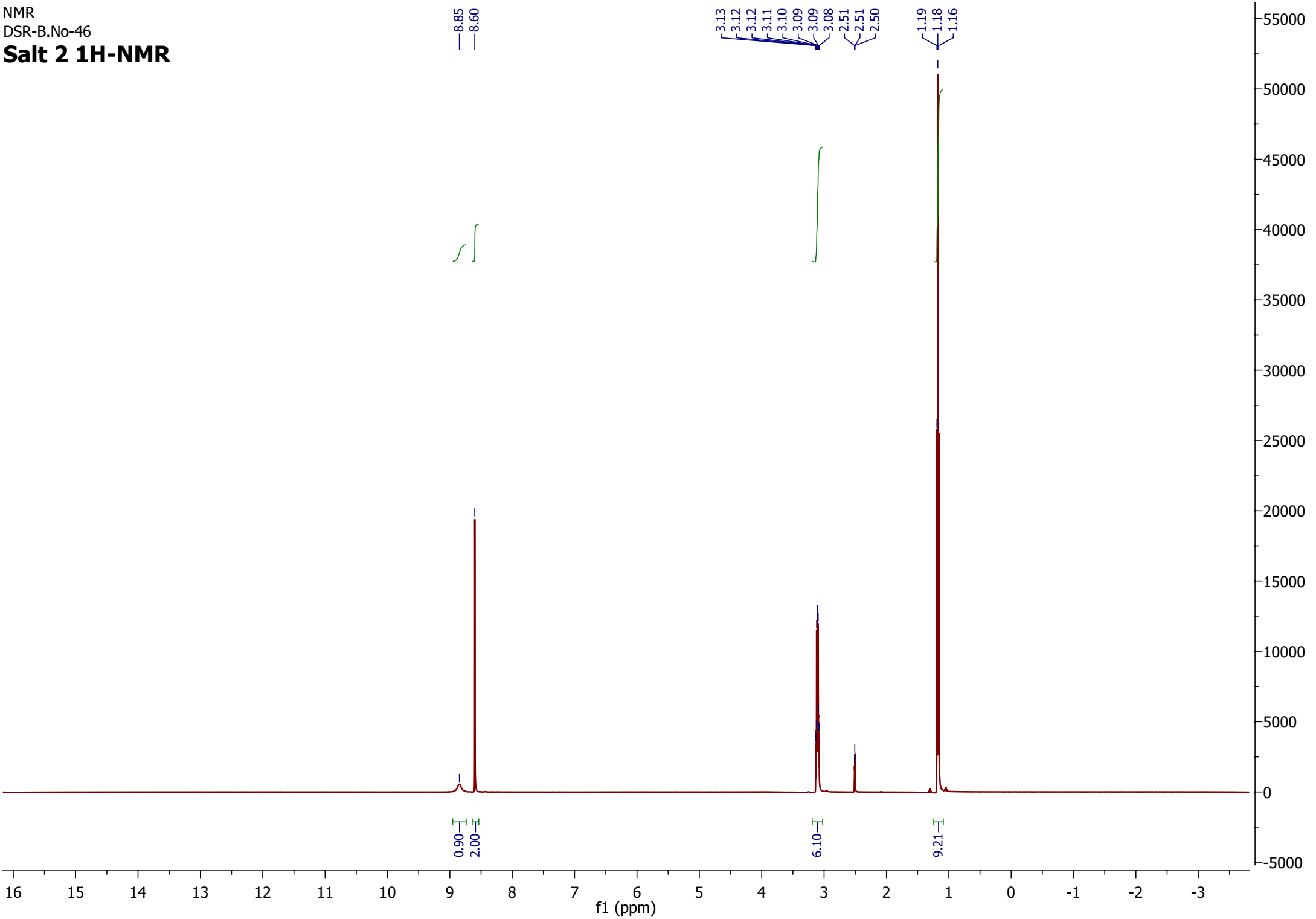

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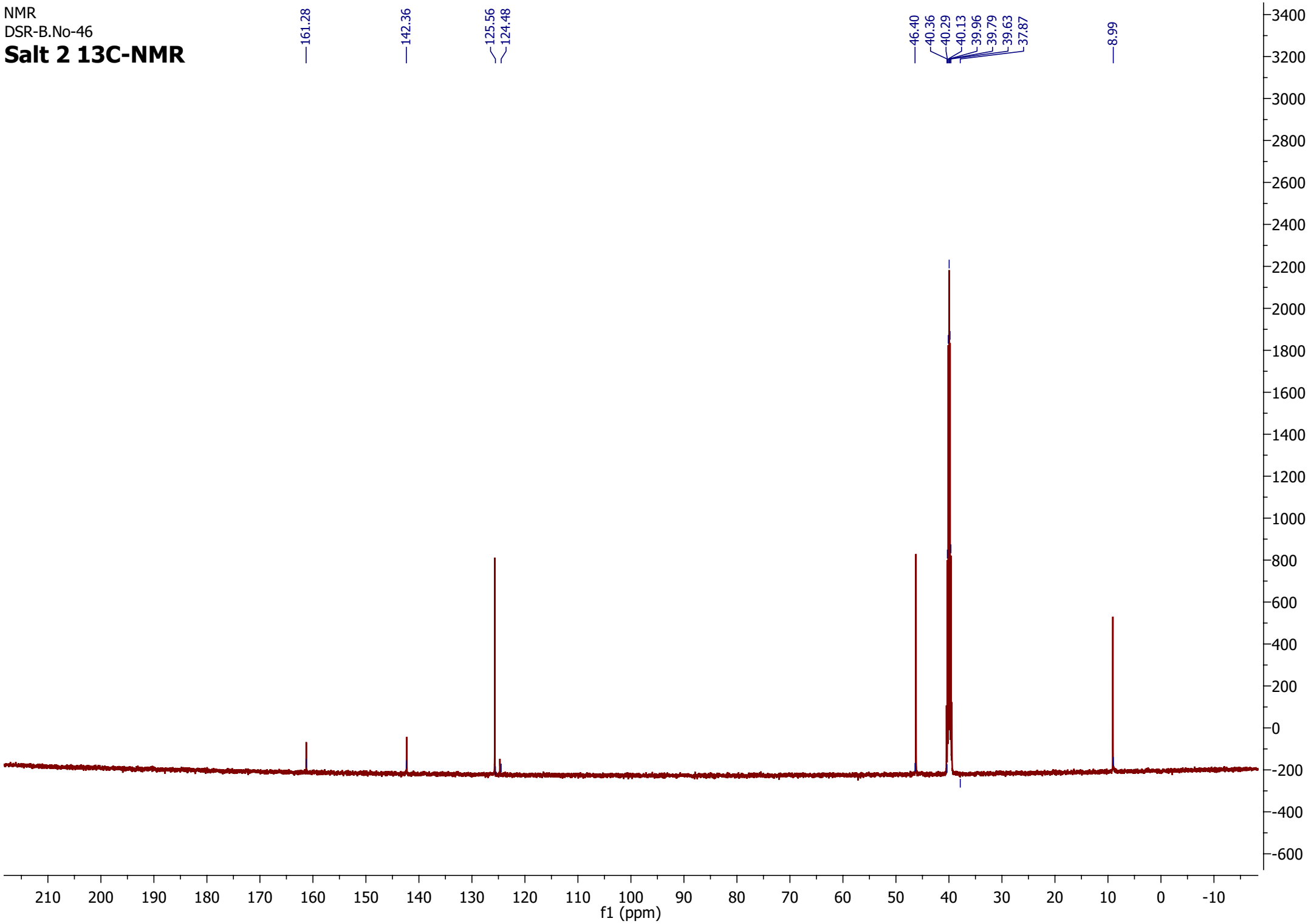

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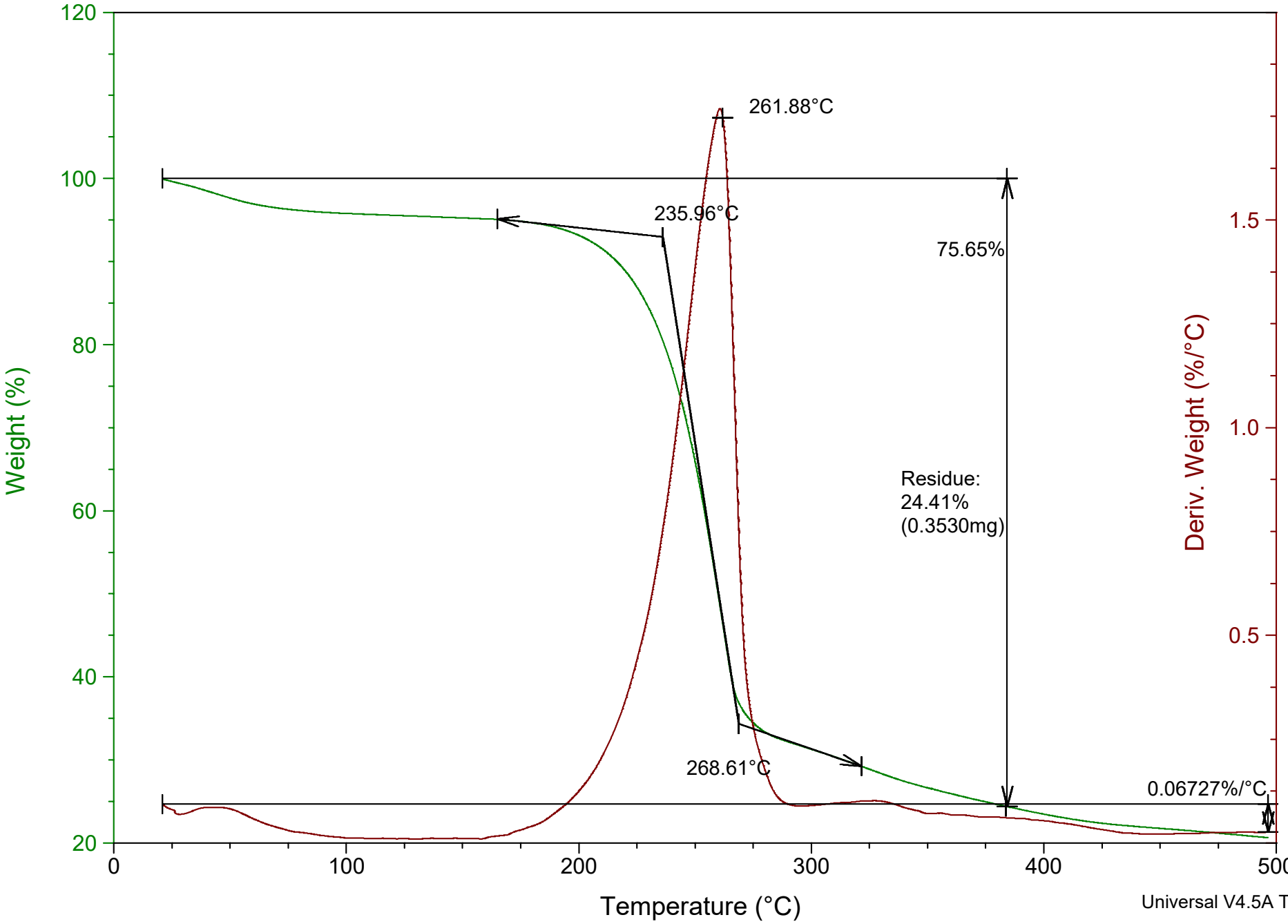
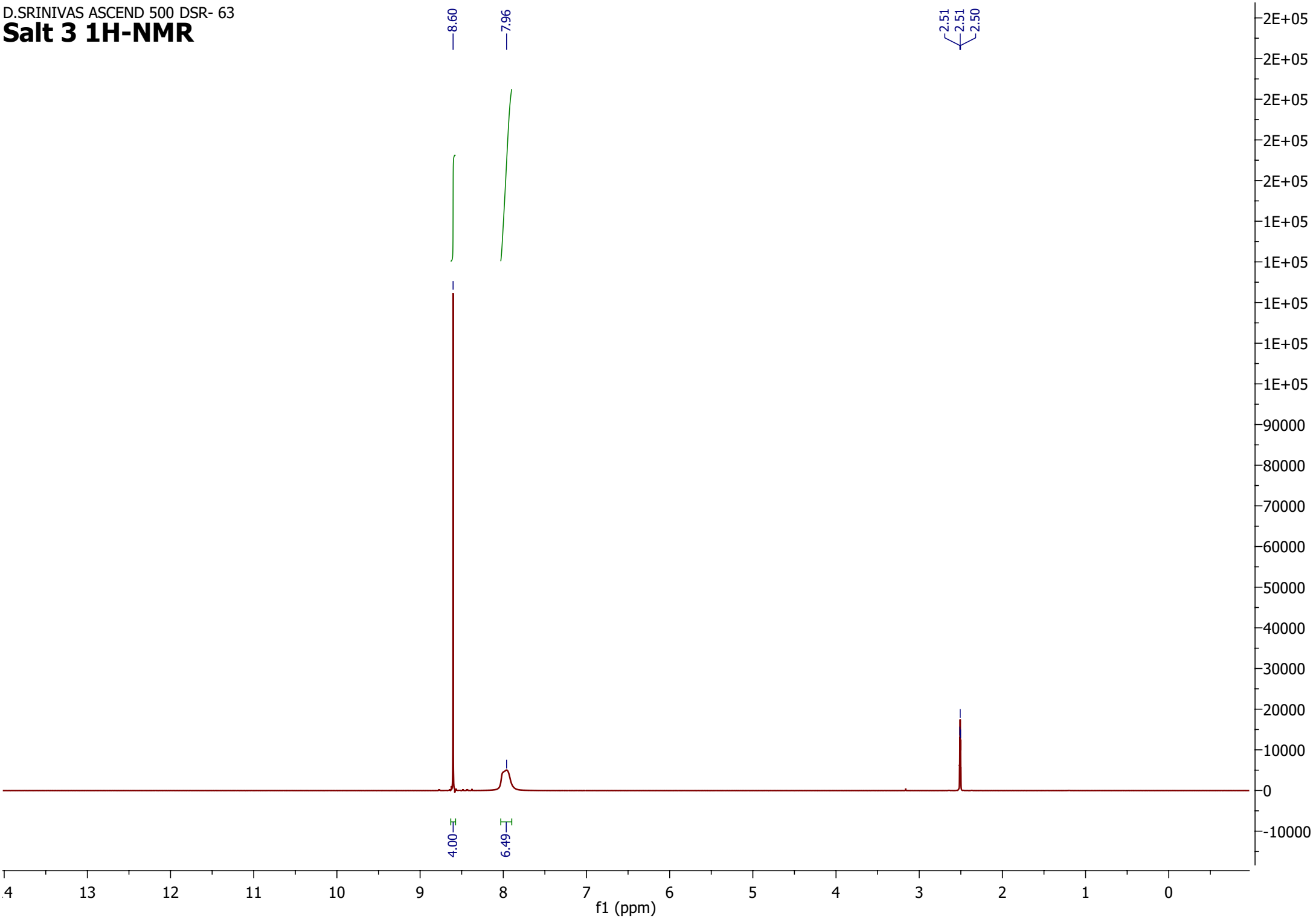


Universal V4.5A TA Instruments

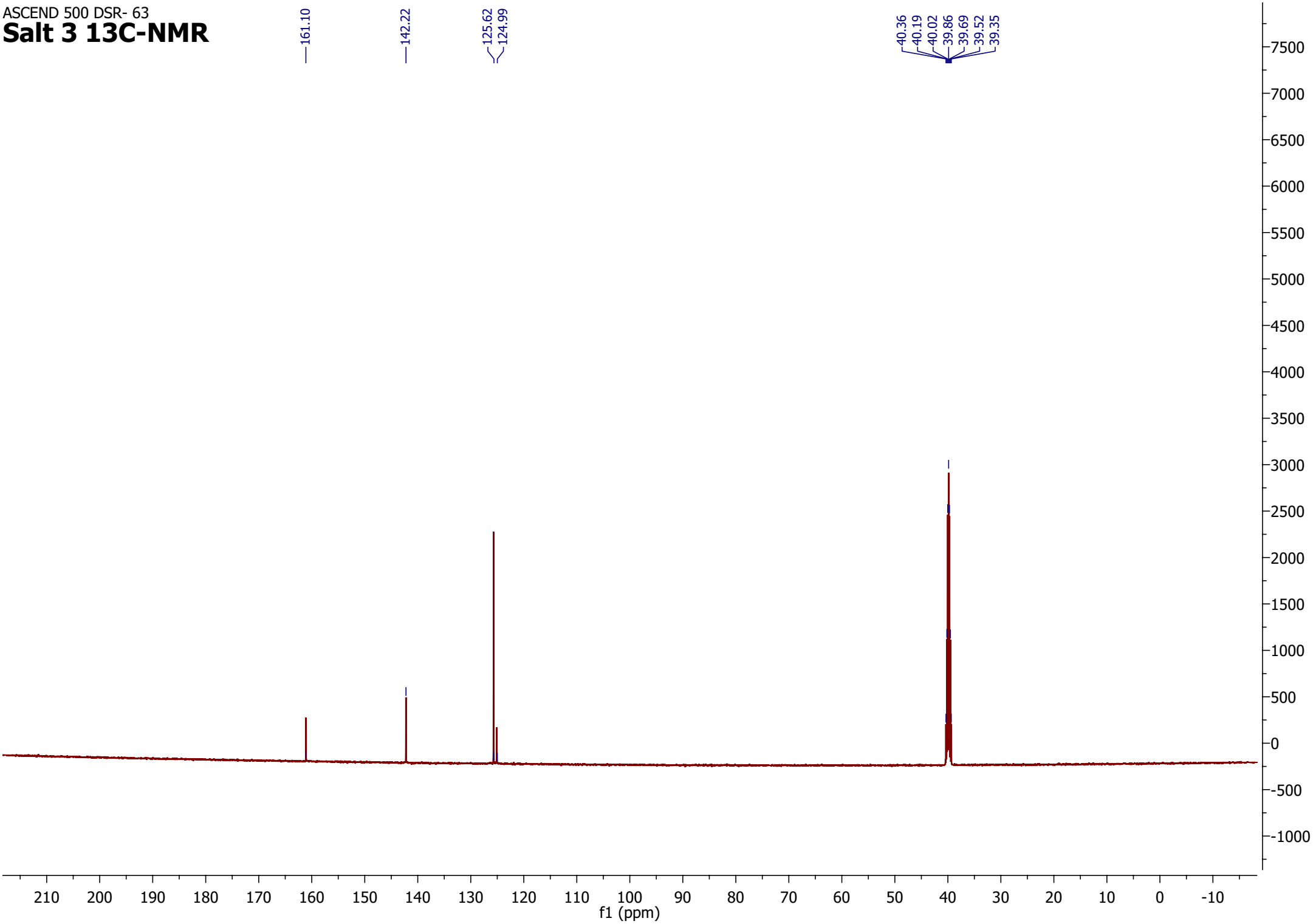
D.SRINIVAS ASCEND 500 DSR- 63

Salt 3 1H-NMR



ASCEND 500 DSR- 63

Salt 3 13C-NMR



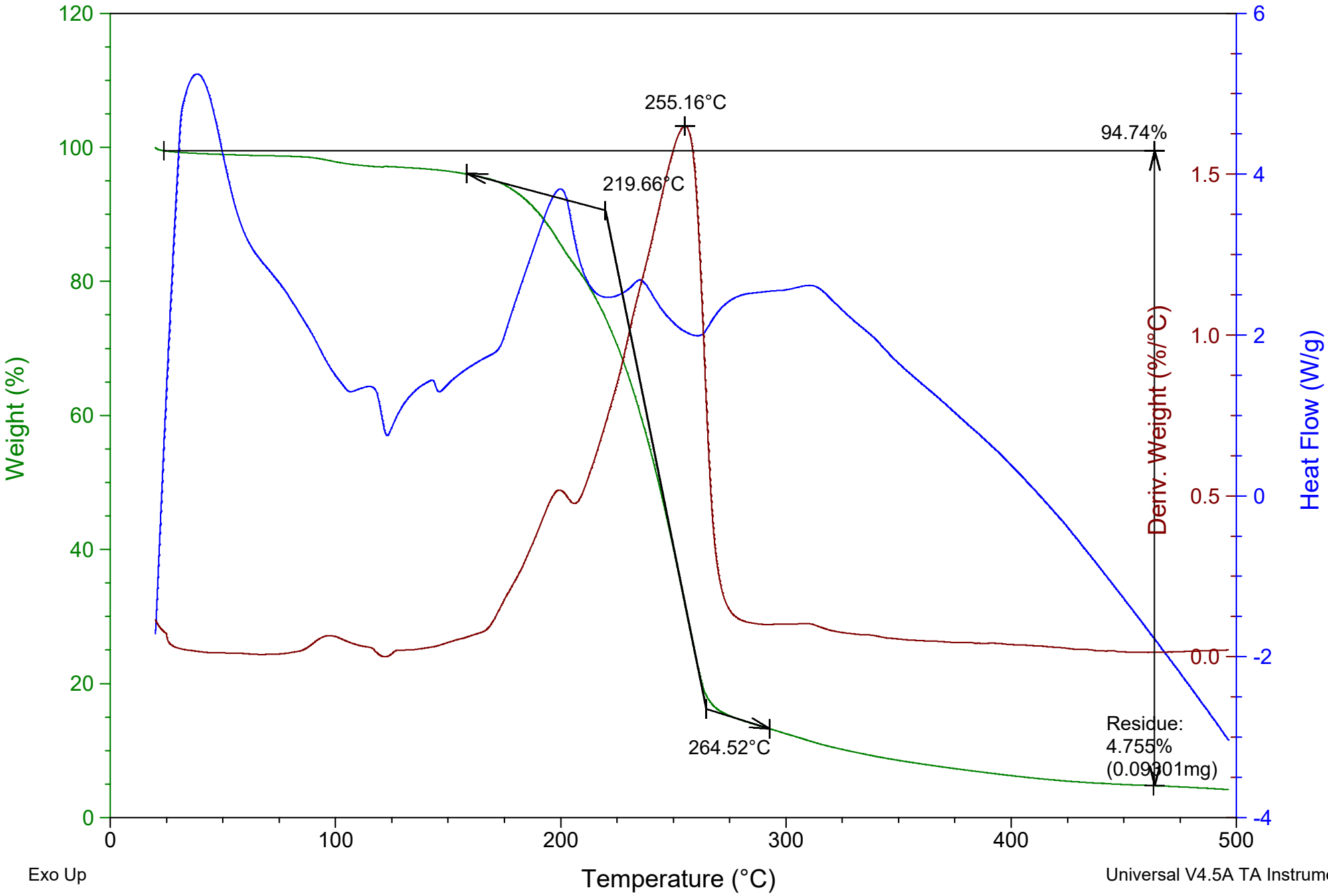
Sample: RMS-63
Size: 1.9560 mg
Method: Ramp

Salt 3

DSC-TGA

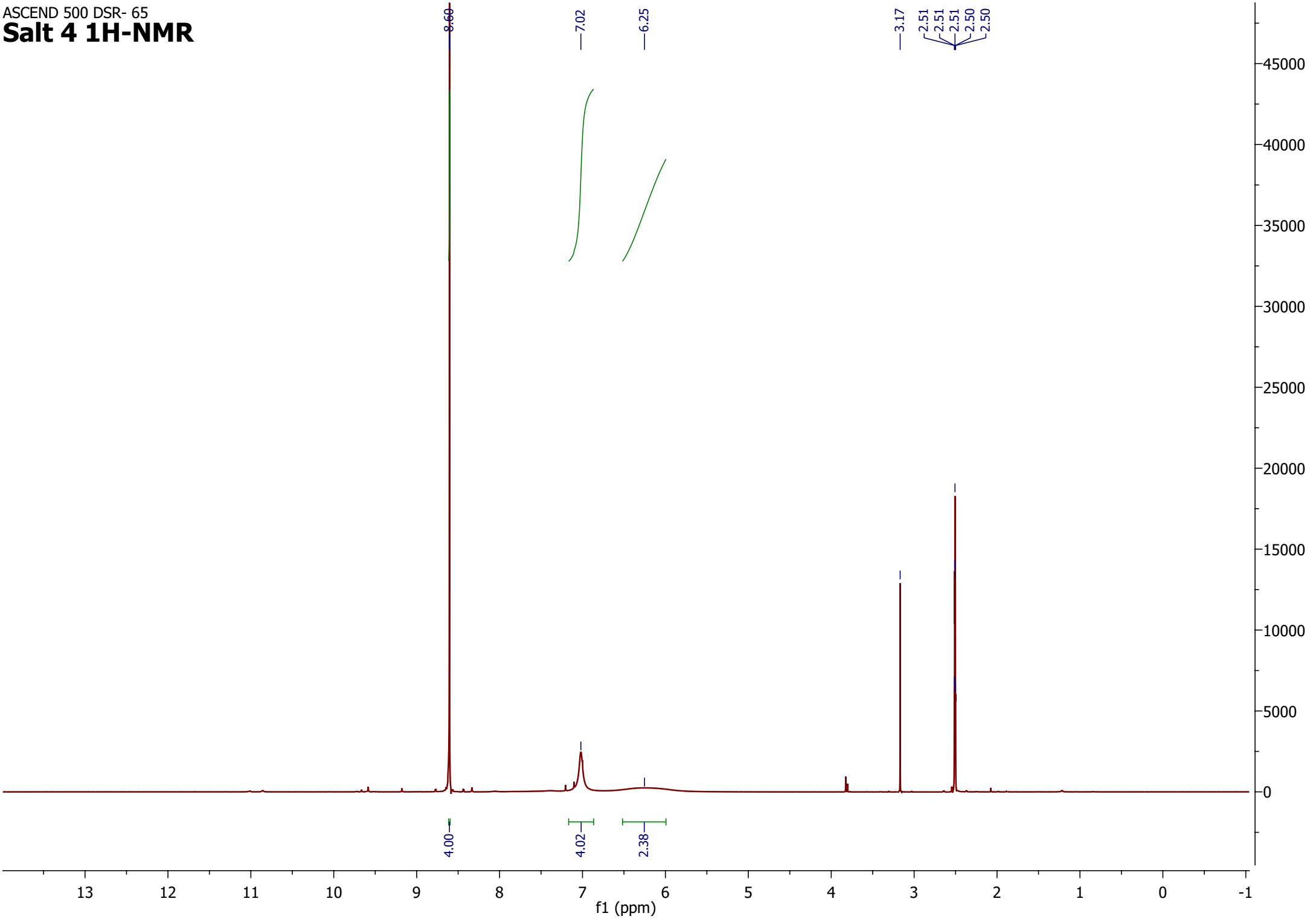
File: C:...\TGA-DATA\2019\NOVEMBER\RMS-63.001

Run Date: 06-Nov-2019 09:38
Instrument: SDT Q600 V20.9 Build 20



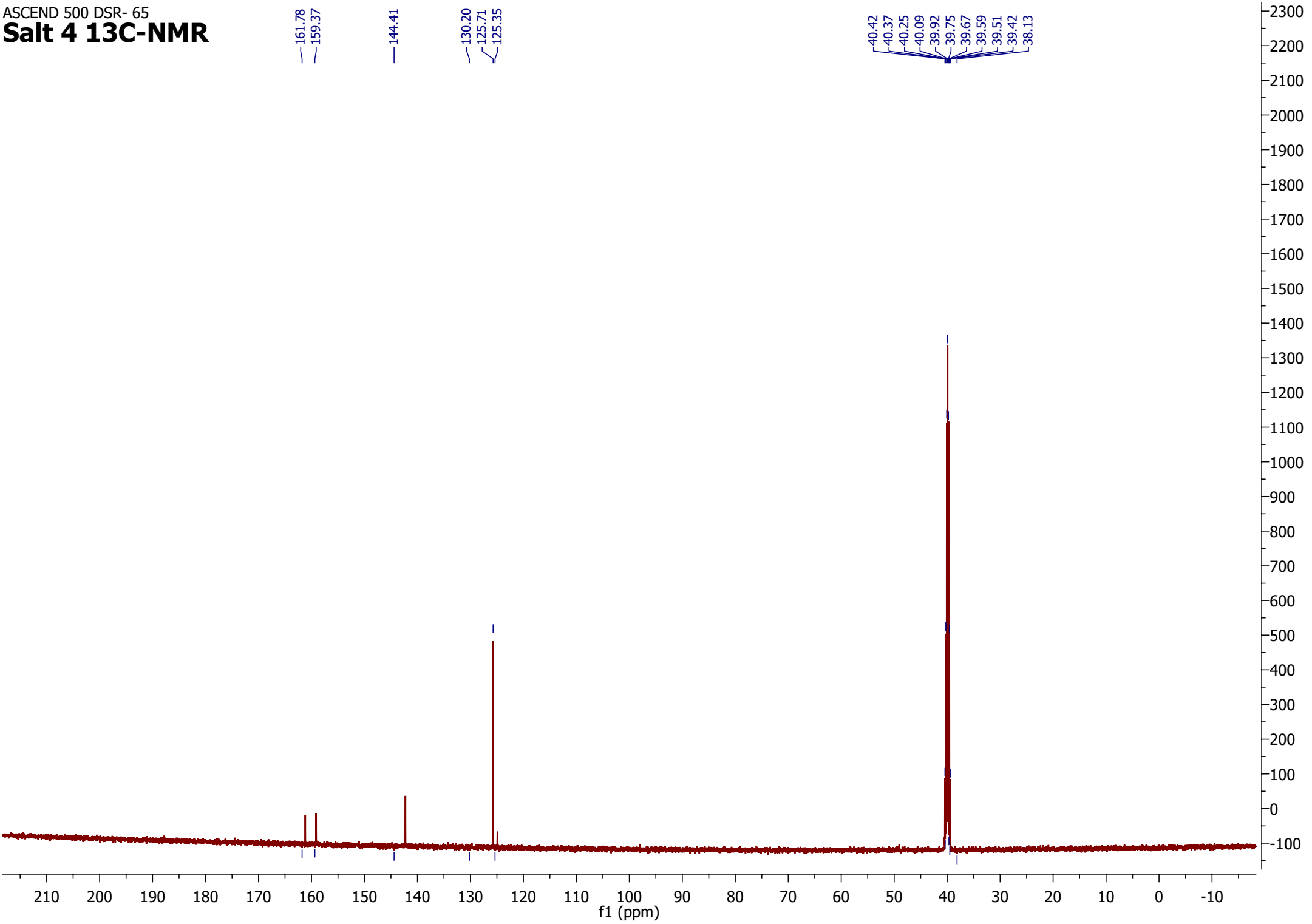
ASCEND 500 DSR- 65

Salt 4 1H-NMR



ASCEND 500 DSR- 65

Salt 4 13C-NMR



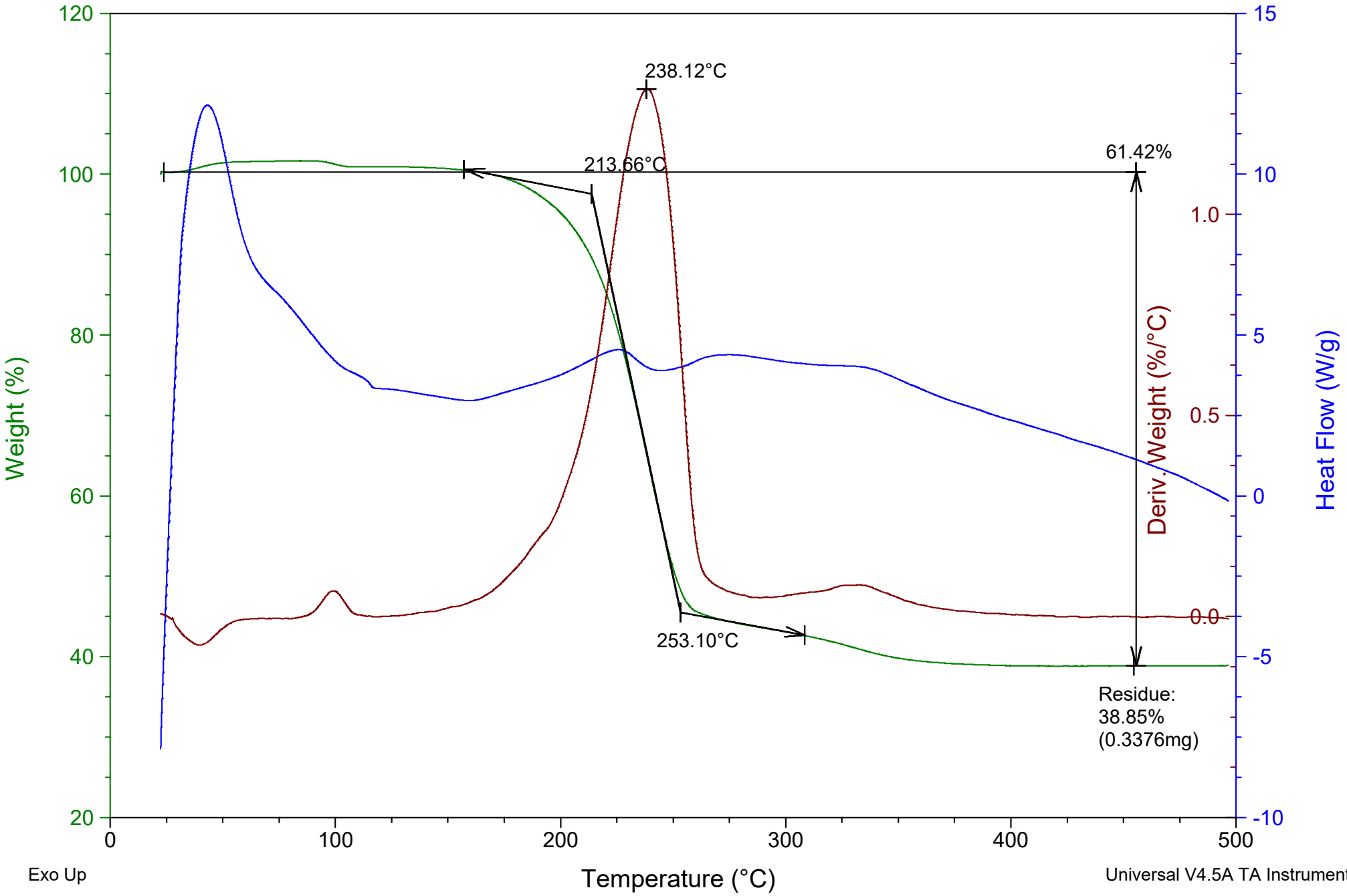
Sample: RMS-65
Size: 0.8690 mg
Method: Ramp

Salt 4

DSC-TGA

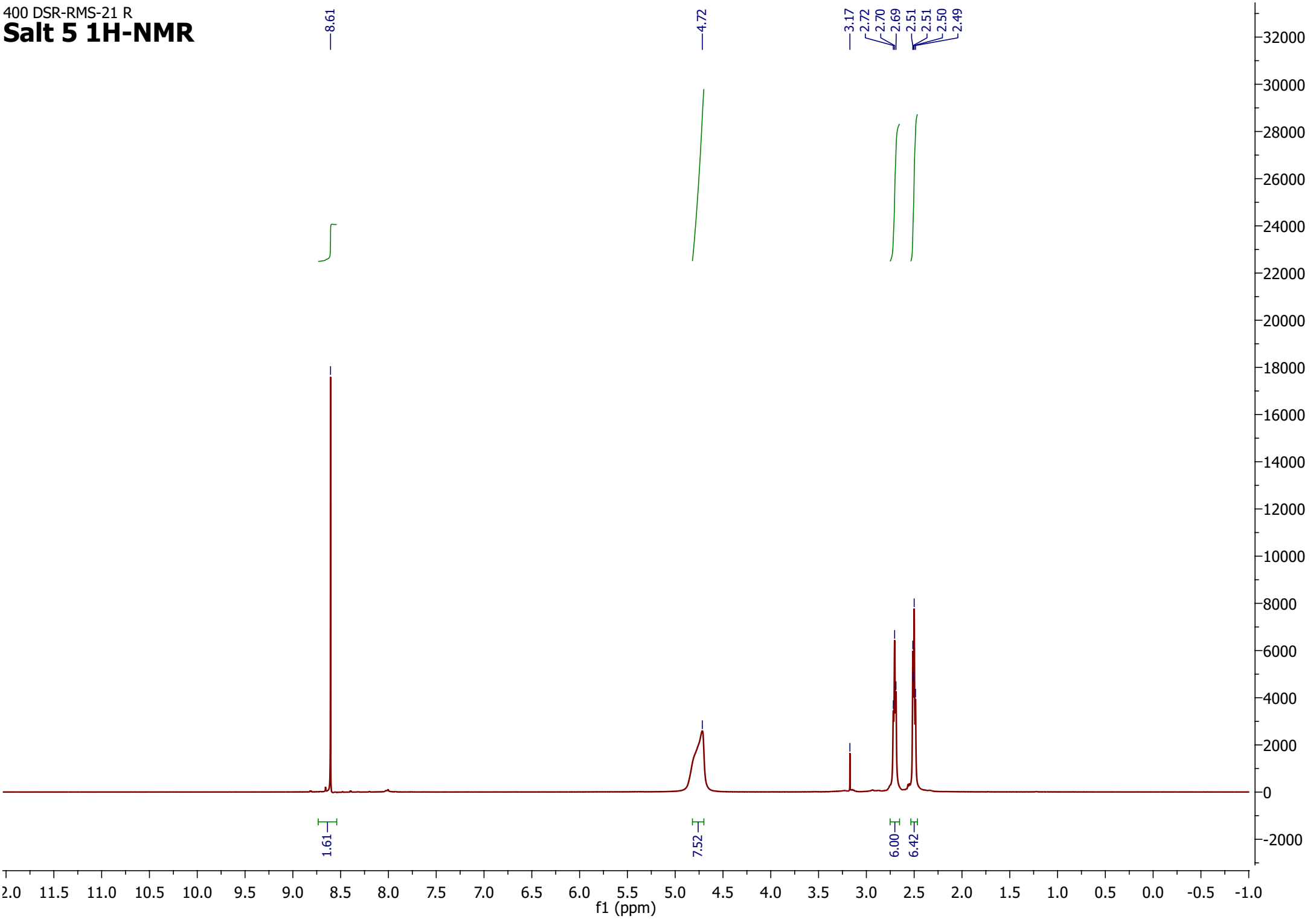
File: C:...\TGA-DATA\2019\NOVEMBER\RMS-65.001

Run Date: 06-Nov-2019 11:45
Instrument: SDT Q600 V20.9 Build 20



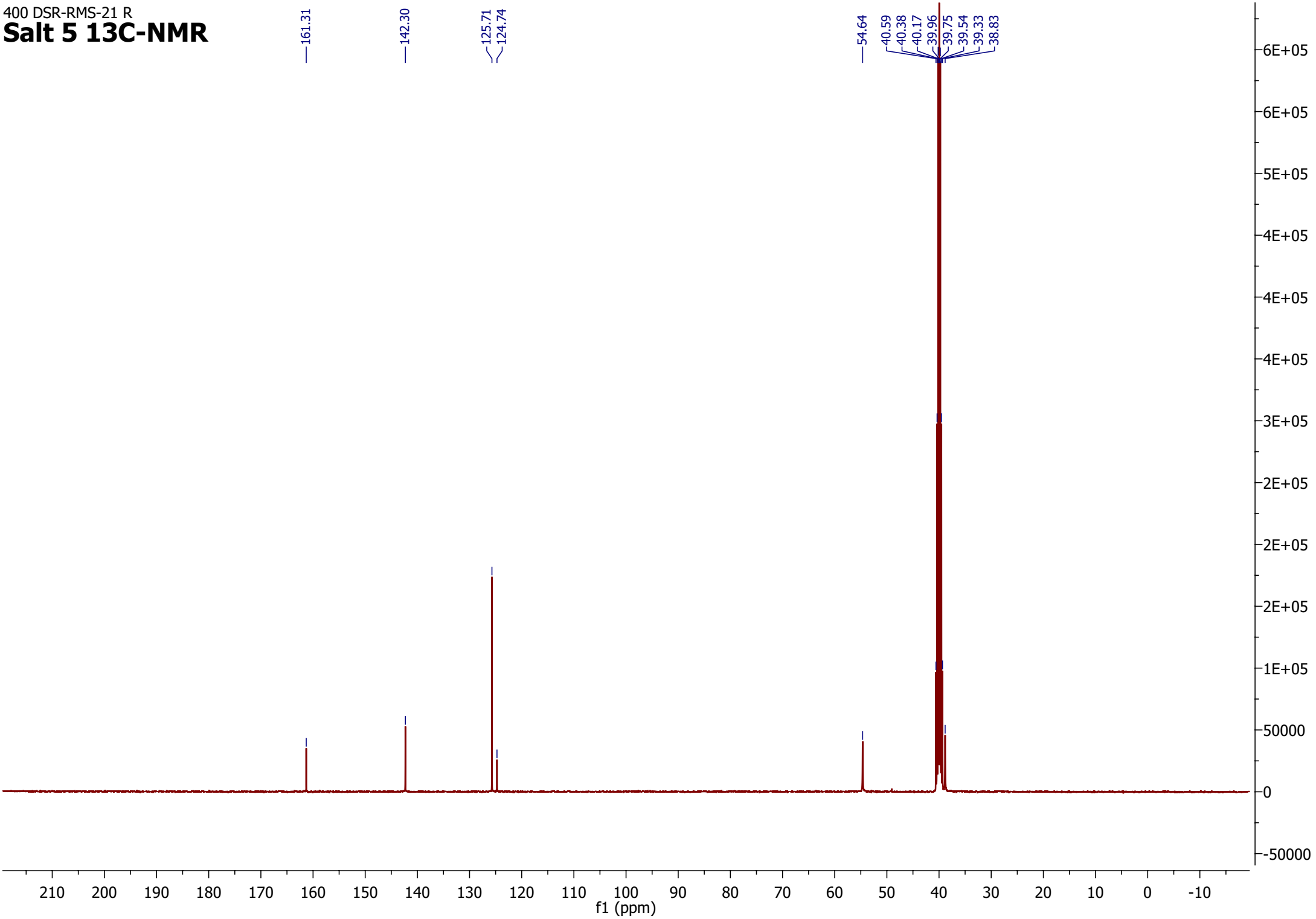
400 DSR-RMS-21 R

Salt 5 1H-NMR



400 DSR-RMS-21 R

Salt 5 13C-NMR

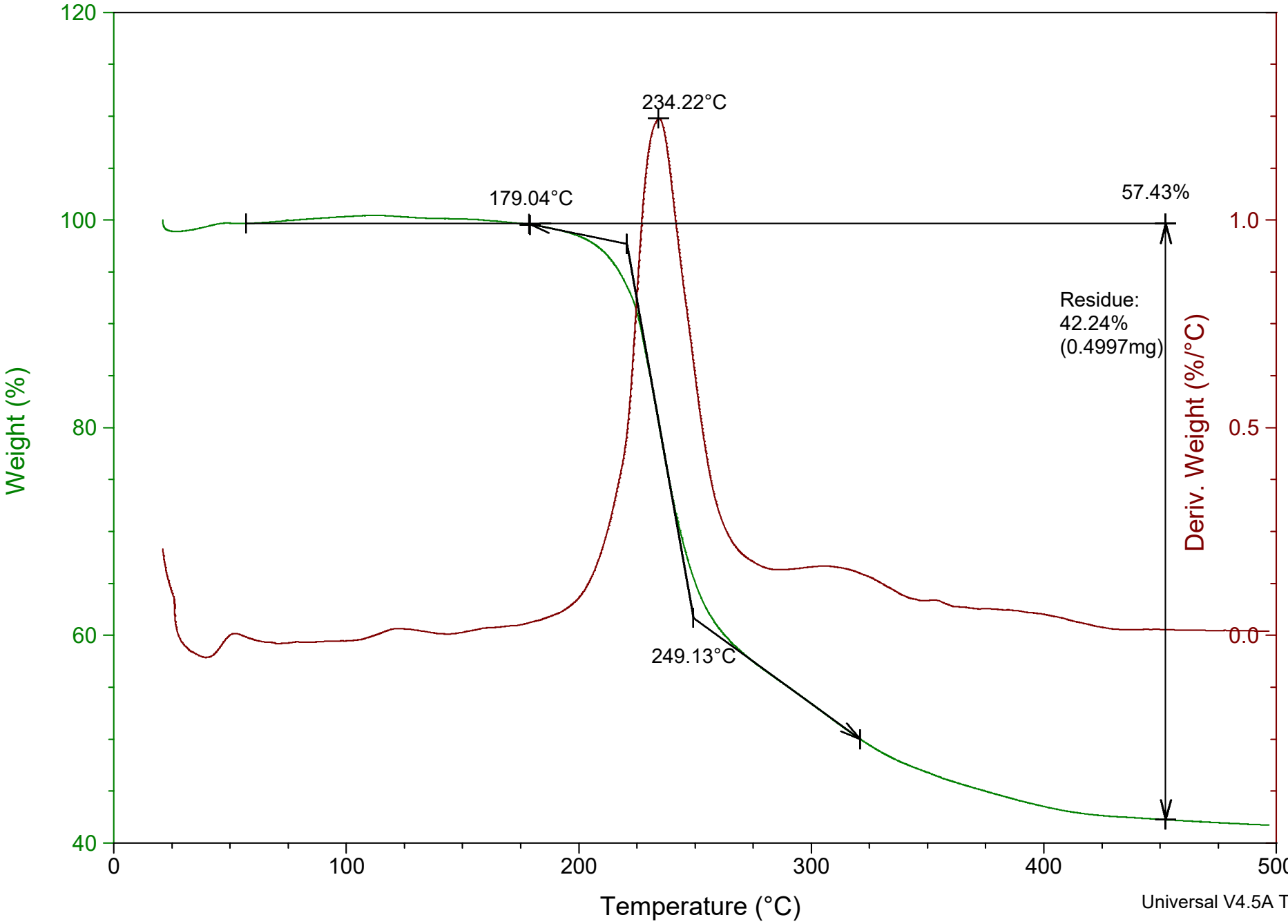


Sample: RMS-21
Size: 1.1830 mg
Method: Ramp
Salt 5

DSC-TGA

File: C:...\TGA-DATA\2019\SEPTEMBER\RMS-21.00

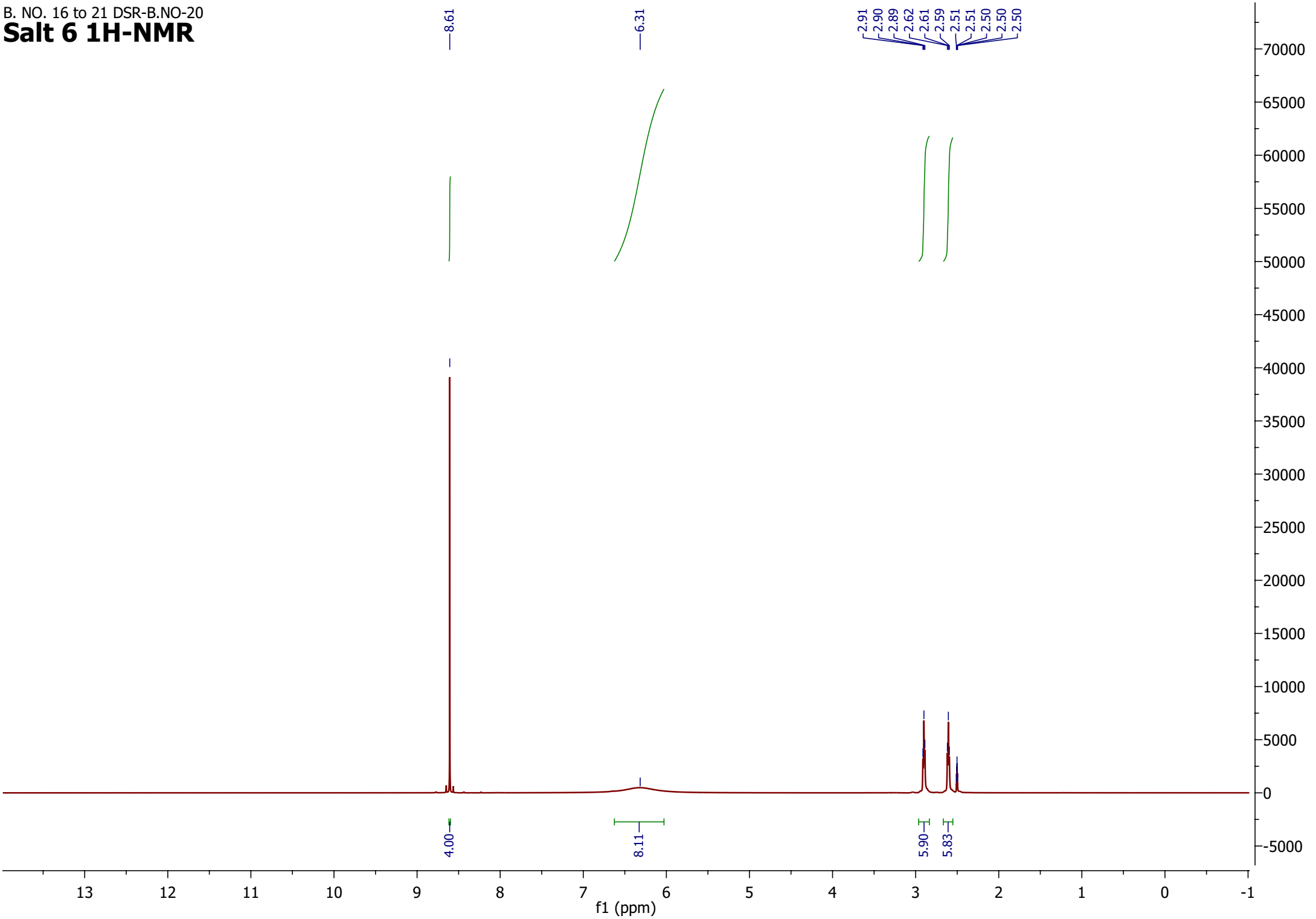
Run Date: 17-Sep-2019 09:35
Instrument: SDT Q600 V20.9 Build 20



Universal V4.5A TA Instruments

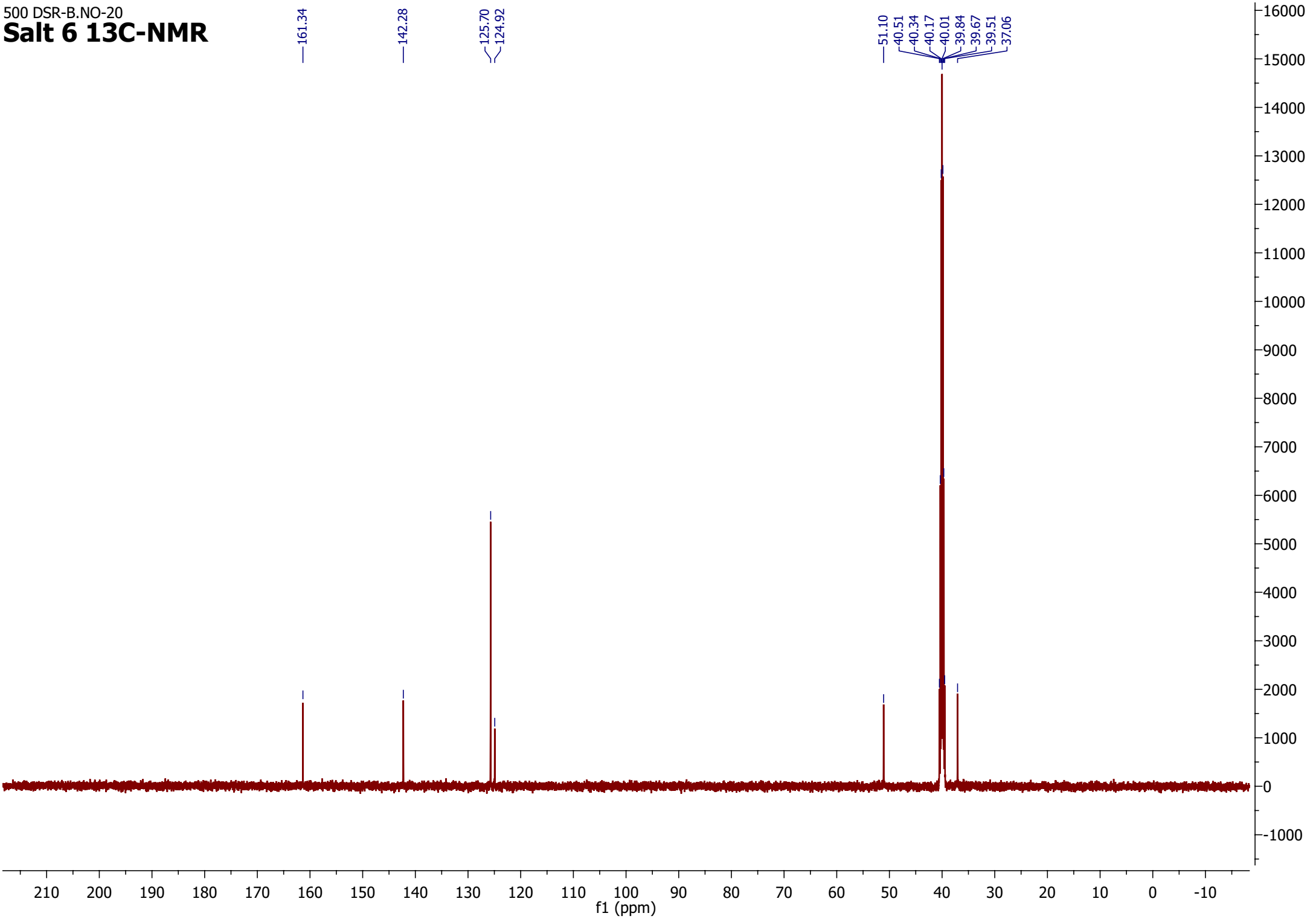
B. NO. 16 to 21 DSR-B.NO-20

Salt 6 1H-NMR



500 DSR-B.NO-20

Salt 6 13C-NMR



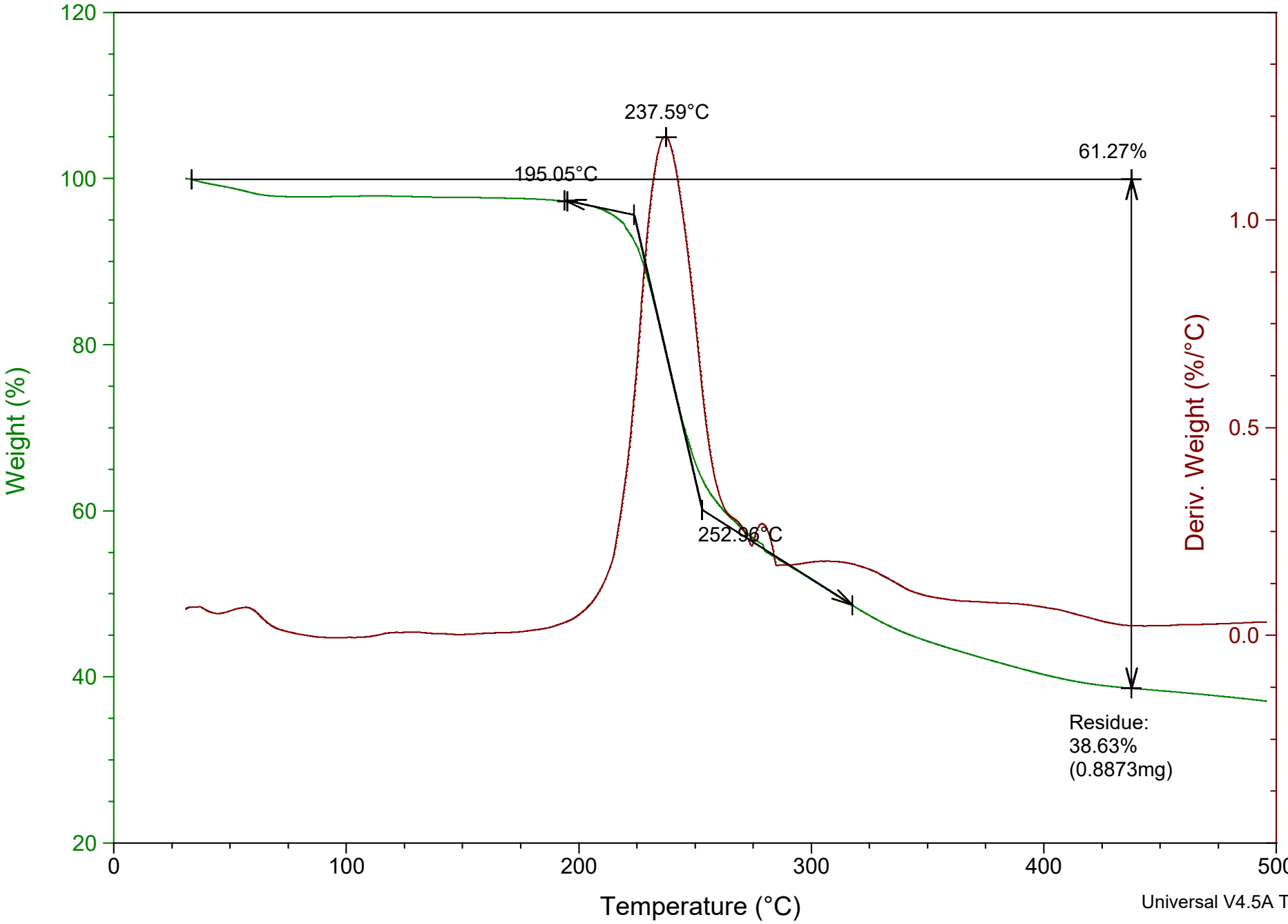
Sample: RMS-20
Size: 2.2970 mg
Method: Ramp

Salt 6

DSC-TGA

File: C:...\TGA-DATA\2019\SEPTEMBER\RMS-20.00

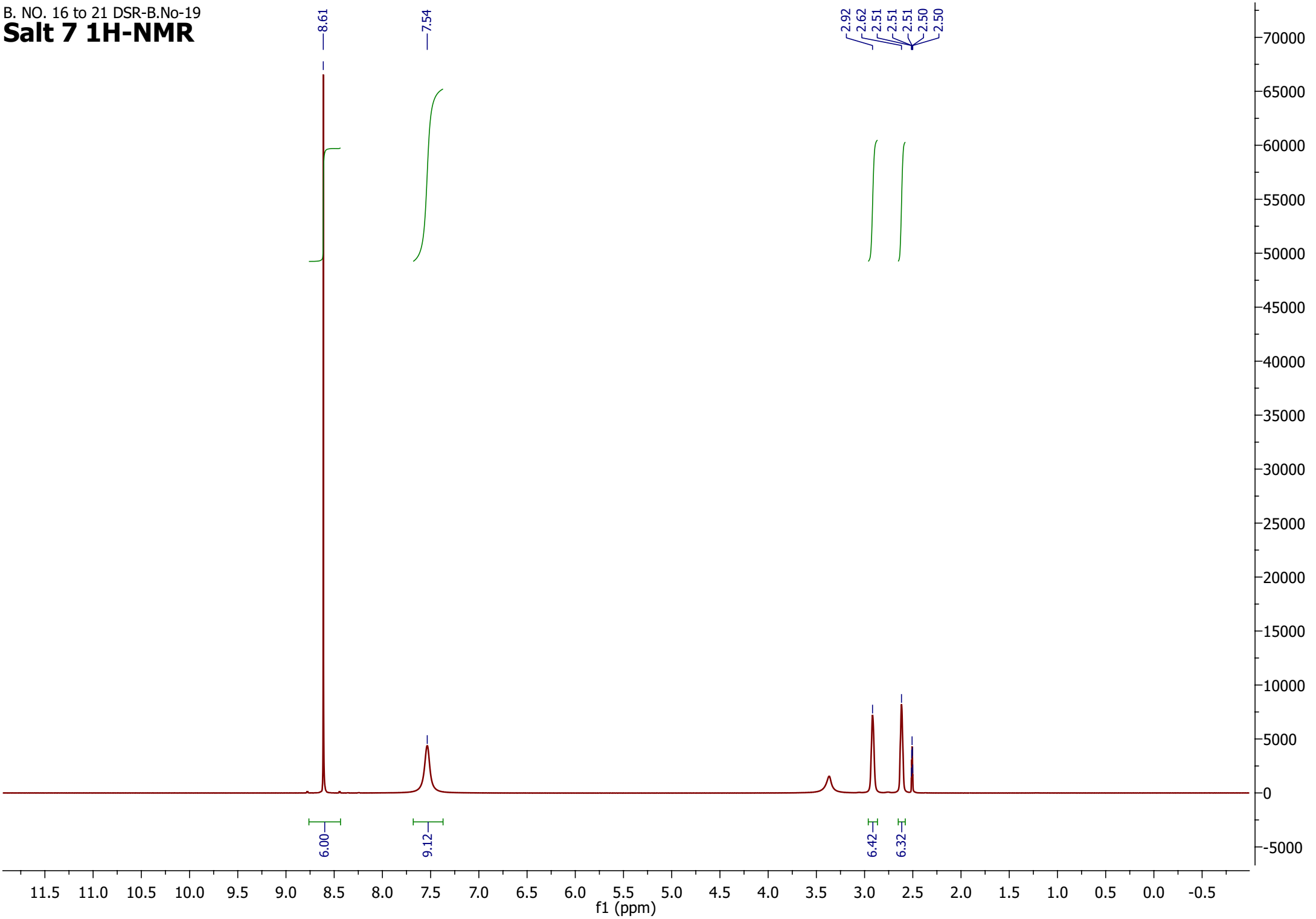
Run Date: 17-Sep-2019 11:17
Instrument: SDT Q600 V20.9 Build 20



Universal V4.5A TA Instruments

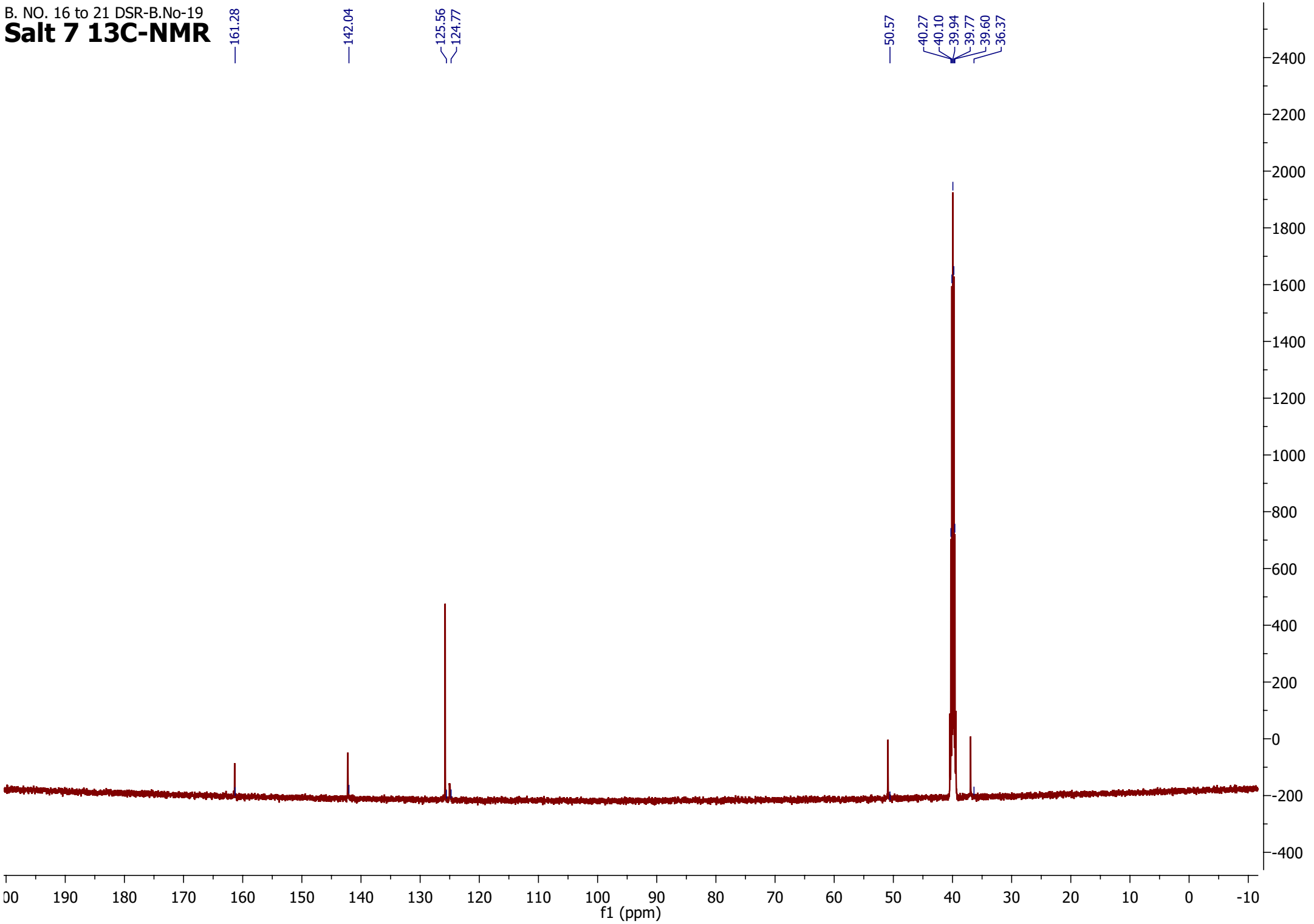
B. NO. 16 to 21 DSR-B.No-19

Salt 7 1H-NMR



B. NO. 16 to 21 DSR-B.No-19

Salt 7 13C-NMR



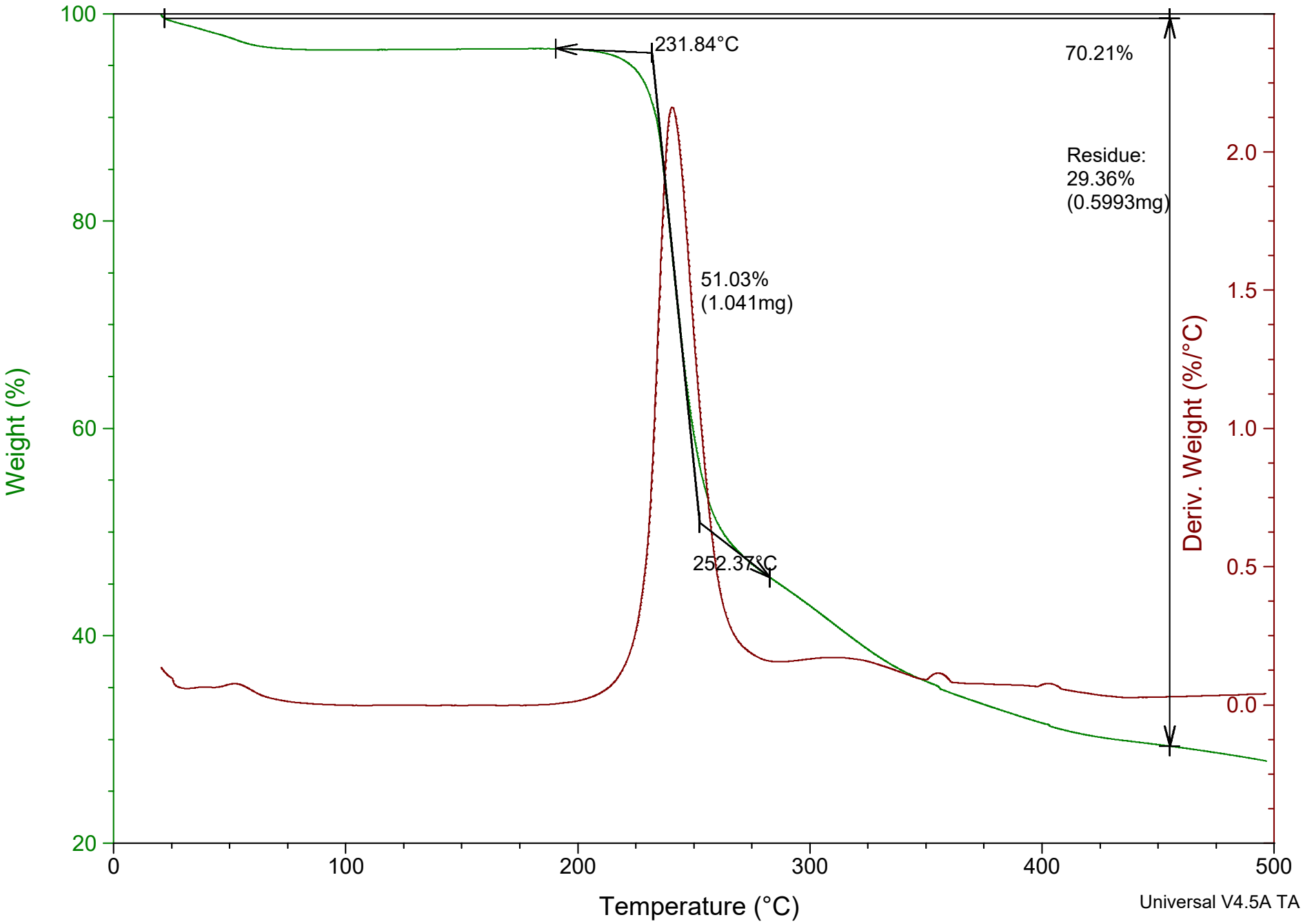
Sample: RMS-19
Size: 2.0410 mg
Method: Ramp

Salt 7

DSC-TGA

File: C:...\TGA-DATA\2019\SEPTEMBER\RMS-19.00

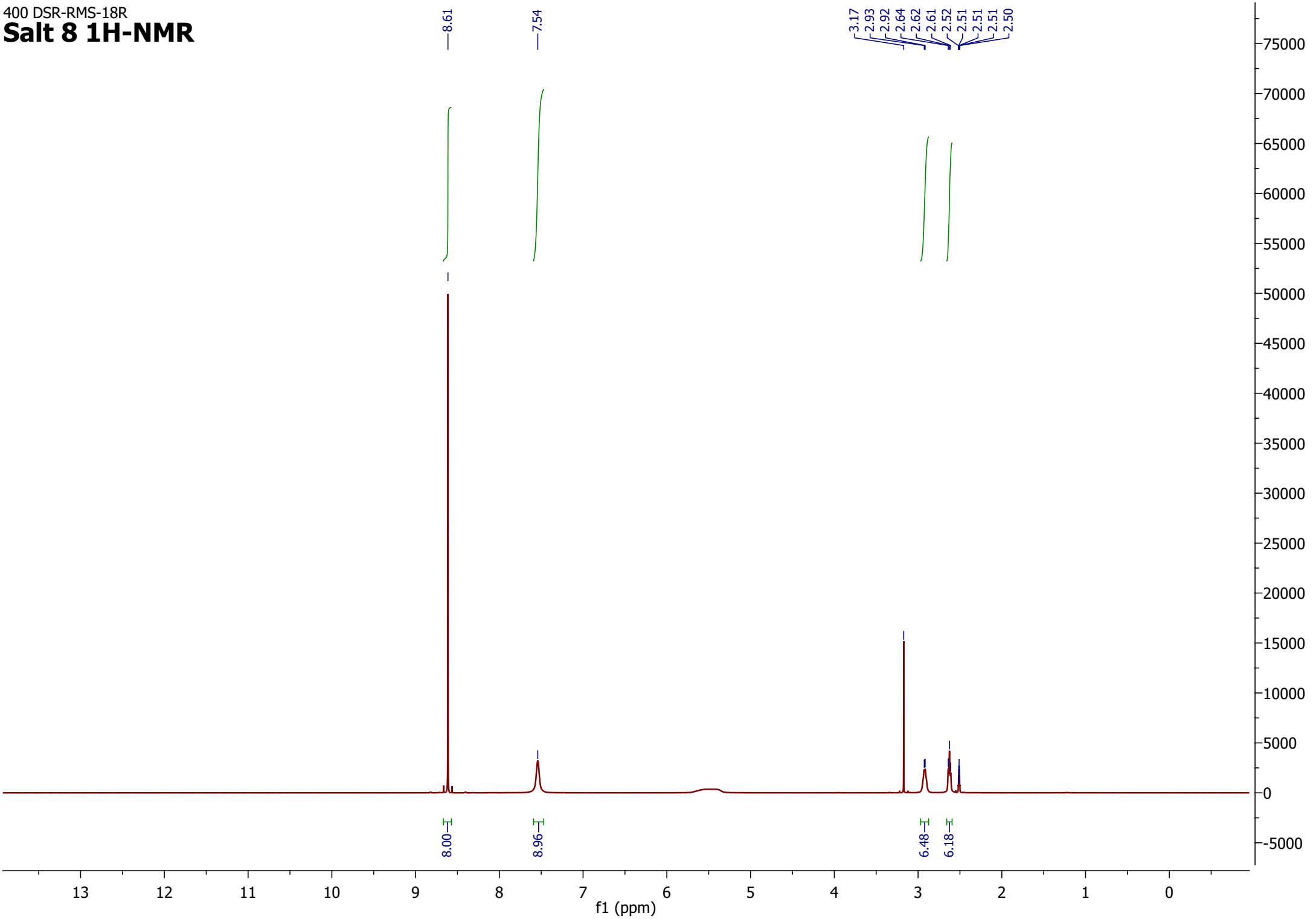
Run Date: 16-Sep-2019 09:42
Instrument: SDT Q600 V20.9 Build 20



Universal V4.5A TA Instruments

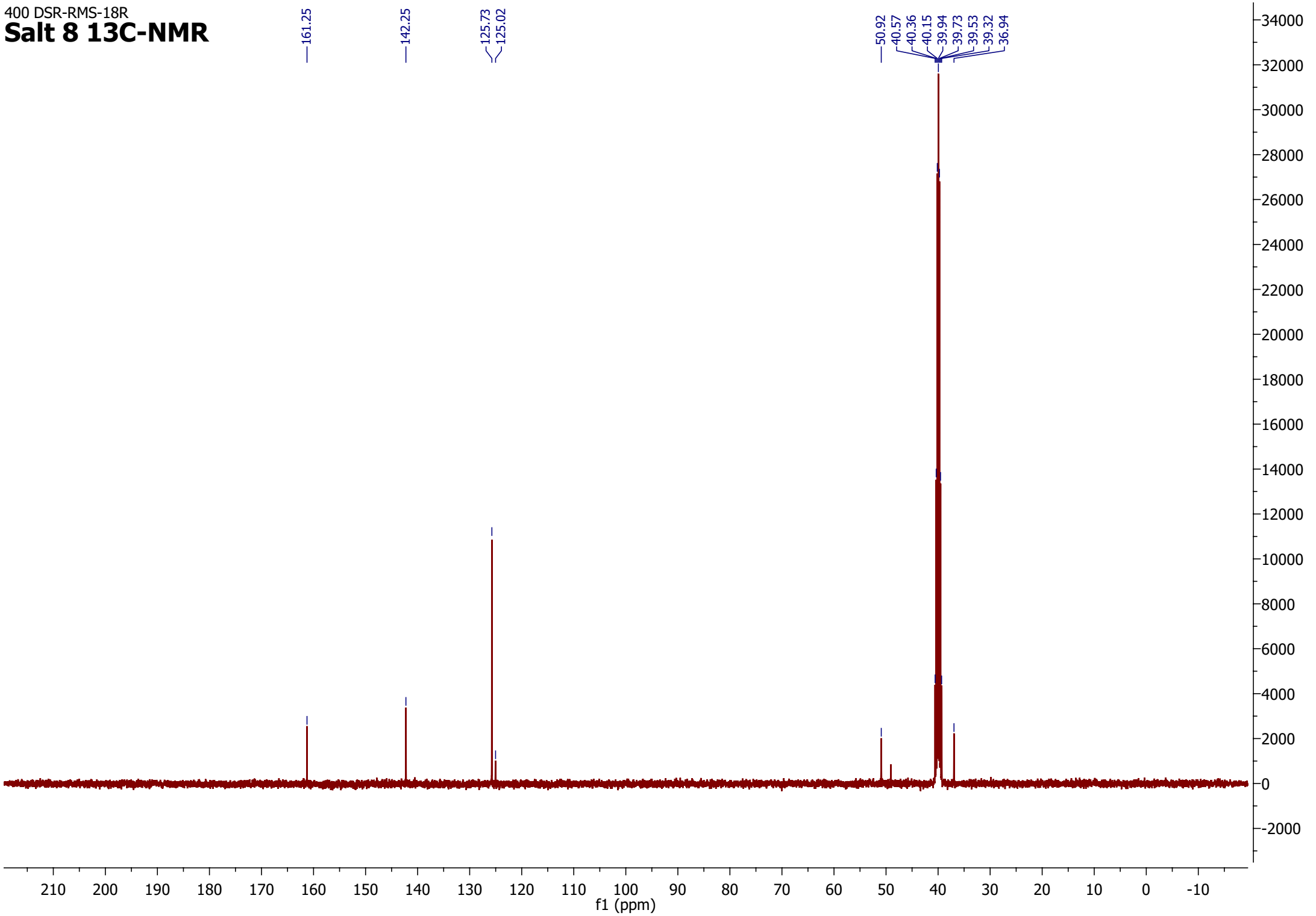
400 DSR-RMS-18R

Salt 8 1H-NMR



400 DSR-RMS-18R

Salt 8 13C-NMR



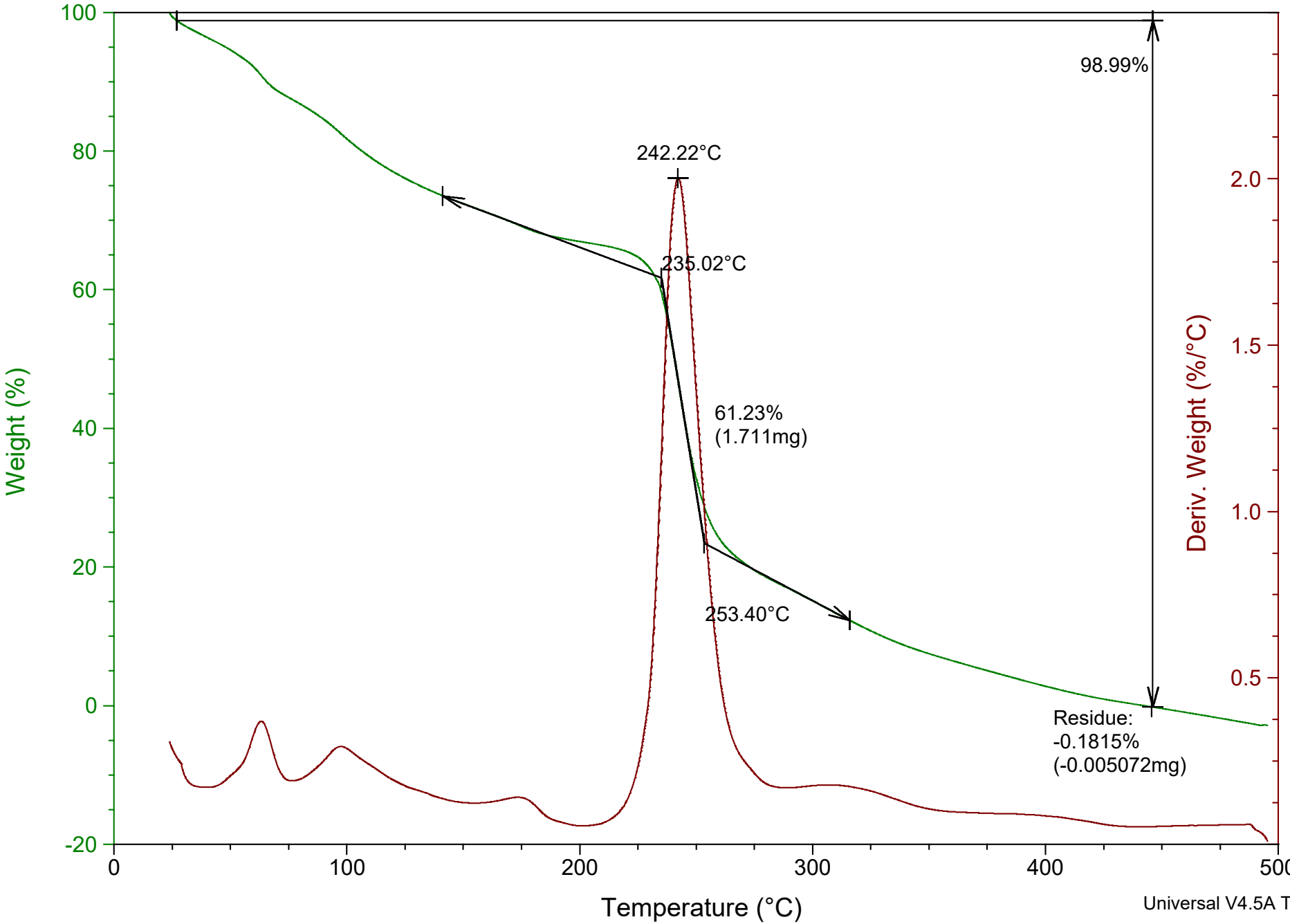
Sample: RMS-18
Size: 2.7940 mg
Method: Ramp

Salt 8

DSC-TGA

File: C:...\TGA-DATA\2019\SEPTEMBER\RMS-18.00

Run Date: 16-Sep-2019 11:39
Instrument: SDT Q600 V20.9 Build 20



Universal V4.5A TA Instruments

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: Salt-1a

```
Bond precision:  C-C = 0.0050 A          Wavelength=0.71073

Cell:            a=9.9819(6)    b=7.1284(4)         c=11.8414(7)
                 alpha=90       beta=114.070(2)     gamma=90
Temperature:     296 K

                Calculated                Reported
Volume          769.31(8)                 769.31(8)
Space group     P 21                      P21
Hall group      P 2yb                     ?
Moiety formula  C6 H2 N3 O7, C6 H13 N4    ?
Sum formula     C12 H15 N7 O7             C12 H15 N7 O7
Mr              369.31                    369.31
Dx,g cm-3       1.594                     1.594
Z               2                         2
Mu (mm-1)       0.133                     0.133
F000            384.0                     384.0
F000'           384.21
h,k,lmax        11,8,14                   11,8,14
Nref            2718[ 1478]               2705
Tmin,Tmax       0.975,0.989               0.949,0.989
Tmin'           0.948

Correction method= # Reported T Limits: Tmin=0.949 Tmax=0.989
AbsCorr = MULTI-SCAN

Data completeness= 1.83/1.00      Theta(max)= 25.000

R(reflections)= 0.0522( 2333)     wR2(reflections)= 0.1263( 2705)

S = 1.147                 Npar= 239
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
STRVA01_ALERT_4_C           Flack parameter is too small
           From the CIF: _refine_ls_abs_structure_Flack   -1.300
           From the CIF: _refine_ls_abs_structure_Flack_su    1.900
PLAT089_ALERT_3_C Poor Data / Parameter Ratio (Zmax < 18) ........       6.18 Note
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of         N3 Check
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.1 Note
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............      0.005 Ang.
```

Alert level G

```
PLAT005_ALERT_5_G No Embedded Refinement Details Found  in the CIF     Please Do !
PLAT032_ALERT_4_G Std. Uncertainty on Flack Parameter Value High .      1.900 Report
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical          ? Check
PLAT899_ALERT_4_G SHELXL97   is Deprecated and Succeeded by SHELXL       2018 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   5 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   4 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   2 ALERT type 2 Indicator that the structure model may be wrong or deficient
   2 ALERT type 3 Indicator that the structure quality may be low
   3 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

Datablock: Salt-1b

Bond precision: C-C = 0.0040 A Wavelength=0.71073

Cell: a=12.462(2) b=6.7318(11) c=18.747(3)
       alpha=90 beta=107.065(5) gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	1503.5(4)	1503.5(4)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	?
Moiety formula	C6 H2 N3 O7, C6 H13 N4	?
Sum formula	C12 H15 N7 O7	C12 H15 N7 O7
Mr	369.31	369.31
Dx,g cm-3	1.632	1.632
Z	4	4
Mu (mm-1)	0.136	0.136
F000	768.0	768.0
F000'	768.42	
h,k,lmax	14,8,22	14,8,22
Nref	2637	2637
Tmin,Tmax	0.968,0.974	0.965,0.975
Tmin'	0.965	

Correction method= # Reported T Limits: Tmin=0.965 Tmax=0.975
AbsCorr = MULTI-SCAN

Data completeness= 1.000 Theta(max)= 25.000

R(reflections)= 0.0519(1674) wR2(reflections)= 0.1764(2637)

S = 1.101 Npar= 235

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT230_ALERT_2_C Hirshfeld Test Diff for N5 --C7 . 5.5 s.u.
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of N2 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of N3 Check
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 2.3 Note

---

Alert level G

PLAT005_ALERT_5_G No Embedded Refinement Details Found in the CIF Please Do !
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 1 Report
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical ? Check
PLAT093_ALERT_1_G No s.u.'s on H-positions, Refinement Reported as mixed Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 1 Note
PLAT899_ALERT_4_G SHELXL97 is Deprecated and Succeeded by SHELXL 2018 Note

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
4 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
6 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

Datablock: Salt-2

Bond precision: C-C = 0.0089 A Wavelength=0.71073

Cell: a=21.997(8) b=6.972(2) c=20.770(7)
alpha=90 beta=90 gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	3185.4(18)	3185.2(18)
Space group	P c a 21	P c a 21
Hall group	P 2c -2ac	?
Moiety formula	C6 H2 N3 O7, C6 H16 N	?
Sum formula	C12 H18 N4 O7	C24 H36 N8 O14
Mr	330.30	660.61
Dx,g cm-3	1.378	1.378
Z	8	4
Mu (mm-1)	0.114	0.114
F000	1392.0	1392.0
F000'	1392.82	
h,k,lmax	25,8,24	25,8,24
Nref	5292[2730]	5275
Tmin,Tmax	0.976,0.982	0.972,0.982
Tmin'	0.972	

Correction method= # Reported T Limits: Tmin=0.972 Tmax=0.982
AbsCorr = MULTI-SCAN

Data completeness= 1.93/1.00 Theta(max)= 24.490

R(reflections)= 0.0770(3053) wR2(reflections)= 0.2159(5275)

S = 1.004 Npar= 421

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT360_ALERT_2_B Short C(sp3)-C(sp3) Bond C3 - C4 . 1.29 Ang.

Alert level C

STRVA01_ALERT_4_C Flack test results are meaningless.
From the CIF: _refine_ls_abs_structure_Flack 0.000
From the CIF: _refine_ls_abs_structure_Flack_su 2.000
THETM01_ALERT_3_C The value of sine(theta_max)/wavelength is less than 0.590
Calculated sin(theta_max)/wavelength = 0.5833
PLAT089_ALERT_3_C Poor Data / Parameter Ratio (Zmax < 18) ..... 6.48 Note
PLAT230_ALERT_2_C Hirshfeld Test Diff for O12 --N6 . 6.5 s.u.
PLAT234_ALERT_4_C Large Hirshfeld Difference O13 --N7 . 0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference O14 --N7 . 0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N1 --C4 . 0.22 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N1 --C6 . 0.21 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C5 --C6 . 0.25 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference C21 --C22 . 0.18 Ang.
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of N3 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of N5 Check
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of N7 Check
PLAT243_ALERT_4_C High 'Solvent' Ueq as Compared to Neighbors of C4 Check

```
PLAT243_ALERT_4_C High   'Solvent' Ueq as Compared to Neighbors of         C6 Check
PLAT244_ALERT_4_C Low    'Solvent' Ueq as Compared to Neighbors of         N1 Check
PLAT244_ALERT_4_C Low    'Solvent' Ueq as Compared to Neighbors of         N8 Check
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.4 Note
PLAT260_ALERT_2_C Large Average Ueq of Residue Including        N1      0.176 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including        N8      0.112 Check
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00889 Ang.
PLAT360_ALERT_2_C Short  C(sp3)-C(sp3) Bond  C5       - C6       .       1.41 Ang.
```

Alert level G

```
PLAT005_ALERT_5_G No Embedded Refinement Details Found  in the CIF     Please Do !
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          2 Report
PLAT032_ALERT_4_G Std. Uncertainty on Flack Parameter Value High .      2.000 Report
PLAT045_ALERT_1_G Calculated and Reported Z Differ by a Factor ...       2.00 Check
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical          ? Check
PLAT072_ALERT_2_G SHELXL First  Parameter in WGHT  Unusually Large       0.13 Report
PLAT093_ALERT_1_G No s.u.'s on H-positions, Refinement Reported as      mixed Check
PLAT850_ALERT_4_G Check Flack Parameter Exact Value 0.00 and s.u.        2.00 Check
PLAT899_ALERT_4_G SHELXL97   is Deprecated and Succeeded by SHELXL       2018 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   1 ALERT level B = A potentially serious problem, consider carefully
  22 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   9 ALERT level G = General information/check it is not something unexpected

   3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  10 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
  14 ALERT type 4 Improvement, methodology, query or suggestion
   2 ALERT type 5 Informative message, check
```

Datablock: Salt-5

Bond precision: C-C = 0.0111 A Wavelength=0.71073

Cell:	a=6.9949(9)	b=12.5916(19)	c=19.969(3)
	alpha=90	beta=90	gamma=90
Temperature:	296 K		

	Calculated	Reported
Volume	1758.8(4)	1758.9(4)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	?
Moiety formula	C6 H2 N3 O7, C6 H19 N4	?
Sum formula	C12 H21 N7 O7	C12 H21 N7 O7
Mr	375.36	375.36
Dx,g cm-3	1.418	1.418
Z	4	4
Mu (mm-1)	0.117	0.117
F000	792.0	792.0
F000'	792.42	
h,k,lmax	8,14,22	8,14,22
Nref	2746[1606]	2646
Tmin,Tmax	0.972,0.988	0.970,0.988
Tmin'	0.970	

Correction method= # Reported T Limits: Tmin=0.970 Tmax=0.988
AbsCorr = MULTI-SCAN

Data completeness= 1.65/0.96 Theta(max)= 23.990

R(reflections)= 0.0686(1141) wR2(reflections)= 0.1967(2646)

S = 0.893 Npar= 235

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT316_ALERT_2_A Too many H on C in C=N Moiety in Main Residue .. C11 Check
PLAT410_ALERT_2_A Short Intra H...H Contact H8A ..H11B . 1.74 Ang.
x,y,z = 1_555 Check
PLAT417_ALERT_2_A Short Inter D-H..H-D H5B ..H6B . 1.60 Ang.
1-x,-1/2+y,3/2-z = 3_646 Check

Alert level B

THETM01_ALERT_3_B The value of sine(theta_max)/wavelength is less than 0.575
Calculated sin(theta_max)/wavelength = 0.5721
PLAT234_ALERT_4_B Large Hirshfeld Difference C11 --C12 . 0.26 Ang.
PLAT241_ALERT_2_B High 'MainMol' Ueq as Compared to Neighbors of C8 Check
PLAT241_ALERT_2_B High 'MainMol' Ueq as Compared to Neighbors of C10 Check
PLAT241_ALERT_2_B High 'MainMol' Ueq as Compared to Neighbors of C12 Check
PLAT242_ALERT_2_B Low 'MainMol' Ueq as Compared to Neighbors of N7 Check
PLAT340_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.01111 Ang.
PLAT360_ALERT_2_B Short C(sp3)-C(sp3) Bond C7 - C8 . 1.26 Ang.
PLAT360_ALERT_2_B Short C(sp3)-C(sp3) Bond C11 - C12 . 1.31 Ang.
PLAT410_ALERT_2_B Short Intra H...H Contact H7A ..H8B . 1.86 Ang.
x,y,z = 1_555 Check
PLAT410_ALERT_2_B Short Intra H...H Contact H7B ..H8A . 1.86 Ang.

```
                                                  x,y,z  =      1_555 Check
PLAT410_ALERT_2_B Short Intra H...H Contact  H8B      ..H9A      .       1.88 Ang.
                                                  x,y,z  =      1_555 Check
PLAT410_ALERT_2_B Short Intra H...H Contact  H11A     ..H12B     .       1.86 Ang.
                                                  x,y,z  =      1_555 Check
PLAT410_ALERT_2_B Short Intra H...H Contact  H11B     ..H12A     .       1.86 Ang.
                                                  x,y,z  =      1_555 Check
PLAT416_ALERT_2_B Short Intra D-H..H-D       H4C      ..H5A      .       1.86 Ang.
                                                  x,y,z  =      1_555 Check
```

Alert level C

```
STRVA01_ALERT_2_C           Chirality of atom sites is inverted?
          From the CIF: _refine_ls_abs_structure_Flack    3.000
          From the CIF: _refine_ls_abs_structure_Flack_su    4.000
PLAT026_ALERT_3_C Ratio Observed / Unique Reflections (too) Low ..        43% Check
PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full value Low .      0.973 Why?
PLAT089_ALERT_3_C Poor Data / Parameter Ratio (Zmax < 18) ........       6.83 Note
PLAT230_ALERT_2_C Hirshfeld Test Diff for    O5       --N3       .        5.7 s.u.
PLAT230_ALERT_2_C Hirshfeld Test Diff for    N1       --C1       .        6.3 s.u.
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C9       --C10      .        6.4 s.u.
PLAT234_ALERT_4_C Large Hirshfeld Difference O6       --N3       .       0.17 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N4       --C12      .       0.22 Ang.
PLAT234_ALERT_4_C Large Hirshfeld Difference N6       --C10      .       0.18 Ang.
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of         C9 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of         N1 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of         N3 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of         C7 Check
PLAT260_ALERT_2_C Large Average Ueq of Residue Including        N4      0.157 Check
PLAT360_ALERT_2_C Short  C(sp3)-C(sp3) Bond  C9       - C10      .       1.39 Ang.
PLAT410_ALERT_2_C Short Intra H...H Contact  H9B      ..H11A     .       1.94 Ang.
                                                  x,y,z  =      1_555 Check
PLAT420_ALERT_2_C D-H Without Acceptor       N4       --H4A      .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N4       --H4B      .     Please Check
PLAT420_ALERT_2_C D-H Without Acceptor       N6       --H6A      .     Please Check
PLAT907_ALERT_2_C Flack x > 0.5, Structure Needs to be Inverted? .       3.00 Check
```

Alert level G

```
PLAT005_ALERT_5_G No Embedded Refinement Details Found  in the CIF     Please Do !
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          7 Report
PLAT032_ALERT_4_G Std. Uncertainty on Flack Parameter Value High .      4.000 Report
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical          ? Check
PLAT093_ALERT_1_G No s.u.'s on H-positions, Refinement Reported as      mixed Check
PLAT899_ALERT_4_G SHELXL97   is Deprecated and Succeeded by SHELXL       2018 Note
```

```
   3 ALERT level A = Most likely a serious problem - resolve or explain
  15 ALERT level B = A potentially serious problem, consider carefully
  21 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   6 ALERT level G = General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  30 ALERT type 2 Indicator that the structure model may be wrong or deficient
   5 ALERT type 3 Indicator that the structure quality may be low
   6 ALERT type 4 Improvement, methodology, query or suggestion
   2 ALERT type 5 Informative message, check
```

Datablock: Salt-7a

Bond precision: C-C = 0.0044 A Wavelength=0.71073

Cell: a=8.4362(9) b=12.5183(14) c=18.3788(19)
alpha=72.109(3) beta=83.298(3) gamma=72.280(3)
Temperature: 296 K

	Calculated	Reported
Volume	1758.9(3)	1758.9(3)
Space group	P -1	P -1
Hall group	-P 1	?
Moiety formula	3(C6 H2 N3 O7), C6 H21 N4, C H4 O	?
Sum formula	C25 H31 N13 O22	C25 H31 N13 O22
Mr	865.63	865.63
Dx,g cm-3	1.635	1.634
Z	2	2
Mu (mm-1)	0.145	0.145
F000	896.0	896.0
F000'	896.58	
h,k,lmax	10,14,21	10,14,21
Nref	6173	6066
Tmin,Tmax	0.969,0.980	0.965,0.980
Tmin'	0.964	

Correction method= # Reported T Limits: Tmin=0.965 Tmax=0.980
AbsCorr = MULTI-SCAN

Data completeness= 0.983 Theta(max)= 25.000

R(reflections)= 0.0592(4258) wR2(reflections)= 0.1774(6066)

S = 1.101 Npar= 546

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT097_ALERT_2_B Large Reported Max. (Positive) Residual Density 0.97 eA-3
PLAT230_ALERT_2_B Hirshfeld Test Diff for O1 --N1 . 7.3 s.u.

Alert level C

CRYSC01_ALERT_1_C The word below has not been recognised as a standard identifier.
Wine
DIFMX02_ALERT_1_C The maximum difference density is > 0.1*ZMAX*0.75
The relevant atom site should be identified.
PLAT213_ALERT_2_C Atom O1 has ADP max/min Ratio ..... 3.1 prolat
PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of N1 Check

```
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of         N9 Check
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor ....        2.3 Note
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.00438 Ang.
```

Alert level G

```
PLAT005_ALERT_5_G No Embedded Refinement Details Found  in the CIF     Please Do !
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............         10 Report
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical          ? Check
PLAT093_ALERT_1_G No s.u.'s on H-positions, Refinement Reported as       mixed Check
PLAT154_ALERT_1_G The s.u.'s on the Cell Angles are Equal ..(Note)      0.003 Degree
PLAT432_ALERT_2_G Short Inter X...Y Contact  O5       ..C24             2.95 Ang.
                                                    x,y,z  =      1_555 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..........          4 Note
PLAT899_ALERT_4_G SHELXL97   is Deprecated and Succeeded by SHELXL       2018 Note
```

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
2 **ALERT level B** = A potentially serious problem, consider carefully
7 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
8 **ALERT level G** = General information/check it is not something unexpected

5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
7 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

Datablock: Salt-7b

Bond precision: C-C = 0.0031 A Wavelength=0.71073

Cell:	a=14.1276(6)	b=10.6978(5)	c=24.1392(11)
	alpha=90	beta=106.656(1)	gamma=90
Temperature:	296 K		

	Calculated	Reported
Volume	3495.2(3)	3495.2(3)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	?
Moiety formula	3(C6 H2 N3 O7), C6 H21 N4, 2(H2 O)	?
Sum formula	C24 H31 N13 O23	C24 H31 N13 O23
Mr	869.62	869.62
Dx,g cm-3	1.653	1.653
Z	4	4
Mu (mm-1)	0.149	0.149
F000	1800.0	1800.0
F000’	1801.19	
h,k,lmax	16,12,28	16,12,28
Nref	6163	6153
Tmin,Tmax	0.970,0.979	0.965,0.979
Tmin’	0.965	

Correction method= # Reported T Limits: Tmin=0.965 Tmax=0.979
AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 25.000

R(reflections)= 0.0495(4813) wR2(reflections)= 0.1682(6153)

S = 1.124 Npar= 557

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT242_ALERT_2_C Low ’MainMol’ Ueq as Compared to Neighbors of N1 Check
PLAT242_ALERT_2_C Low ’MainMol’ Ueq as Compared to Neighbors of N3 Check
PLAT242_ALERT_2_C Low ’MainMol’ Ueq as Compared to Neighbors of N4 Check
PLAT242_ALERT_2_C Low ’MainMol’ Ueq as Compared to Neighbors of N6 Check
PLAT242_ALERT_2_C Low ’MainMol’ Ueq as Compared to Neighbors of N7 Check
PLAT242_ALERT_2_C Low ’MainMol’ Ueq as Compared to Neighbors of N9 Check
PLAT250_ALERT_2_C Large U3/U1 Ratio for Average U(i,j) Tensor .... 2.1 Note

---

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 6 Note
PLAT005_ALERT_5_G No Embedded Refinement Details Found in the CIF Please Do !
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 9 Report
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical ? Check
PLAT072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large 0.10 Report
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels ..... 6 Note
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. # 3 Note
C6 H2 N3 O7
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd. # 6 Note
H2 O

```
PLAT860_ALERT_3_G Number of Least-Squares Restraints .....          4 Note
PLAT899_ALERT_4_G SHELXL97   is Deprecated and Succeeded by SHELXL    2018 Note
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   7 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  10 ALERT level G = General information/check it is not something unexpected

   1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   9 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   4 ALERT type 4 Improvement, methodology, query or suggestion
   2 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

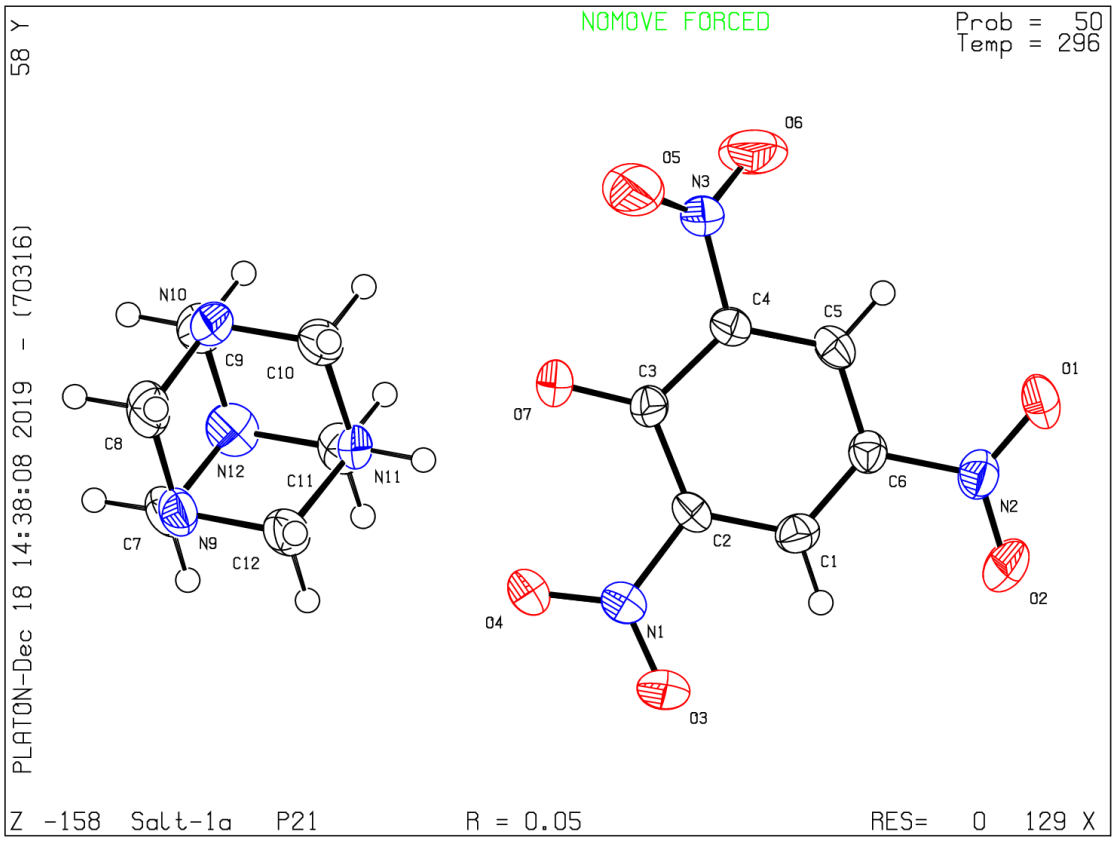
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

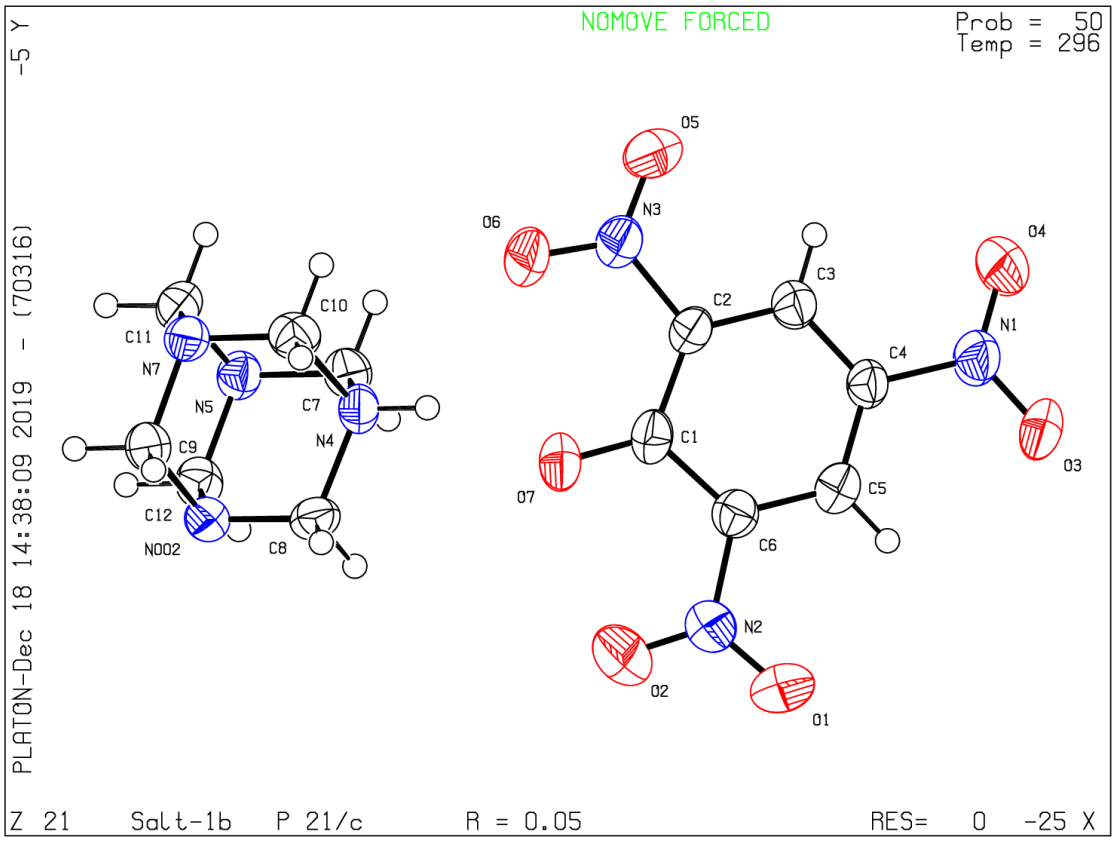
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 16/12/2019; check.def file version of 13/12/2019

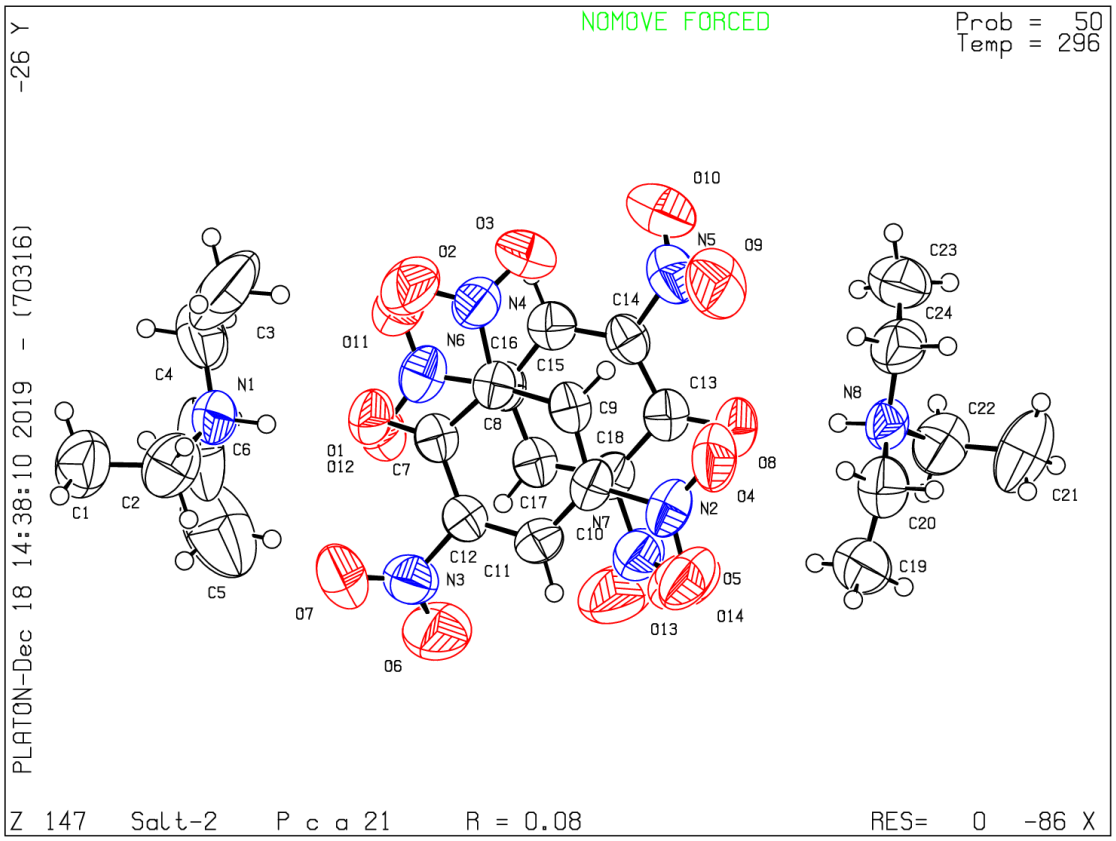
Datablock Salt-1a - ellipsoid plot



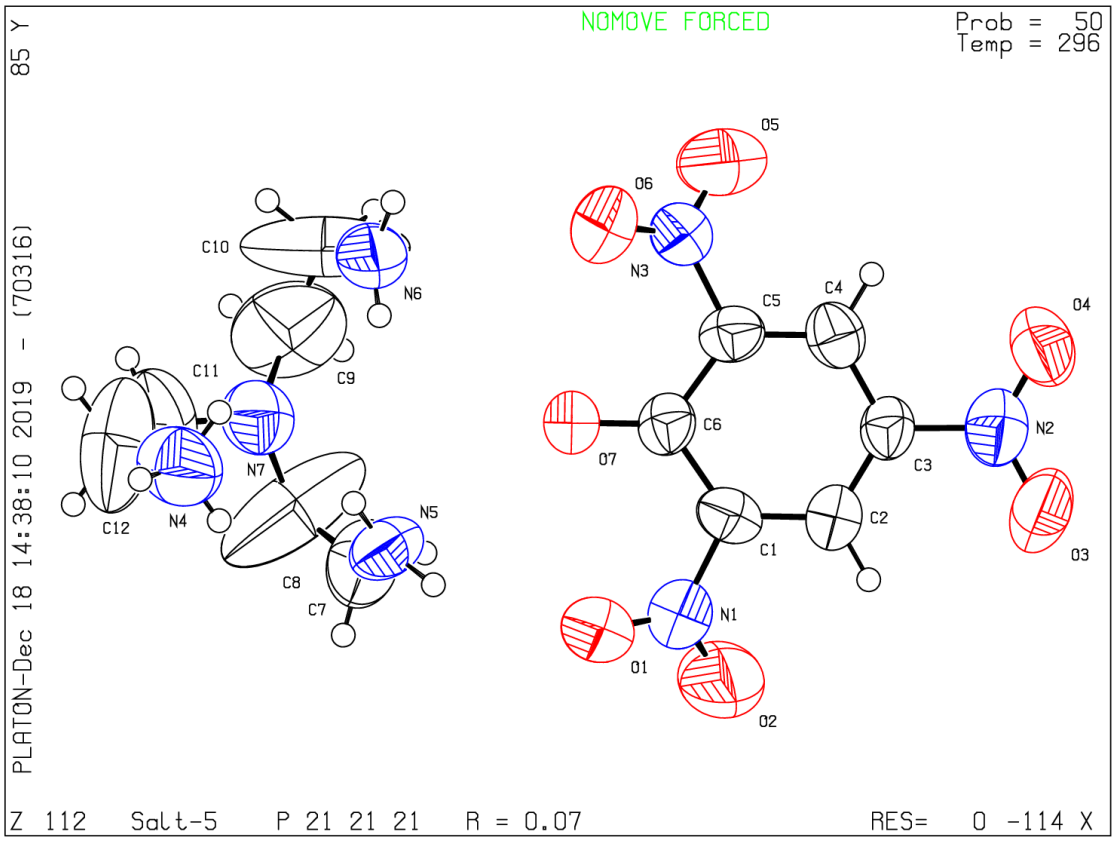
Datablock Salt-1b - ellipsoid plot



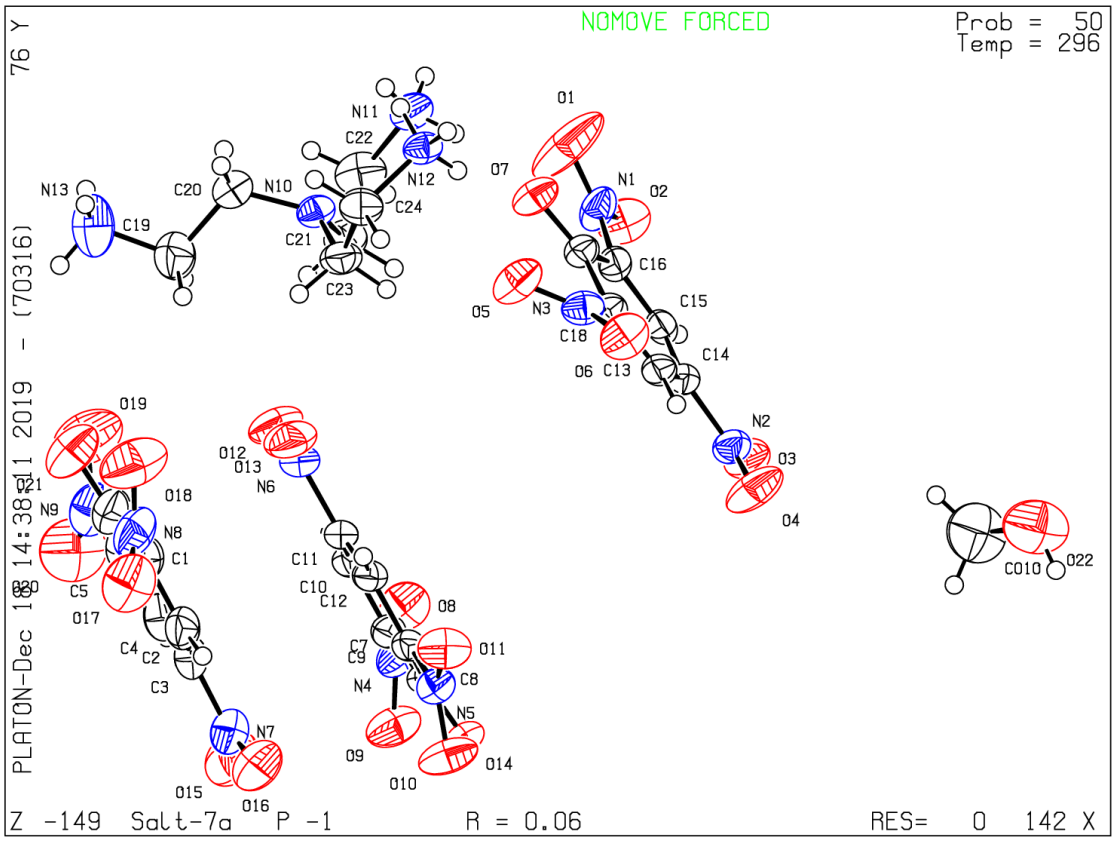
Datablock Salt-2 - ellipsoid plot



Datablock Salt-5 - ellipsoid plot



Datablock Salt-7a - ellipsoid plot



Datablock Salt-7b - ellipsoid plot