Electronic Supplementary Material (ESI) for RSC Advances.

Site specific role of bifunctional graphitic carbon nitride catalyst for the sustainable synthesis of 3,3-spirocyclic oxindoles in aqueous media

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Supporting Information **Page no.**

1. General

All the chemicals used were of research grade (purchased from Sigma Aldrich, Acros etc.) and used without further purification. The melting points of all compounds were determined on a Toshniwal apparatus in capillary and uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO d_6 using TMS as an internal standard on a JEOL NMR spectrometer at 400 and 100 MHz respectively. Chemical shifts are expressed in parts per million (ppm) using tetramethylsilane (TMS) as an internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet and m = multiplet. Mass spectrum of representative compound was recorded on Waters-Xeevo G_2S Q-Tof. X-ray diffraction (XRD) measurements for phase determination were recorded by Philips powder diffractometer (PW3040/60) with Cu K_α radiation (1.54060nm) operating in a continuous mode to collect 2θ values with a scan rate of 0.02°/min. SEM and EDX measurements were performed using a FEI Quanta 200F SEM. The size and morphology of the synthesized material was observed by transmission electron microscopy (TEM) using a JEOL 1011 at an accelerating voltage of 200kV. (XPS) were measured on a commercial SPECS spectrometer (Germany), equipped with an Al-Kα X-ray source (1486.5eV). The UV-Vis spectra were recorded using Ocean optics USB 2000 spectrophotometer in the solution form. The Raman spectra were recorded by micro-Raman spectrometer (Jobin Yvon Horibra LABRAM-HR visible 400-1100 nm). IR spectra were recorded on a Shimadzu FT IR- 8400S spectrophotometer using KBr pellets. The Elemental analysis of the samples has been done by Elemental Analyzer Perkin Elmer PE 2400 and ELEMENTAR Vario EL III.

2. Synthesis of g-C_3N_4

Melamine (5 g) was placed in a crucible (enclosed with a lid) and heated at 550^0C (at a rate of 4°C/min) in a muffle furnace for 3 h. After that, obtained material was crushed into fine powder with the help of a pestle-mortar and referred as g-C_3N_4.

3. Synthesis of Sg-C_3N_4

The as prepared g-C_3N_4 and 30% aqueous H_2SO_4 was placed in flask. The flask was attached to a 12 mm tip diameter probe and the reaction mixture was sonicated for the 4h at 50% power of the processor and 230W output in a 4 s pulse mode. The resulting mixture was poured in ice-cold water and centrifuged (12000 rpm for 10 min twice). The obtained solid material was dried under vacuum for 24 h and referred as Sg-C_3N_4.

4. Synthesis of spiro-pyrano chromene derivatives

A mixture of isatins (2.0 mmol), malononitrile/ ethyl cyanoacetate (2.0 mmol), 4-hydroxycoumarin (2.0 mmol) and 20 wt% Sg-C_3N_4 in 20 ml water were mixed, and the reaction mixture was heated under reflux for appropriate time. The progress of the reaction was checked on TLC. After completion of the reaction the solid product was filtered along with the catalyst. The precipitate was dissolved in ethyl acetate and the catalyst was recovered by centrifugation (12000 rpm). The above residual solution was removed under reduced pressure. The crude product was subjected to purification by recrystallization using ethanol.

5. Synthesis of spiro indole-3,1′-naphthalene tetracyclic system

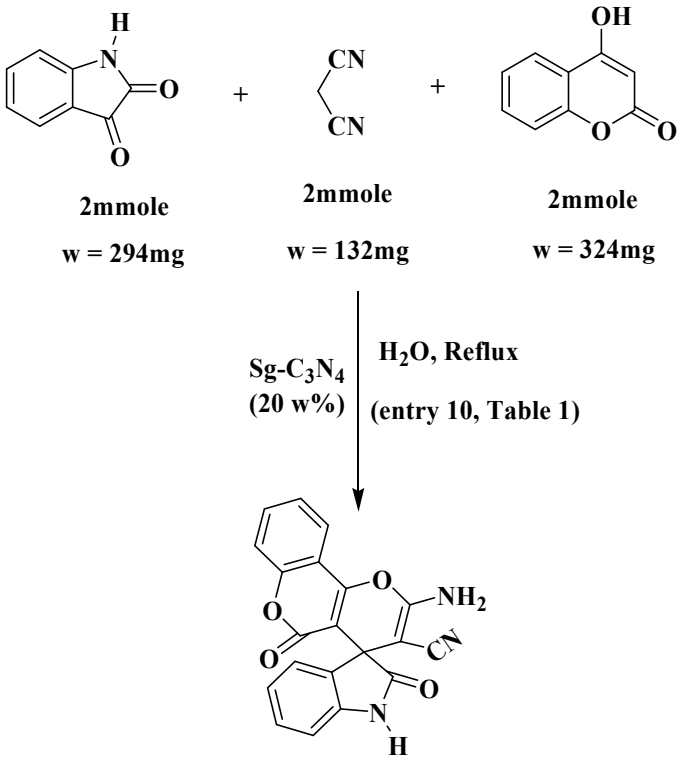
A mixture of isatins (2.0 mmol), malononitrile (4.0 mmol), cyclic ketones (2.0 mmol) and 20 wt% Sg-C_3N_4 in 20 ml water were mixed, and the reaction mixture was heated under reflux for appropriate time. The progress of the reaction was checked on TLC. After completion of the reaction the solid product was filtered along with the catalyst. The precipitate was dissolved in ethyl acetate and the catalyst was recovered by centrifugation (12000 rpm). The above residual solution was removed under reduced pressure. The crude product was subjected to purification by recrystallization using ethanol.

6. Heterogeneous nature and recyclability of Sg-C_3N_4

To confirm the heterogeneous nature of Sg-C_3N_4 in reaction, the model reaction was carried out again under similar reaction conditions with the catalyst procured from a previous cycle. After 4 min, the catalyst was separated from the reaction mixture. The reaction was continued with filtrate for another 5h and the reaction conversion was monitored for every 1h. It was observed that further increment in conversion was not observed even after 8h. These results revealed that reaction was occurring only due to the Sg-C_3N_4. This whole experiment confirms the heterogeneous nature of present catalytic system.

Recycling experiments were performed by choosing the model reaction Sg-C_3N_4 as a solid catalyst. When reaction was completed, the reaction mixture was filtered and solid precipitate was dried along with the catalyst. Then, the solid precipitate was dissolved in ethanol and catalyst was recovered by filtration. The recovered catalyst was washed with water and ethanol and reused in succeeding 7 reaction cycles with slight loss of catalytic activity. The characteristics obtained from XRD, SEM, TEM of fresh and used catalysts are similar, which suggest the retention of structure and morphology of Sg-C_3N_4 after repeated use as catalyst.

Calculation of TOF



Calculation of %ge yield

$$\%\text{ge yield} = \frac{\text{Experimental yield}}{\text{Theoritical yield}} \times 100$$

$$\text{eg for the product 4a (Table 1, entry 10)} = \frac{685.4\text{mg}}{714\text{mg}} \times 100$$

$$= 96\%$$

Calculation of TOF Value

$$\text{TOF} = \frac{\text{No. of Moles of final product produced}}{\text{Amount of loaded Catalyst x Time (min.)}}$$

$$\text{wt\% of loaded Catalyst} = \frac{\text{Amount loaded Catalyst}}{\text{Total Amount}} \times 100$$

For the product 4a (Table 1, entry 10)

Assuming amount of loaded Catalyst = x gm

$$\frac{20}{100} = \frac{x}{0.294 + 0.132 + 0.324 + x}$$

$$\frac{1}{5} = \frac{x}{0.750 + x}$$

$$0.750 + x = 5x$$

$$0.750 = 4x$$

$$x = \frac{0.750}{4} = 0.1875\text{gm}$$

$$\text{TOF} = \frac{0.6854}{357 \times 0.1875 \times 10} = \frac{0.6854}{669.375}$$

TOF = 1.024×10^{-3} mol gm^{-1} min^{-1}

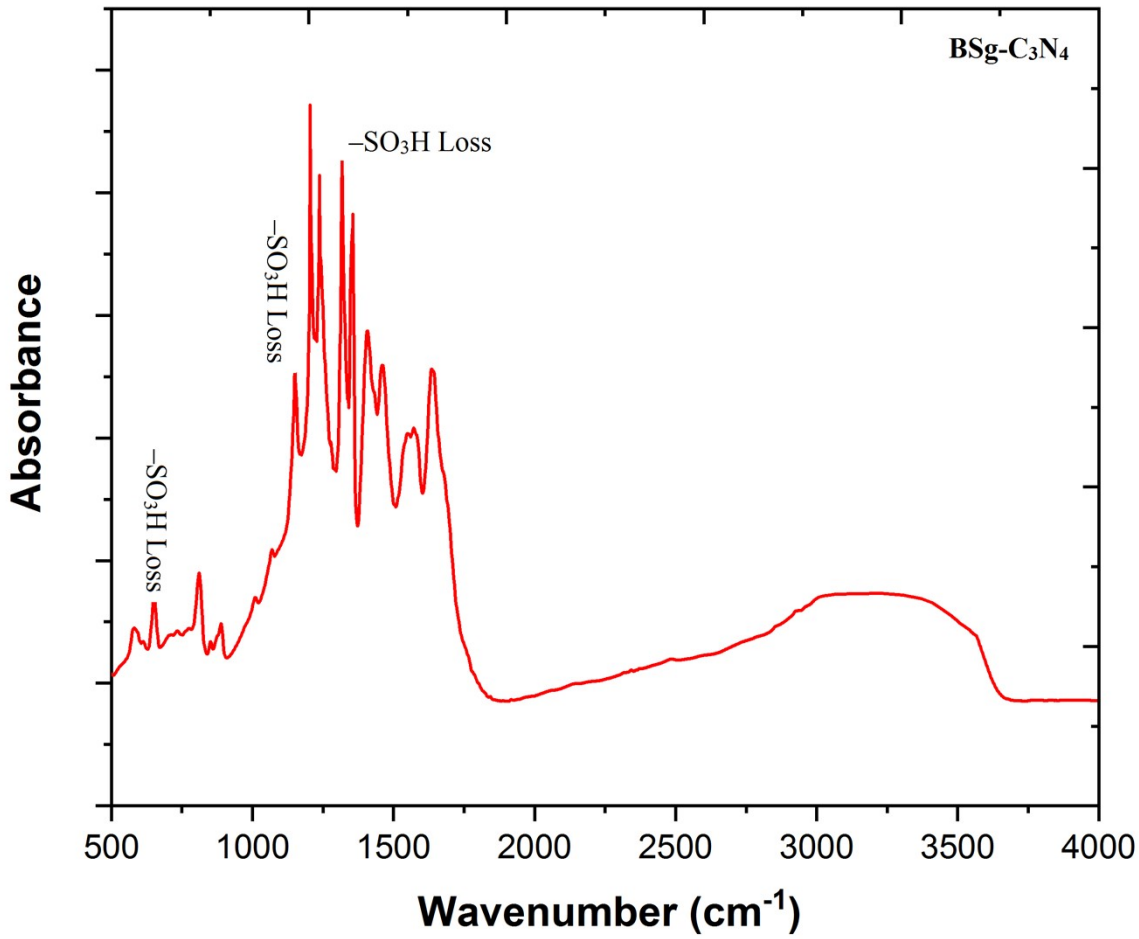


Fig S1: FT-IR spectra of BSg-C_3N_4

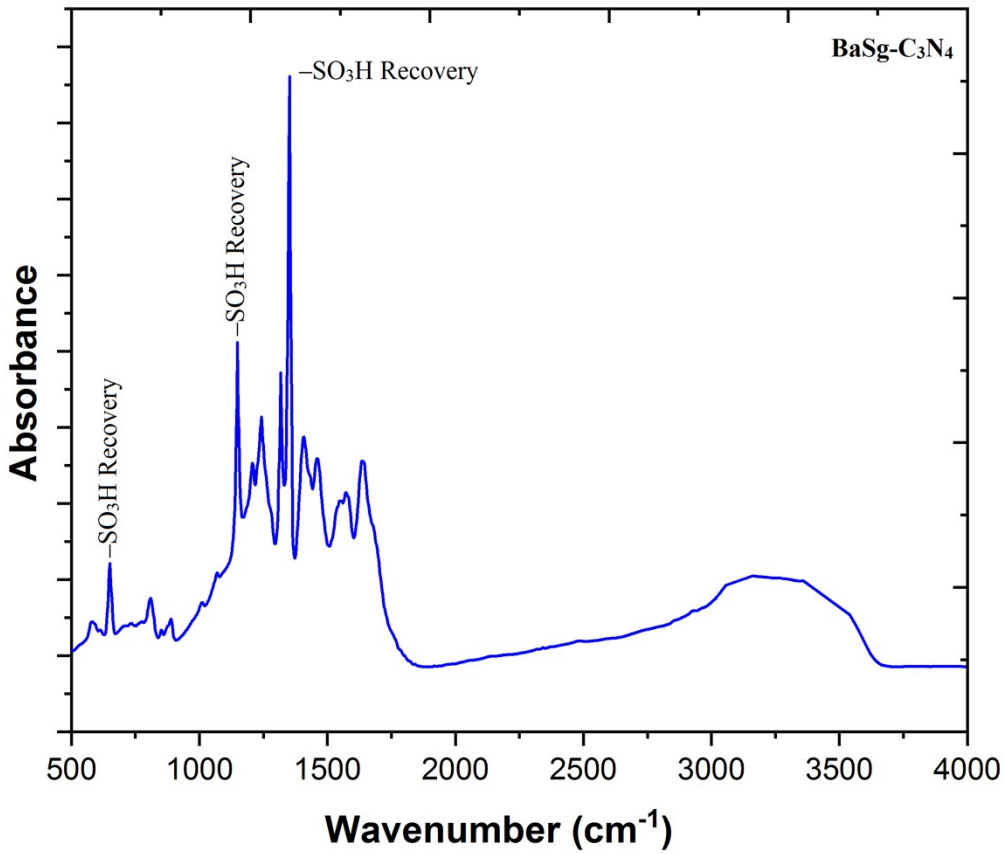


Fig S2: FT-IR spectra of BaSg-C_3N_4

Element	Atomic %
C K	33.48
O K	21.54
N K	44.98
Total	100.00

Table S1: EDAX elemental analysis of g-C_3N_4

Element	Atomic %
C K	19.00
O K	24.10
N K	49.92
S K	6.98
Total	100.00

Table S2: EDAX elemental analysis of Sg-C_3N_4

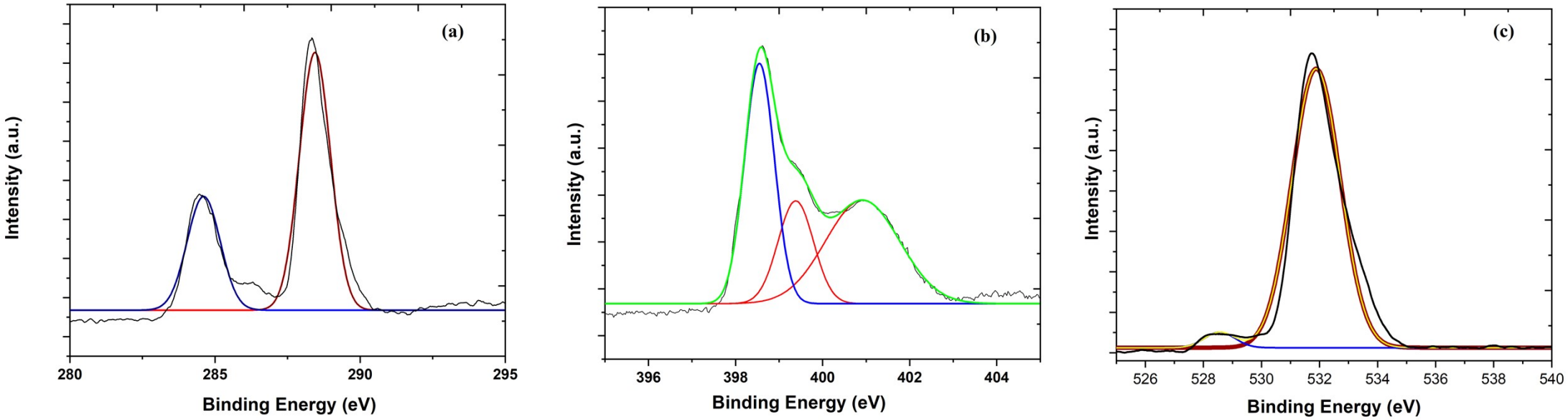


Fig.S3: XPS spectrum of **(a)** C1s spectrum of g-C_3N_4 **(b)** N1s spectrum of g-C_3N_4 **(c)** O1s spectrum of g-C_3N_4

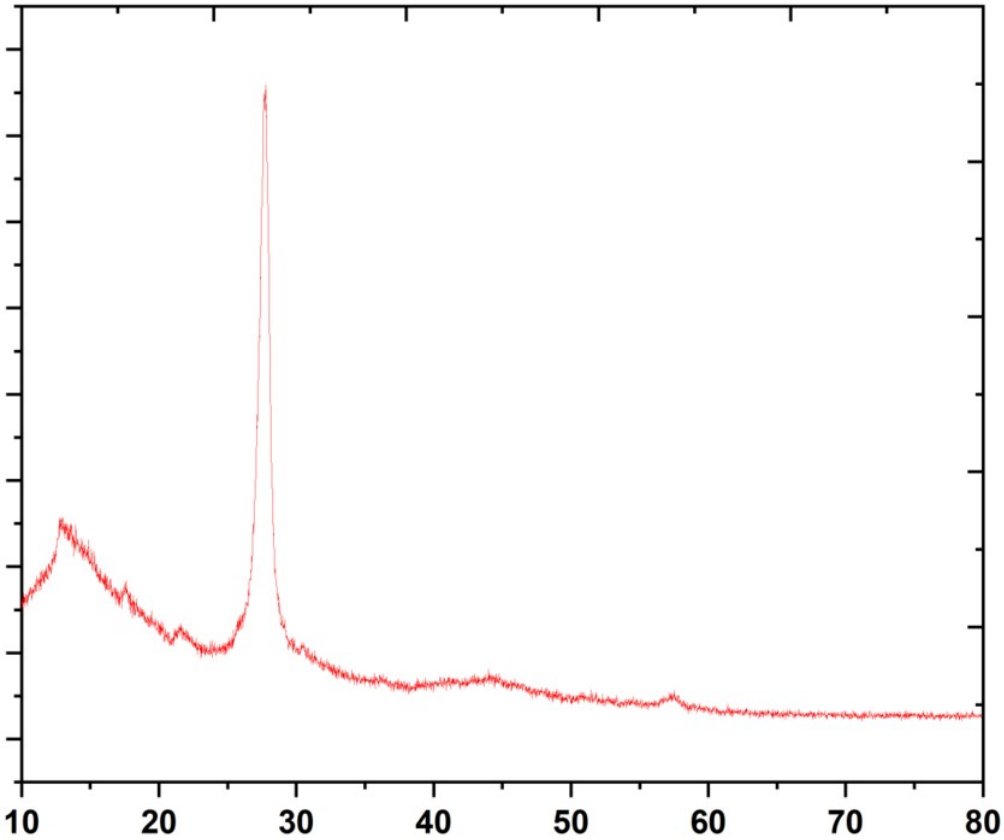


Fig.S4: XRD patterns of reused Sg-C_3N_4

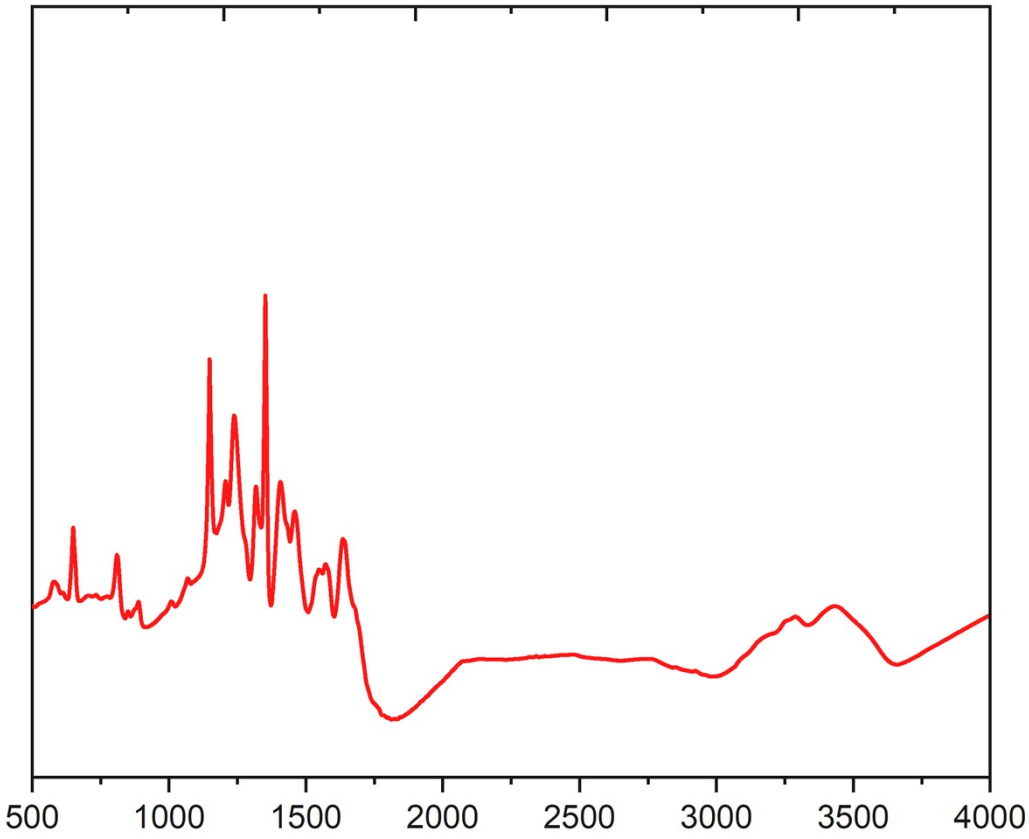


Fig.S5: FT-IR spectra of reused Sg-C_3N_4

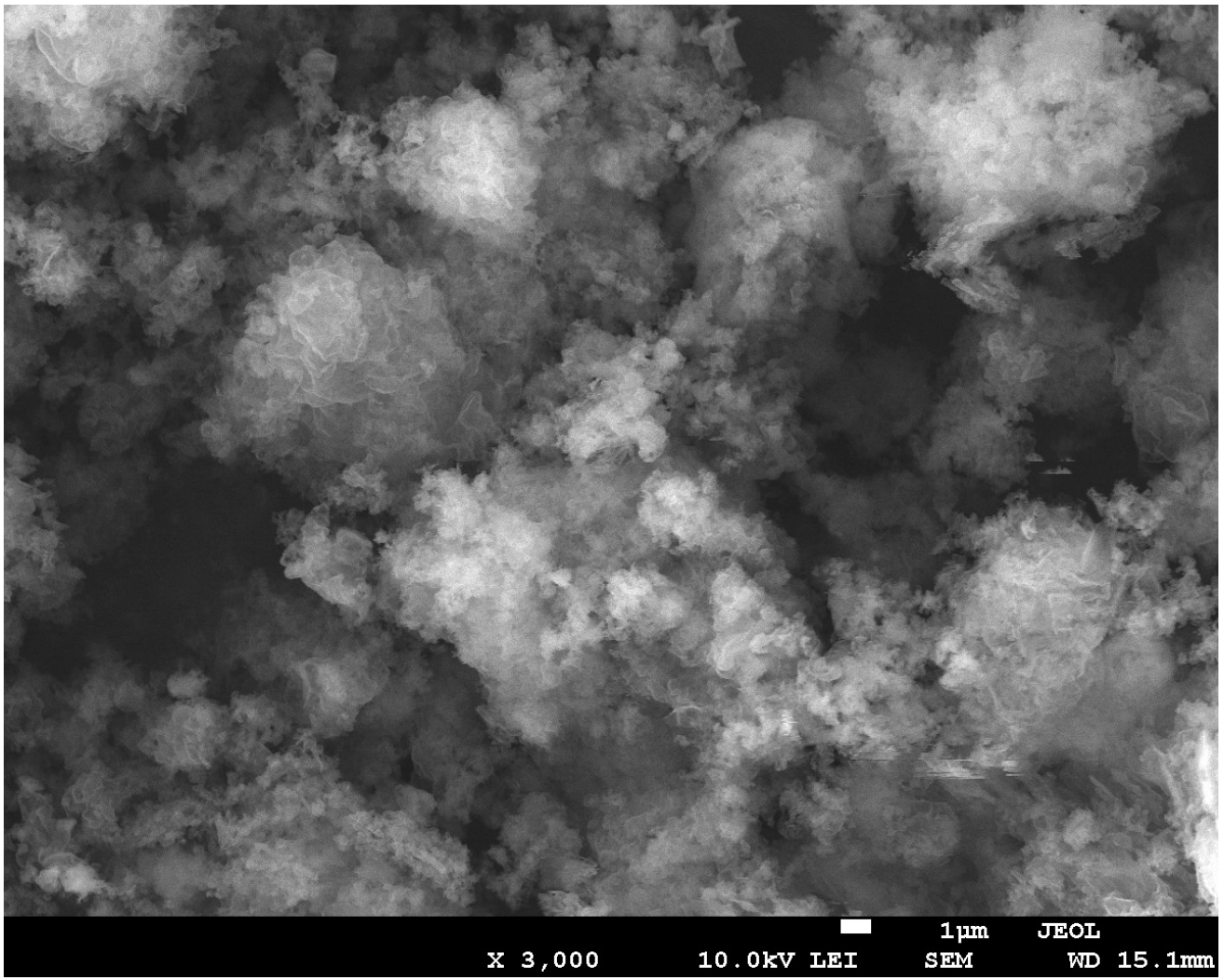


Fig.S6: SEM images of reused Sg-C_3N_4

Elemental Analysis (CNOS)

Table S3

SI. No	Sample	N%	C%	S%	O%
1	**Sg-C_3N_4**	49.41	19.82	6.39	24.38
2	**g-C_3N_4**	44.11	34.24	ND	21.65

9. Spectral data of synthesized compounds (6a-6k)

(6a)[1]: ^{1}H-NMR (DMSO-$d_6$300 MHz);δ (ppm) 11.34(s,1H,NH), 7.51-7.26(m,3H,NH_2, ArH), 7.06-6.86(m,3H,ArH), 5.92(s,1H, CH), 2.91(s,1H,CH_2), 2.50 (s, 1H, CH), 2.18-2.12(d,J=18MHz,1H,CH_2), 1.93(s,1H,CH_2), 1.61-1.48(m,3H,CH_2).^{13}C NMR (75 MHz, DMSO-d_6): δ 173.6,143.3,142.7, 131.3, 125.8, 125.4, 124.1, 123.4, 122.9, 115.9, 111.1, 110.6, 81.9, 55.0, 42.6, 37.4, 24.9, 23.8, 20.6. +ESI MS (m/z): 342.13 $[M+H]^+$

(6b)[1]: ^{1}H-NMR (DMSO-d_6 300 MHz); δ (ppm) 7.55-6.92 (m, 6H, NH_2,ArH), 5.91 (s,1H, CH), 3.29(s, 3H,N-CH_3), 3.05-3.02 (d, J=9.9MHz, 1H,CH_2), 2.50(s,1H, CH_2), 2.26-1.06(m, 4H, CH_2), 0.79-0.77(d, J=6MHz,3H,CH_3).^{13}C NMR (75 MHz, DMSO-d_6): δ 171.9, 144.6, 142.7, 131.4, 125.6, 125.1, 124.1, 123.9, 122.1, 115.9, 111.0, 110.5-110.2, 81.9, 56.4, 54.6, 42.7, 33.8, 32.0, 31.1, 27.5-27.1, 21.9.+ESI MS (m/z): 355.14 $[M]^+$

(6c)[1]: ^{1}H-NMR (DMSO-d_6 300 MHz); δ (ppm) 11.39 (s,1H, NH), 10.85 (s, 2H, NH_2), 7.66-6.84 (m, 5H, ArH, CH), 5.78 (s, 1H, CH), 3.94-3.73 (m,4H,CH_2), 3.34-3.14 (m, 2H, CH_2), 2.28-2.13 (m, 1H, CH_2), 1.52-1.44(m,1H, CH), 0.74-0.62 (m, 1H, CH_2).^{13}C NMR (75 MHz, DMSO-d_6): δ 173.2, 143.3-143.2, 142.6, 131.5, 130.1, 126.9-126.3, 125.3-125.1, 124.4-124.2, 123.6, 122.4, 121.1, 111.2-111.0, 110.5-110.2, 106.6-106.2, 81.4-81.1, 64.5-64.4, 54.8-54.2, 42.5, 37.0, 35.9, 35.7, 32.6.+ESI MS (m/z): 400.14 $[M+H]^+$

(6d)[2]: ^{1}H-NMR (DMSO-d_6 300 MHz); δ (ppm) 7.56 (s, 2H, NH_2), 7.52-7.46(t, J=7.8MHz, 1H, ArH), 7.26-7.23 (d, J=7.8MHz, 1H, ArH), 7.18-7.13 (m, 1H, ArH), 6.95-6.93 (d, J=7.5MHz, 1H, ArH), 5.93 (s, 1H, CH), 3.28 (s, 3H, N-CH_3), 2.98-2.95 (d, J=9MHz, 1H, CH), 2.50 (s, 1H, CH_2),2.18-1.45 (m, 4H, CH_2), 0.45-0.34(m,1H, CH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 172.0, 144.6, 142.6, 131.4, 125.8, 125.1, 124.2, 124.1, 122.2, 115.9, 110.5, 110.2, 82.0, 54.7, 42.6, 37.5, 27.1, 24.9, 23.8, 20.6. +ESI MS (m/z): 355.14 $[M]^+$

(6e)[2]: ^{1}H-NMR (DMSO-d_6 300 MHz); δ (ppm) 10.64 (s,1H, NH), 8.12 (s, 2H, NH_2), 7.26 (s, 1H, ArH), 7.05-6.98 (m, 1H, ArH), 6.81-6.59 (m, 2H, ArH), 5.60 (s, 1H, CH), 3.28-2.73 (m, 2H,CH_2), 2.32 (s, 1H, CH), 2.02-1.90 (m, 2H, CH_2), 1.31-1.22(m,3H, CH_3), 0.71-0.57 (m, 1H, CH).

^{13}C NMR (75 MHz, DMSO-d_6): δ 174.6, 147.9, 142.7, 129.9-129.5, 127.8-127.0, 126.3, 124.7-124.5, 122.3, 121.5, 120.8, 117.4-117.1, 116.4, 115.5, 110.0, 109.5, 82.2, 55.3, 33.8, 32.2, 27.8, 22.0. +ESI MS (m/z): 356.14 $[M+H]^+$

(6f)[2]: ^{1}H-NMR (DMSO-d_6 300 MHz); δ (ppm) 7.69 (s, 2H, NH_2), 7.54-7.49 (m, 1H, ArH), 7.28-7.15 (m, 2H, ArH), 6.97-6.94 (d, J=7.2MHz, 1H, ArH), 5.79 (s, 1H, CH), 3.93-3.74 (m, 4H,OCH_2), 3.33-3.17 (m, 3H, CH_3), 2.50-2.16 (m, 2H, CH_2), 1.42-1.39 (d, J=10.5MHz, 1H, CH), 0.67-0.59 (m, 2H, CH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 171.5, 144.6, 143.2, 131.7, 125.1, 124.3, 121.7, 121.2, 115.7, 110.9, 110.4, 106.2, 81.1, 64.5, 64.4, 54.2, 42.6, 37.0, 35.9, 32.6, 27.2.+ESI MS (m/z): 413.15 $[M]^+$

(6g)[2]: ^{1}H-NMR (DMSO-d_6 300 MHz); δ (ppm) 7.72 (s, 2H, NH_2), 7.69-6.89 (m, 4H, ArH), 5.79 (s, 1H, CH), 5.67 (s, 1H, CH), 5.28-5.21 (m, 2H, CH), 4.50-4.31 (m, 2H, CH_2), 3.90-3.64 (m, 3H, OCH_2), 3.35-3.18 (m, 1H, OCH_2), 2.29-2.11 (m, 2H, CH_2), 1.45-1.40 (m, 1H, CH), 0.79-0.57 (m, 2H, CH_2). ^{13}C NMR (75 MHz, DMSO-d_6): δ 171.4, 143.6-143.2, 131.8-131.4, 125.3-125.0, 124.3, 123.6-123.2, 122.4, 121.7-121.1, 118.3, 117.9, 115.7, 111.3-111.0, 110.9-110.5, 106.5-106.1, 81.1-81.0, 64.5-64.4, 63.0, 54.5-54.1, 42.6-42.4, 37.2, 36.9, 35.9-35.6, 32.6.+ESI MS (m/z): 439.16 $[M]^+$

(6h)[2]: ^{1}H-NMR (DMSO-d_6 300 MHz); δ (ppm) 11.25 (s, 1H, NH), 7.50 (s, 2H, NH_2), 7.20 (d, J=8.0MHz, 1H, ArH), 6.91 (d, J=8.0MHz, 1H, ArH), 6.64 (s, 1H, ArH), 5.87-5.97 (m, 1H, CH), 2.82-2.94 (m, 1H, CH), 2.30 (s, 3H, CH_3), 2.08-2.21 (m, 1H, CH_2), 1.82-2.02 (m, 1H, CH_2), 1.36-1.70 (m, 3H, CH_2), 0.47 (q, J=12.1MHz, 1H, CH_2).^{13}C NMR (75 MHz, DMSO-d_6): δ 173.1, 142.2, 140.4, 131.5, 131.2, 125.6, 125.4, 123.6, 122.7, 115.5, 110.7, 110.5, 110.2, 81.5, 54.5, 42.1, 37.0, 24.4, 23.4, 21.1, 20.1.+ESI MS (m/z): 356.14$[M+H]^+$

(6i)[1]: ^{1}H-NMR (DMSO-d_6 300 MHz); δ (ppm) 11.54 (s, 1H, NH), 7.65 (s, 2H, NH_2), 7.48 (d, J=8.4MHz, 1H, ArH), 7.05 (d, J=8.4MHz, 1H, ArH), 6.77 (s, 1H, ArH), 5.90-6.03 (m, 1H, CH), 2.86-3.02 (m, 1H, CH), 2.06-2.31 (m, 1H, CH_2), 1.87-2.07 (m, 1H, CH_2), 1.36-1.76 (m, 3H, CH_2), 0.49 (q, J=12.1MHz, 1H, CH_2).^{13}C NMR (75 MHz, DMSO-d_6): δ 172.9, 142.0, 131.0, 126.7, 124.9, 124.7, 124.4, 124.3, 115.3, 112.4, 110.3, 110.1, 81.5, 54.8, 42.0, 37.0, 24.5, 23.4, 20.2.+ESI MS (m/z): 376.08$[M+H]^+$

(6j)[3]: ^{1}H-NMR (DMSO-d_6 300 MHz); δ (ppm) 11.55 (s, 1H, NH), 7.55-7.71 (m, 3H, ArH, NH_2), 7.02 (d, J=8.4MHz, 1H, ArH), 6.91 (s, 1H, ArH), 5.91-6.02 (m, 1H, CH), 2.86-3.01 (m, 1H, CH), 2.08-2.31 (m, 1H, CH_2), 1.87-2.05 (m, 1H, CH_2), 1.37-1.75 (m, 3H, CH_2), 0.48(q, J=12.1MHz, 1H, CH_2).^{13}C NMR (75 MHz, DMSO-d_6): δ 172.7, 142.3, 142.0, 133.7, 127.3, 124.6, 124.6, 124.3, 115.2, 114.1, 112.7, 110.3, 110.1, 81.5, 54.6, 42.0, 37.1, 24.4, 23.3, 20.1.+ESI MS (m/z): 419.03$[M]^+$

(6k)[3]: ^{1}H-NMR (DMSO-d_6 300 MHz); δ (ppm) 7.54 (s, 2H, NH_2), 7.47 (t, J=7.7MHz, 1H, ArH), 7.27 (d, J=7.7 MHz, 1H, ArH), 7.14 (t, J=7.7MHz, 1H, ArH), 6.95 (d, J=7.7MHz, 1H, ArH), 5.88-5.97 (m, 1H, CH), 3.78-3.92 (m, 2H, CH_2), 2.90-3.01 (m, 1H, CH), 2.07-2.21 (m, 1H, CH_2), 1.82-1.98 (m, 1H, CH_2), 1.56-1.68 (m, 1H, CH_2), 1.36-1.54 (m, 2H, CH_2), 1.17 (t, J=7.0MHz, 3H, CH_3), 0.41 (q, J=12.1MHz, 1H, CH_2).^{13}C NMR (75 MHz, DMSO-d_6): δ 171.1, 143.2, 142.1, 131.0, 125.2, 124.8, 123.7, 123.6, 122.1, 115.4, 110.5, 110.0, 109.7, 81.5, 54.1, 42.1, 37.0, 34.7, 24.5, 23.2, 20.1, 12.1. +ESI MS (m/z):369.15$[M]^+$

Spectral data of synthesized compounds (4a-4l)

(4a): ^{1}H-NMR (DMSO-d_6 400 MHz); δ (ppm)10.63(s, 1H, NH), 7.91-7.89 (m,1H,ArH), 7.74-7.70 (m,1H,ArH), 7.62 (s, 2H, NH_2), 7.52-7.44 (m,2H,ArH), 7.19-7.15 (m,2H, ArH), 6.91-6.87 (t, J=7.6MHz, 1H,ArH), 6.82-6.80 (d, J=7.6MHz, 1H,ArH).^{13}C NMR (100 MHz, DMSO-d_6): δ 177.6, 158.9, 158.8, 155.6, 152.5, 142.7, 134.2, 133.5, 129.4, 125.5, 124.6, 123.1, 122.5, 117.5, 117.2, 112.9, 110.0, 101.9, 57.5, 48.1. +ESI MS (m/z): 358.07 $[M+H]^+$

(4b): ^{1}H-NMR (DMSO-d_6 400 MHz); δ (ppm): 10.52 (s, 1H, NH), 8.15 (s, 2H, NH_2), 7.97 (s, 1H, ArH), 7.70-7.67(m, 1H, ArH), 7.48-7.39 (m, 2H, ArH), 7.15-7.13 (m, 2H, ArH),6.82-6.69(m, 1H, ArH), 3.78-3.71 (m, 2H, CH_2), 0.83-0.79(m, 3H, CH_3).^{13}C NMR (100 MHz, DMSO-d_6):δ 179.2, 167.5, 159.2, 154.6, 152.4, 143.6, 137.2, 133.9, 128.1, 125.4, 125.3, 124.1, 123.4, 116.8, 113.1, 110.1, 75.5, 59.7, 56.5, 48.1, 31.2, 19.0. +ESI MS (m/z): 438.06 $[M]^+$

(4c)[4]: ^{1}H-NMR (DMSO-d_6 400 MHz); δ (ppm): 7.94-7.92(m, 1H, ArH), 7.76-7.72 (m, 3H, NH_2, ArH), 7.54-7.42 (m, 4H, ArH), 7.29-7.17(m, 5H, ArH), 6.97-6.94 (m, 1H, ArH), 6.77-6.75 (d, J=8MHz,1H, ArH), 4.98-4.88 (m, 2H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 176.4, 159.1, 158.9, 155.8, 152.6, 143.2, 136.4, 134.3, 132.7, 129.5, 128.9, 127.7, 127.6, 125.6, 124.6, 123.4, 123.2, 117.5, 117.2, 113.0, 109.6, 101.6, 57.2, 56.5, 19.0. +ESI MS (m/z): 448.12 $[M+H]^+$

(4d)[4]: ^{1}H-NMR (DMSO-d_6 400 MHz); δ (ppm): 8.14(s, 2H, NH_2), 8.00-7.98 (d, J=7.2MHz,1H, ArH), 7.71-7.68 (m, 1H, ArH), 7.50-7.46 (m, 1H, ArH), 7.41-7.39 (d, J=8MHz,1H, ArH), 7.20-7.16 (d, J=7.6MHz, 1H, ArH), 7.05-7.03 (d, J=6.8MHz,1H, ArH), 6.90-6.82 (m, 2H, ArH), 3.69-3.64 (m, 2H, CH_2), 3.12 (m, 3H, N-CH_3), 0.73-0.69 (t, J=7.2MHz, 3H, CH_3).^{13}C NMR (100 MHz, DMSO-d_6): δ 199.7, 167.5, 159.2, 158.3, 152.4, 145.8, 134.2, 134.0, 128.6, 125.4, 123.5, 123.4, 122.3, 116.9, 112.9, 107.7, 104.1, 75.6, 59.5, 26.8, 14.0. +ESI MS (m/z): 418.11 $[M]^+$

(4e)[4]: ^{1}H-NMR (DMSO-d_6 400 MHz); δ (ppm): 10.52 (s, 1H, NH), 7.91-7.89 (d, J=8MHz,1H, ArH), 7.75-7.71 (m, 1H, ArH), 7.60 (s, 2H, NH_2), 7.52-7.44 (m, 2H, ArH), 6.98-6.96 (d, J=11.2MHz, 2H, ArH), 6.70-6.68 (d, J=7.6MHz,1H,ArH), 2.15 (s, 3H, CH_3).^{13}C NMR (100 MHz, DMSO-d_6): δ 177.6, 158.9, 158.7, 155.5, 152.5, 140.2, 134.1, 133.6, 131.4, 129.6, 125.5, 125.2, 123.1, 117.5, 117.2, 113.0, 109.7, 102.0, 57.7, 21.0.+ESI MS (m/z): 372.09 $[M+H]^+$

(4f)[4]: ^{1}H-NMR (DMSO-d_6 400 MHz); δ (ppm): 7.92-7.90 (t, 1H, ArH), 7.73-7.69 (m, 3H, -NH_2, ArH), 7.51-7.44 (m, 2H, ArH), 7.27-7.22 (m, 2H, ArH), 6.99-6.90 (m, 2H, ArH), 5.39-5.35 (m, 1H, =CH_2), 5.14-5.12 (d,d 1H, =CH_2), 4.39-4.25 (m, 1H, CH), 3.29 (S, 2H, CH).^{13}C NMR (100 MHz, DMSO-d_6): δ 175.9, 159.0, 158.8, 155.7, 152.6, 143.2, 134.3, 132.7, 132.0, 129.5, 125.5, 124.5, 123.3, 123.2, 117.4, 117.2, 112.9, 109.6, 101.7, 57.2, 47.8, 42.6. +ESI MS (m/z): 397.10 $[M]^+$

(4g)[4]: ^{1}H-NMR (DMSO-d_6 400 MHz); δ (ppm): 7.94-7.90 (m, 1H, ArH), 7.72-7.68 (m, 3H, NH_2, ArH), 7.50-7.45 (m, 2H, ArH), 7.26-7.20 (m, 2H, ArH), 6.98-6.92 (m, 2H, ArH), 2.15 (s, 3H, CH_3).^{13}C NMR (100 MHz, DMSO-d_6): δ 175.8, 159.1, 155.6, 152.6, 143.1, 132.6, 132.1, 129.4, 125.5, 124.4, 123.2, 123.1, 117.1, 109.5, 101.7, 57.1, 47.4, 37.4. +ESI MS (m/z): 371.09 $[M]^+$

(4h)[5]: ^{1}H-NMR (DMSO-d_6 400 MHz); δ (ppm): 8.17 (s, 2H, NH_2), 8.02-7.97 (d, J=7.2MHz, 1H, ArH), 7.72-7.69 (m, 1H, ArH), 7.51-7.45(m, 1H, ArH), 7.42-7.38 (d, J=8MHz, 1H, ArH), 7.21-7.17 (d, J=7.6MHz, 1H, ArH), 7.04-7.02 (d, J=6.8MHz, 1H, ArH), 6.91-6.81 (m, 2H, ArH),5.78 (s, 1H, CH),4.51-4.32 (m, 2H, CH_2), 3.68-3.65 (m, 2H, CH_2), 2.35-2.21 (m, 2H, CH_2), 0.72-0.68 (t, J=7.2MHz, 3H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ 199.7, 167.4, 159.1, 158.2, 152.6, 145.9, 134.3, 134.1, 131.5, 128.7, 125.5, 123.6, 123.3, 122.2, 116.7, 115.6, 112.8, 107.6, 104.1, 75.8,64.6, 59.6, 14.2. +ESI MS (m/z): 418.11 $[M]^+$

(4i)[5]: ^{1}H-NMR (DMSO-d_6 400 MHz); δ (ppm): 10.55 (s, 1H, NH), 8.15 (s, 2H, NH_2), 8.16-7.99 (d, J=7.2MHz, 1H, ArH), 7.72-7.69 (m, 1H, ArH), 7.50-7.44(m, 1H, ArH), 7.40-7.36 (d, J=8MHz, 1H, ArH), 7.25-7.15 (d, J=7.6MHz, 1H, ArH), 7.04-7.02 (d, J=6.8 MHz, 1H, ArH), 6.91-6.81 (m, 2H, ArH), 3.68-3.63 (m, 2H, CH_2), 0.72-0.66 (t, J=7.2 MHz, 3H, CH_3).^{13}C NMR (100 MHz, DMSO-d_6): δ 199.3, 167.33, 159.1, 158.3, 152.2, 145.9, 134.3, 134.1, 128.5, 125.2, 123.5, 123.2, 122.1, 116.4, 112.9, 107.6, 104.2, 75.4, 59.4, 14.0. +ESI MS (m/z): 405.10 $[M+H]^+$

(4j)[5]: ^{1}H-NMR(DMSO-d_6 400 MHz); δ (ppm): 10.61 (s, 1H, NH),7.85 (m, 2H, ArH), 7.69 (m, 2H, ArH),7.49 (s, 2H, NH_2), 7.37 (d, 1H, J=7.6MHz, ArH), 7.19 (d, J=7.7Hz, 1H, ArH), 6.99 (s, 1H, ArH). ^{13}C NMR 100 MHz, DMSO-d_6): δ175.9, 160.3, 158.3, 156.6, 145.9, 140.5,133.4, 130.9, 126.7, 129.2, 125.5, 123.3, 120.8, 119.3, 117.2, 114.1, 112.4, 102.5, 59.4, 48.8.+ESI MS (m/z): 391.03 $[M]^+$

(4k)[6]: ^{1}H-NMR (DMSO-d_6 400 MHz); δ (ppm): 10.21 (s, 1H, NH), 8.01 (1H, d, J=7.9MHz, ArH), 7.99 (s, 2H, NH_2), 7.67 (d, J=7.6MHz, 1H,ArH), 7.50 (d, J=7.8MHz, 1H, ArH), 7.29 (t, J=7.2MHz, 1H,ArH), 7.10 (m, 2H, ArH), 6.90 (d, J=7.2MHz, 1H, ArH), 3.70(s, 3H, OCH_3).^{13}C NMR (100 MHz, DMSO-d_6): δ178.7, 160.4, 158.3, 156.2, 152.1, 145.9, 140.9, 133.3, 130.2, 125.9, 125.1, 119.6, 118.4, 117.4, 114.4, 112.9, 111.4, 101.3,61.2, 57.9, 49.1.+ESI MS (m/z): 387.08 $[M]^+$

(4l)[6]: ^{1}H-NMR (DMSO-d_6 400 MHz); δ (ppm): 10.21 (s, 1H, NH), 7.90 (s, 2H, NH_2), 7.54 (d, J=8.0MHz, 1H, ArH), 7.49 (m, 2H, ArH), 7.28 (t, J=7.5MHz, 1H, ArH), 7.09 (m, 2H, ArH). ^{13}C NMR (100MHz, DMSO-d_6): δ 176.5, 158.9, 158.7, 157.0, 146.7, 141.4, 140.8, 132.7, 131.2, 126.7, 125.9, 122.8, 122.3, 120.1, 116.0, 114.1, 109.2, 102.6, 61.8, 49.3.+ESI MS (m/z): 403.06 $[M+H]^+$

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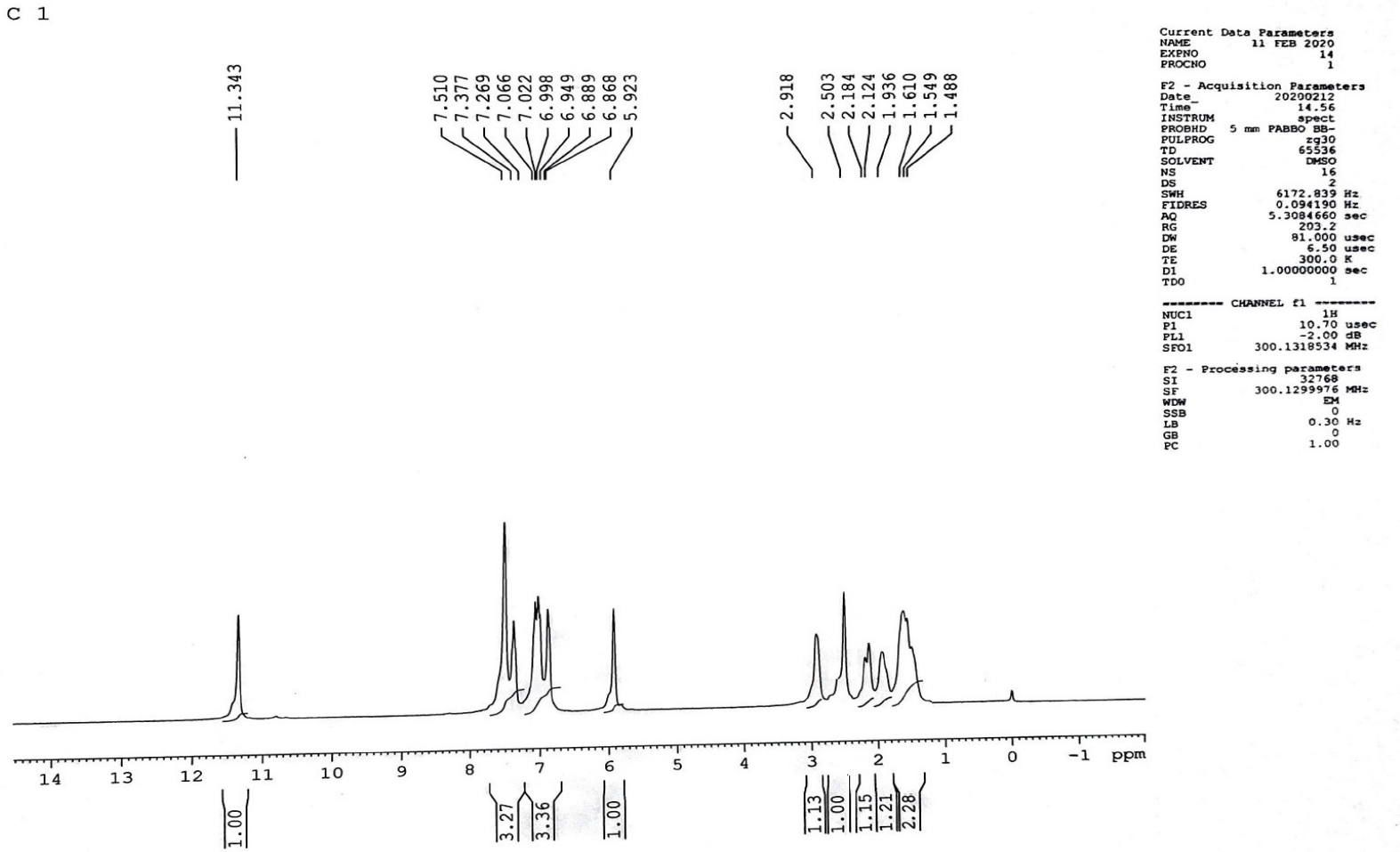

Figure 1: ^{1}H-NMR spectrum of (6a)

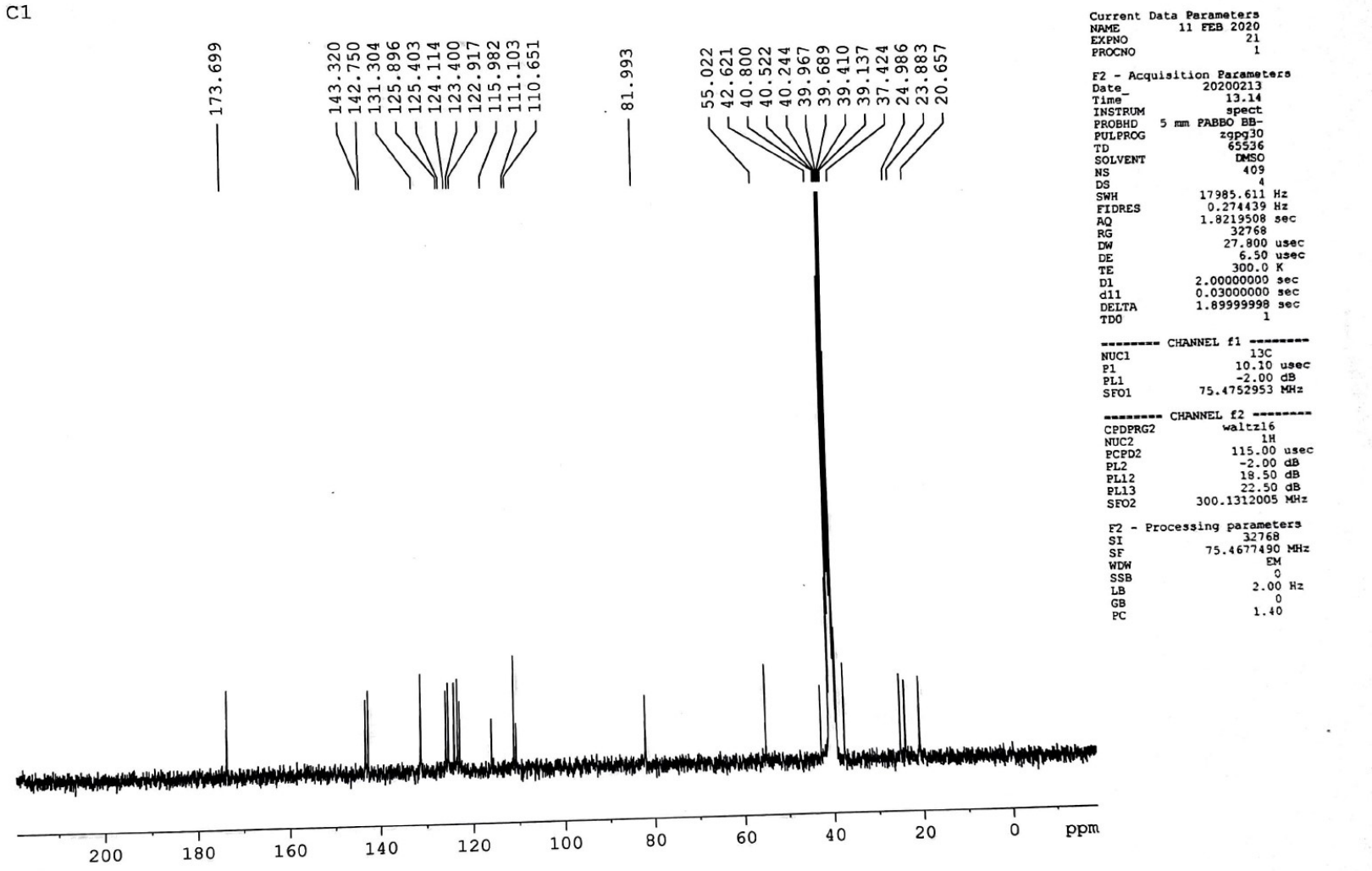

Figure 2: ^{13}C NMR **spectrum of (6a)**

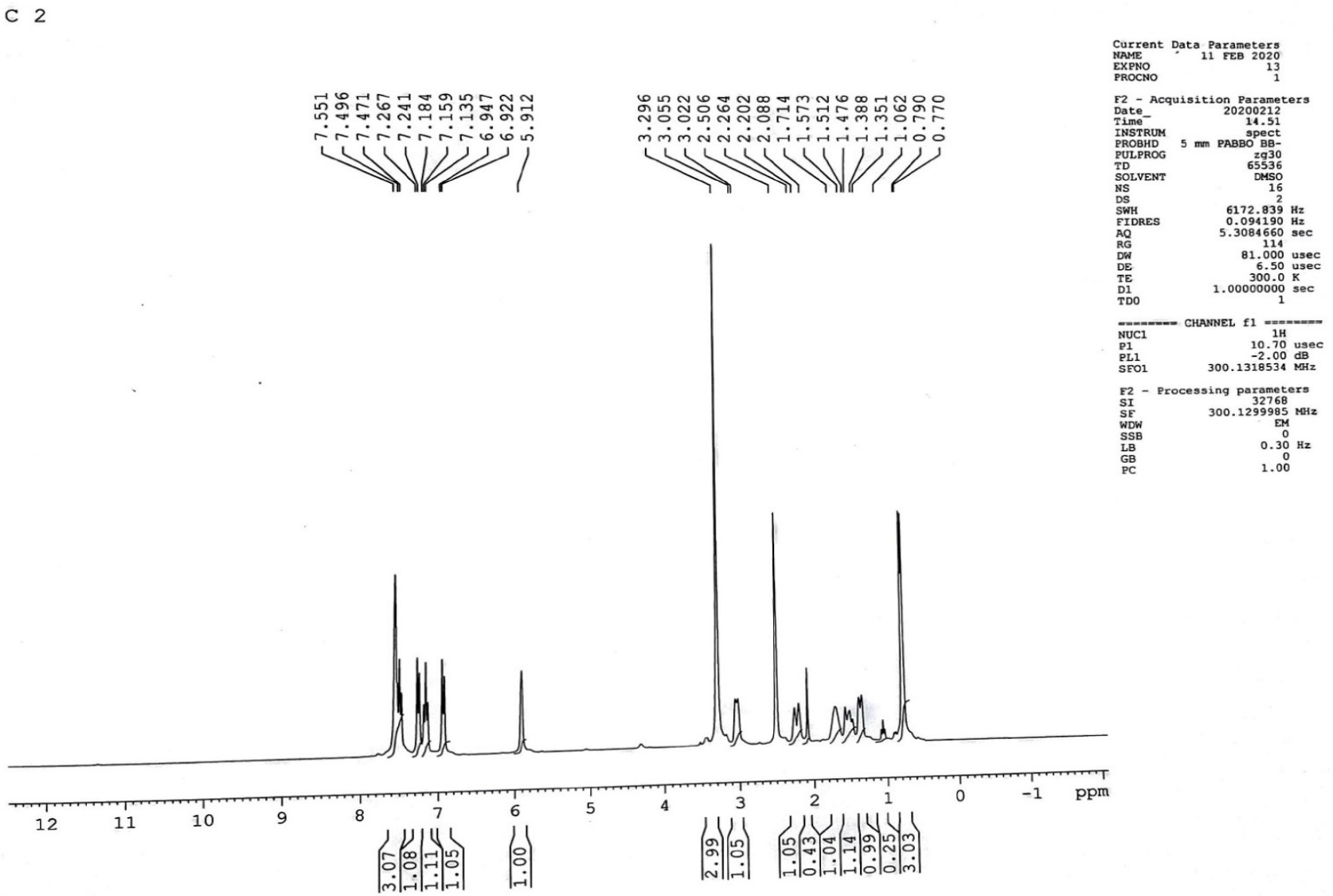

Figure 3: ^{1}H-NMR spectrum of (6b)

C2

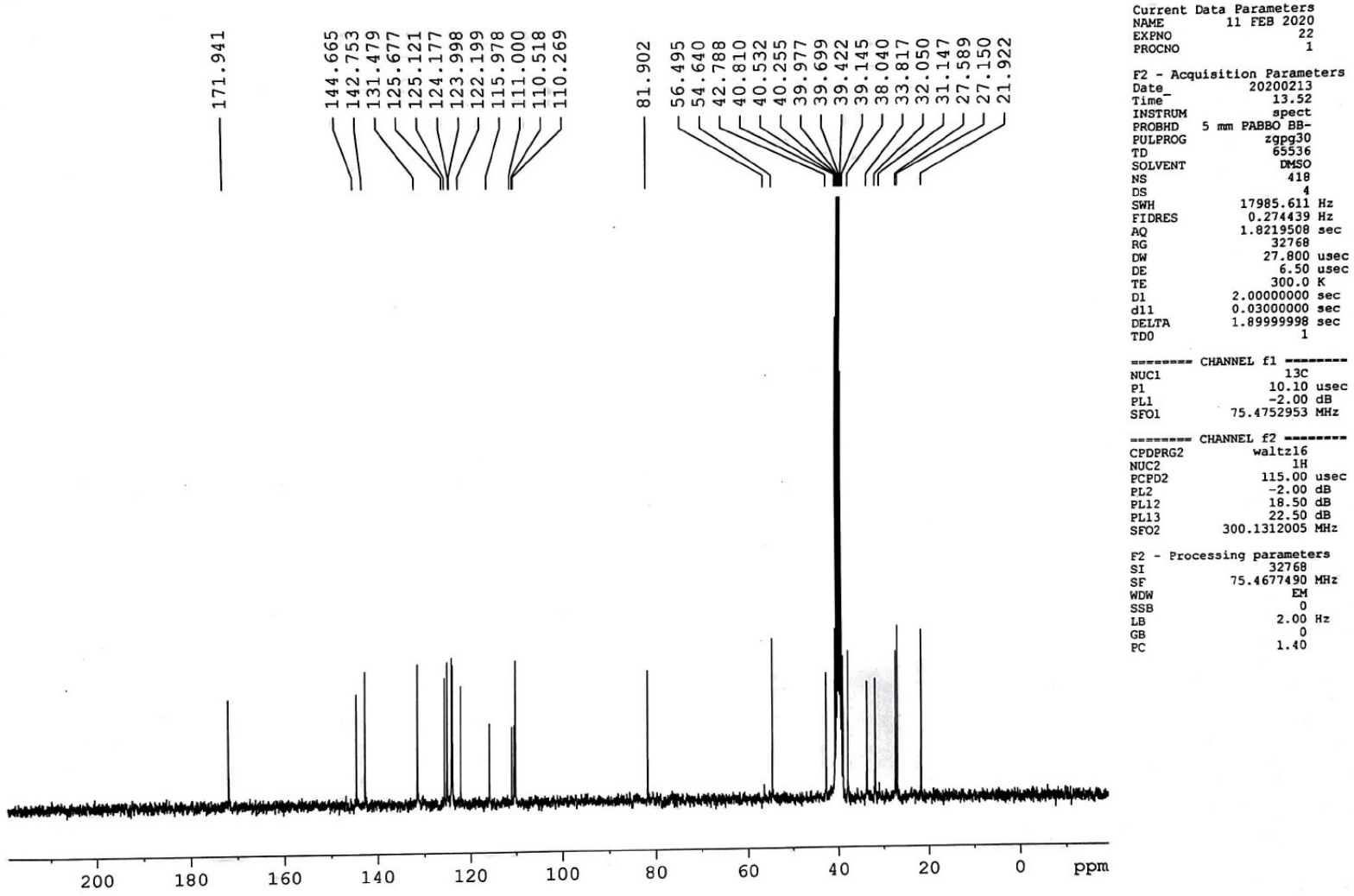

Figure 4: ^{13}C NMR **spectrum of (6b)**

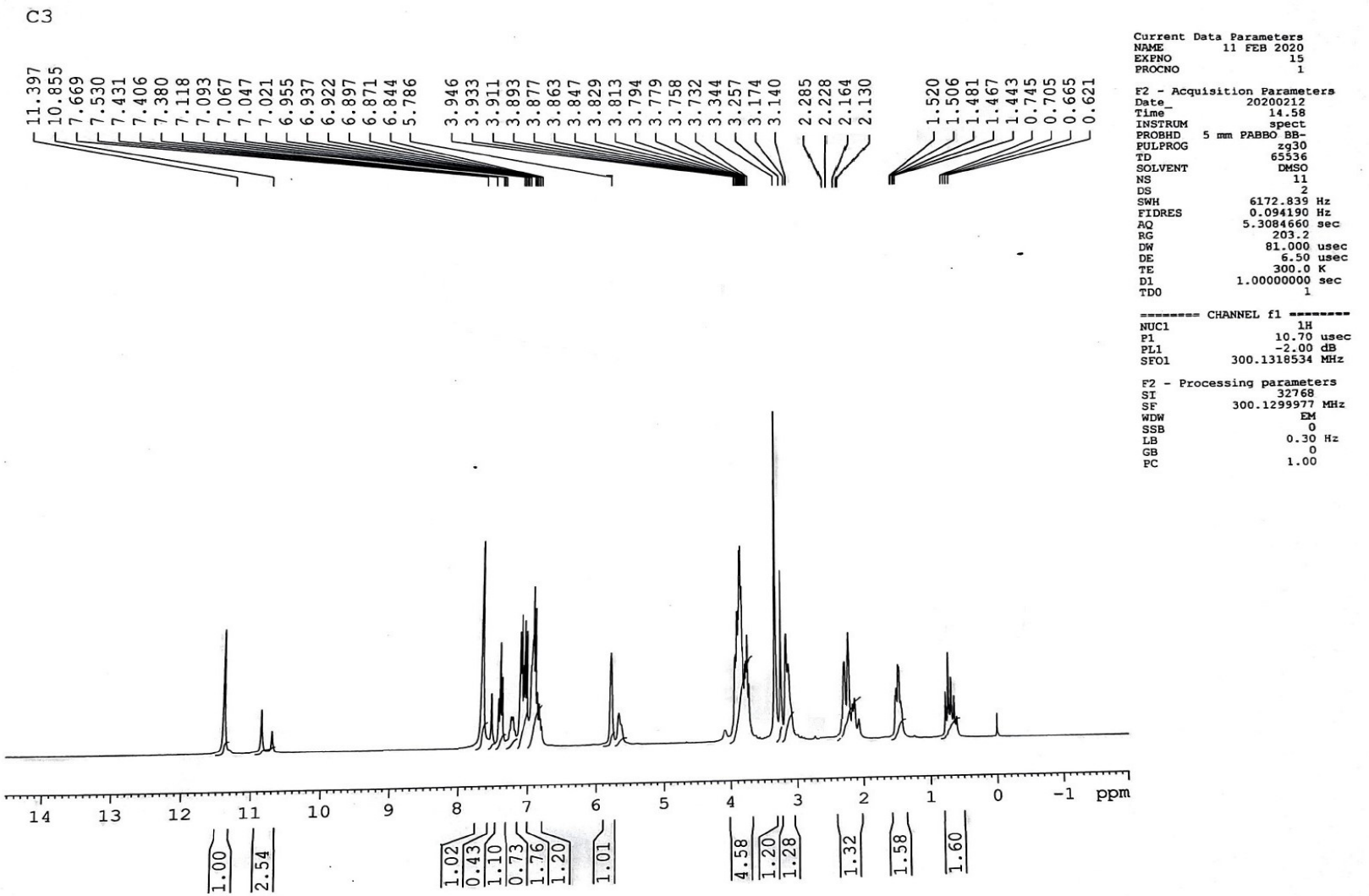

Figure 5: ^{1}H-NMR spectrum of (6c)

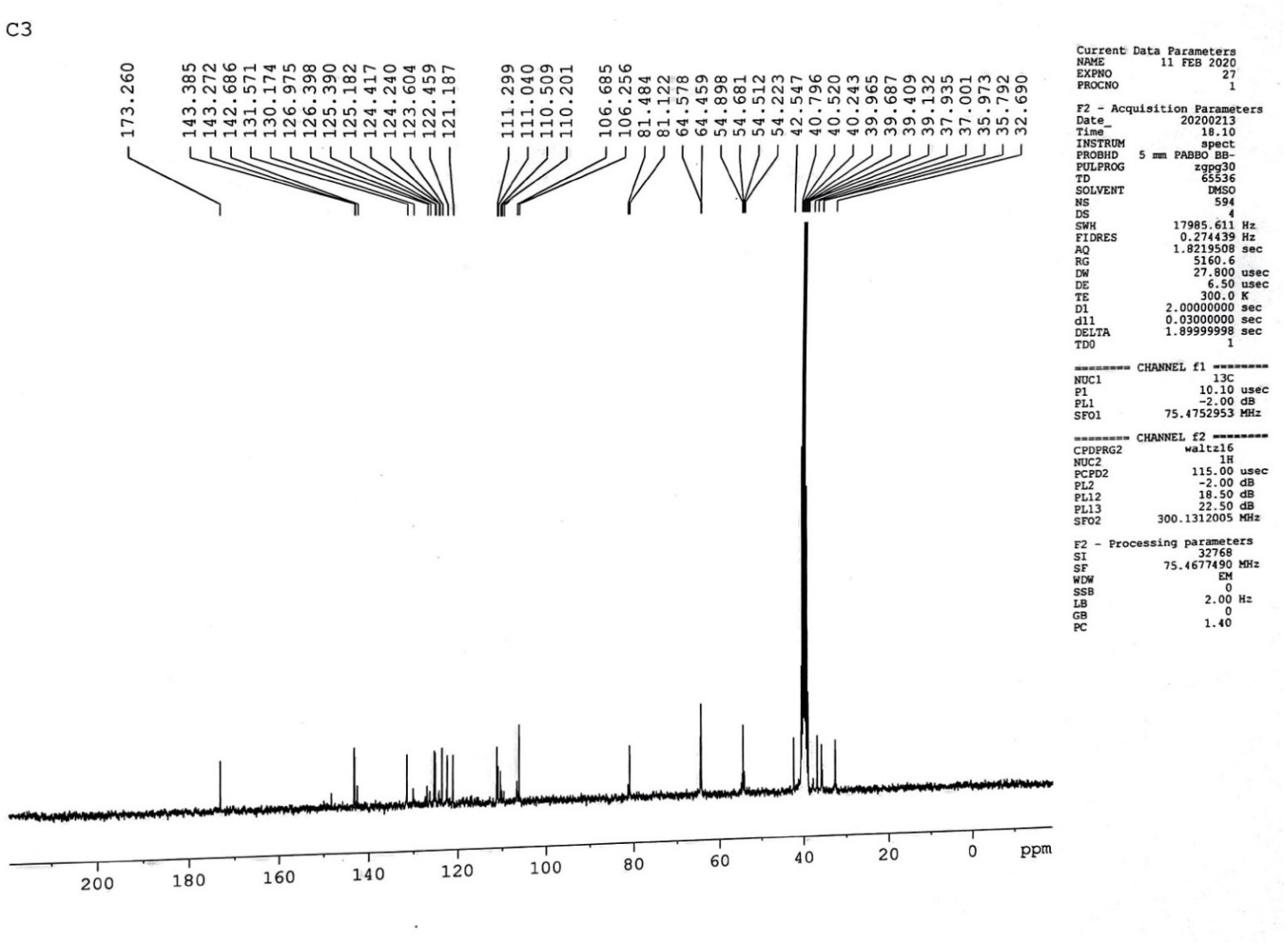

Figure 6: ^{13}C NMR **spectrum of (6c)**

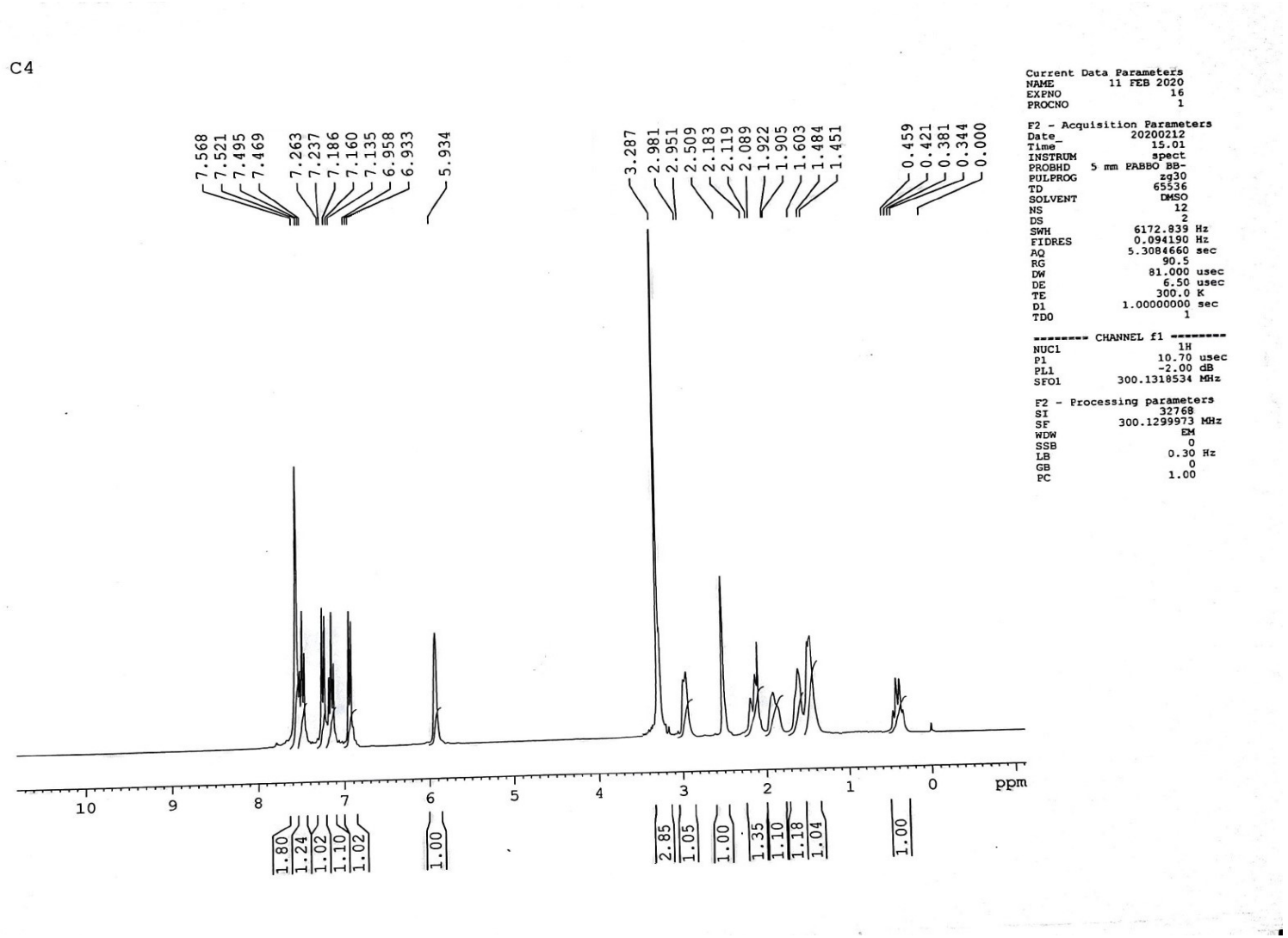

Figure 7: ^{1}H-NMR spectrum of (6d)

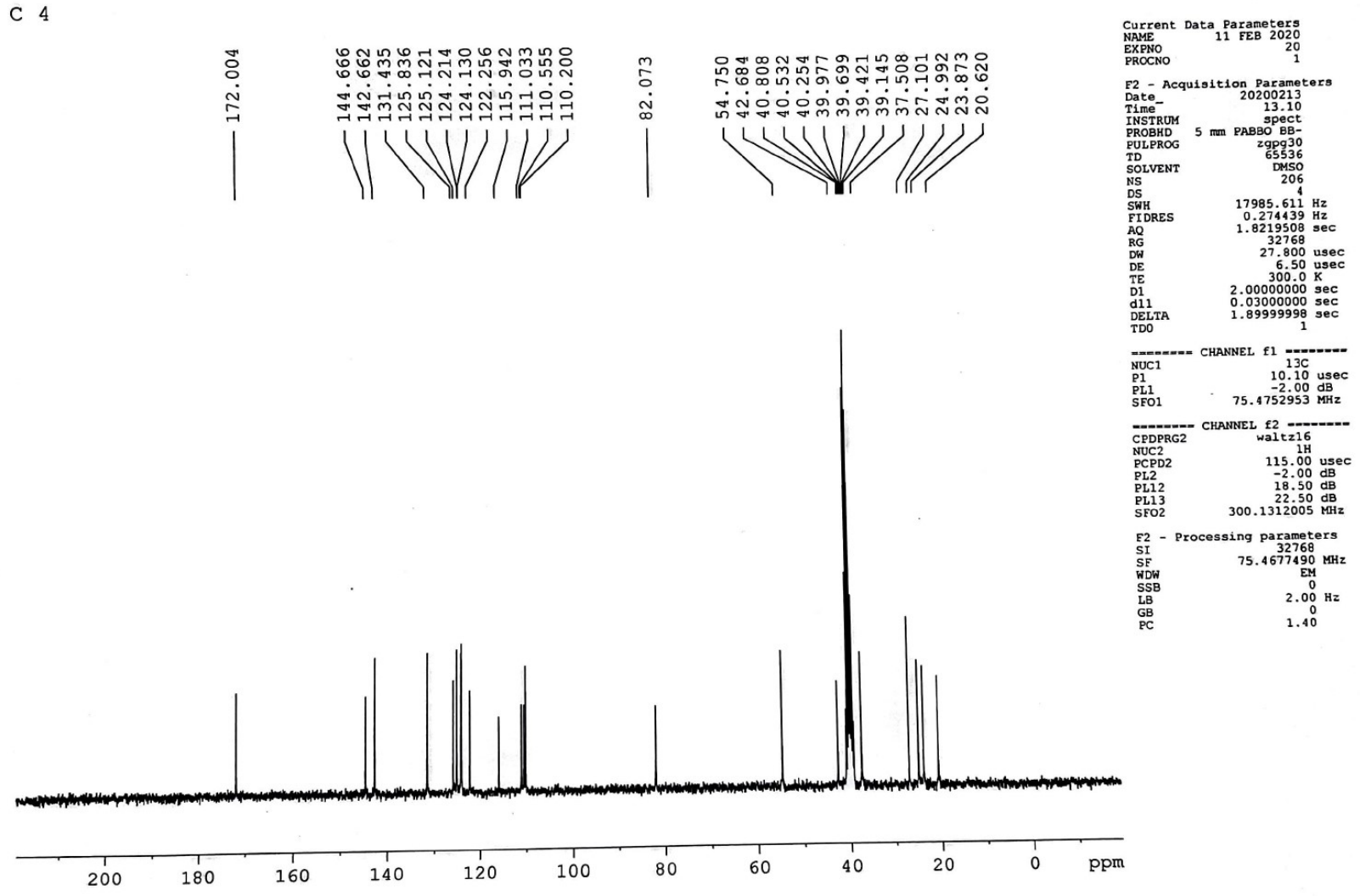

Figure 8: ^{13}C NMR **spectrum of (6d)**

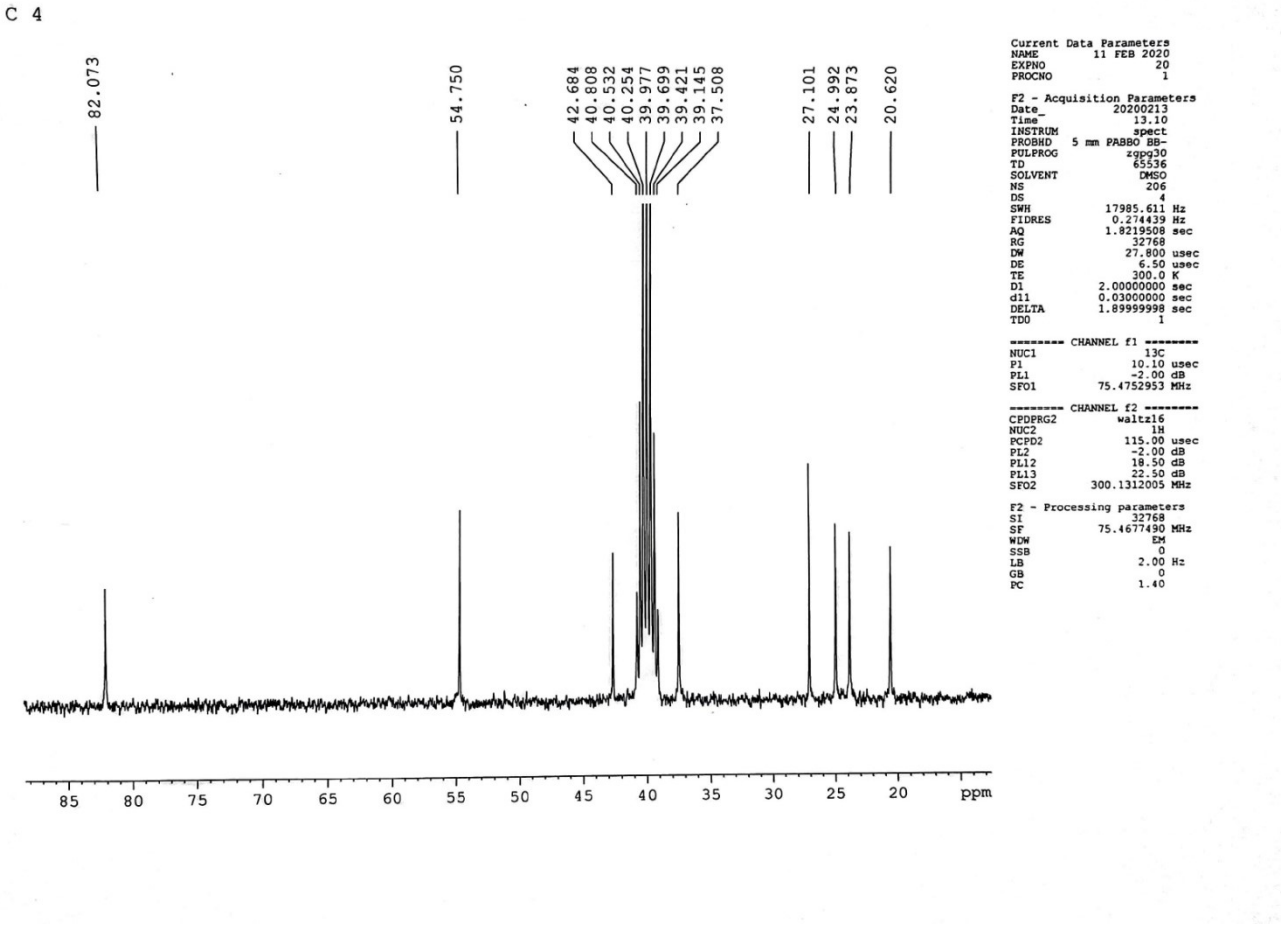

Figure 8a: ^{13}C NMR **spectrum of (6d) Zoom**

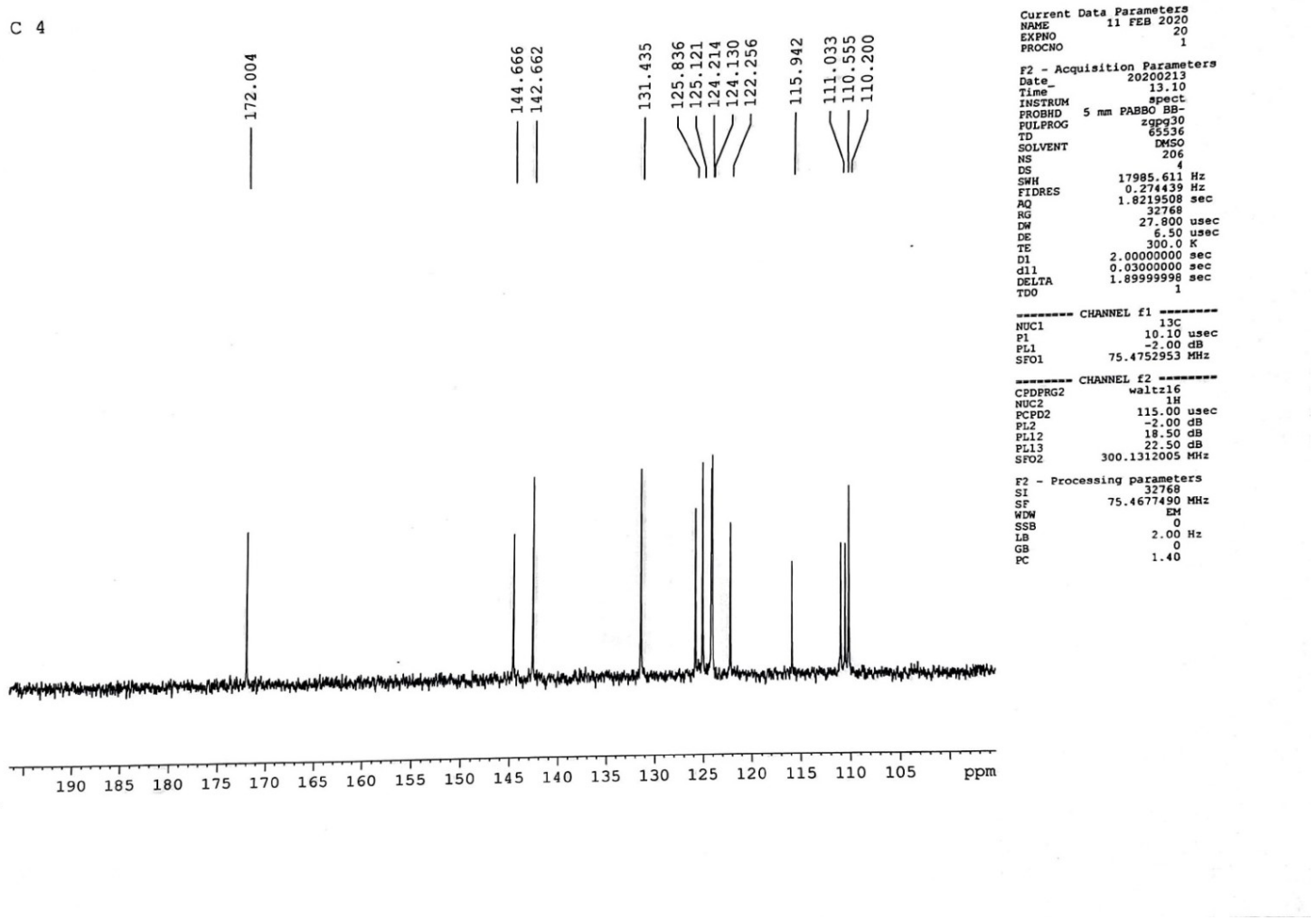

Figure 8b: ^{13}C NMR **spectrum of (6d) Zoom**

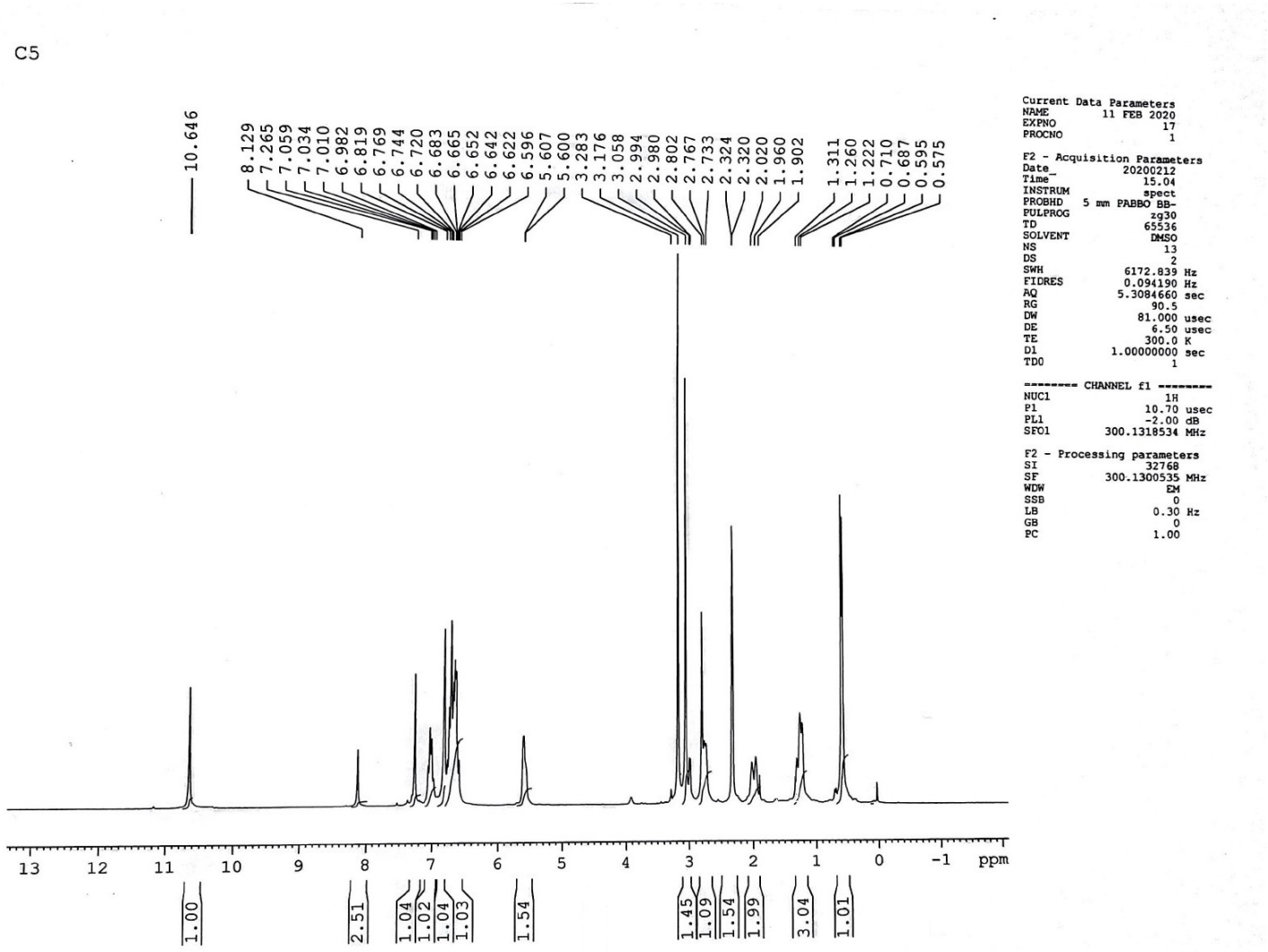

Figure 9: ^{1}H-NMR spectrum of (6e)

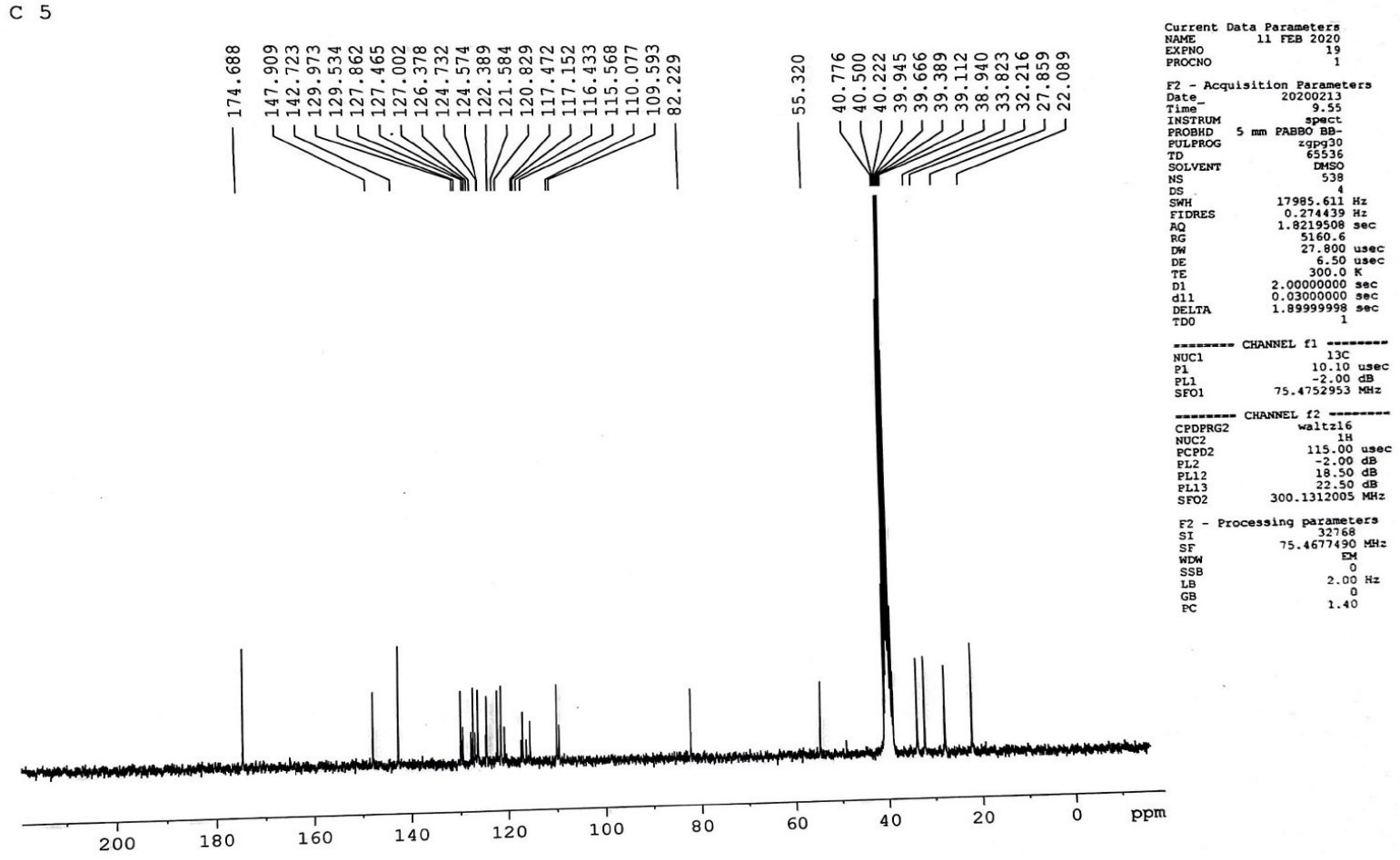

Figure 10: ^{13}C NMR **spectrum of (6e)**

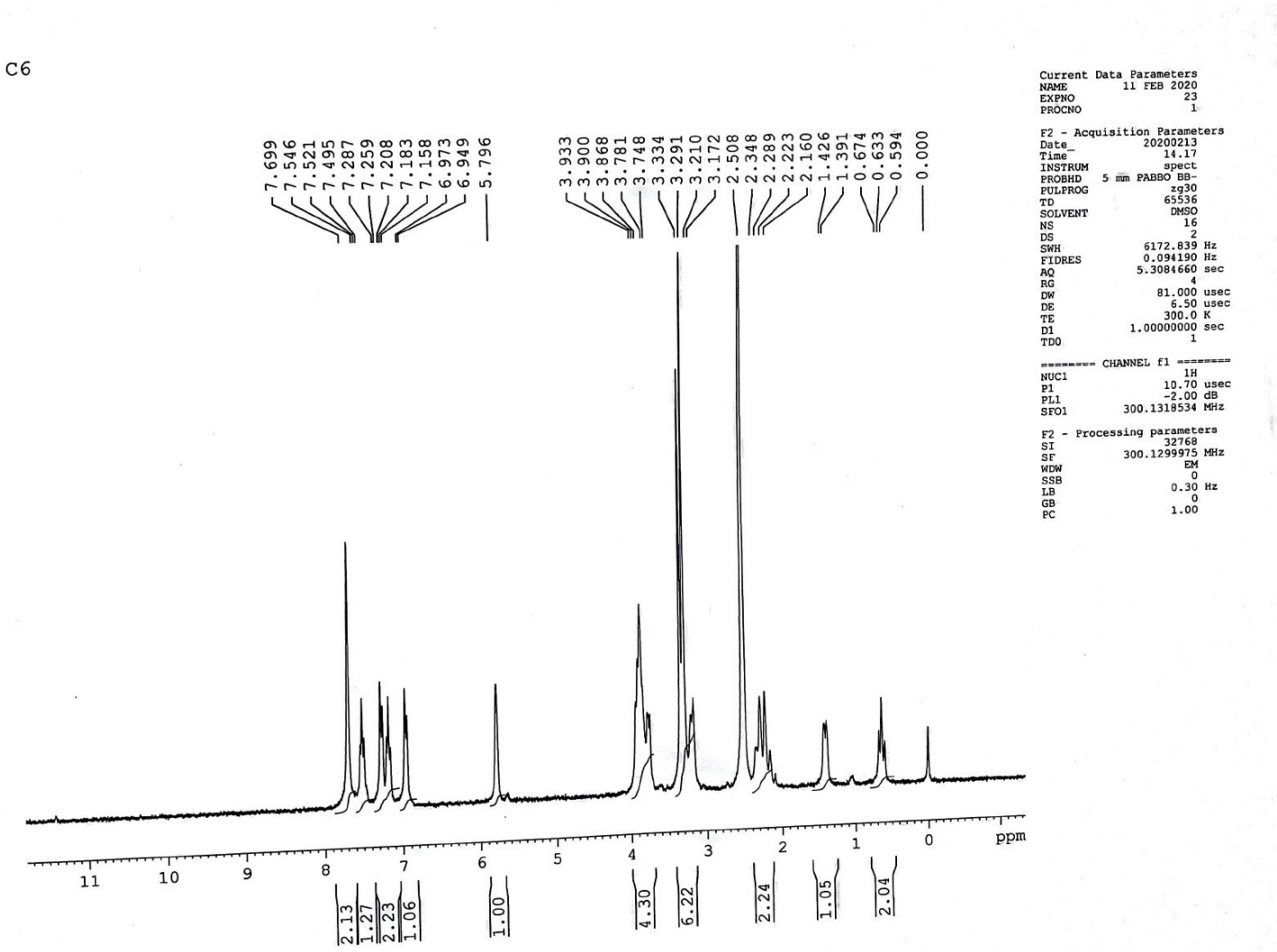

Figure 11: ^{1}H-NMR spectrum of (6f)

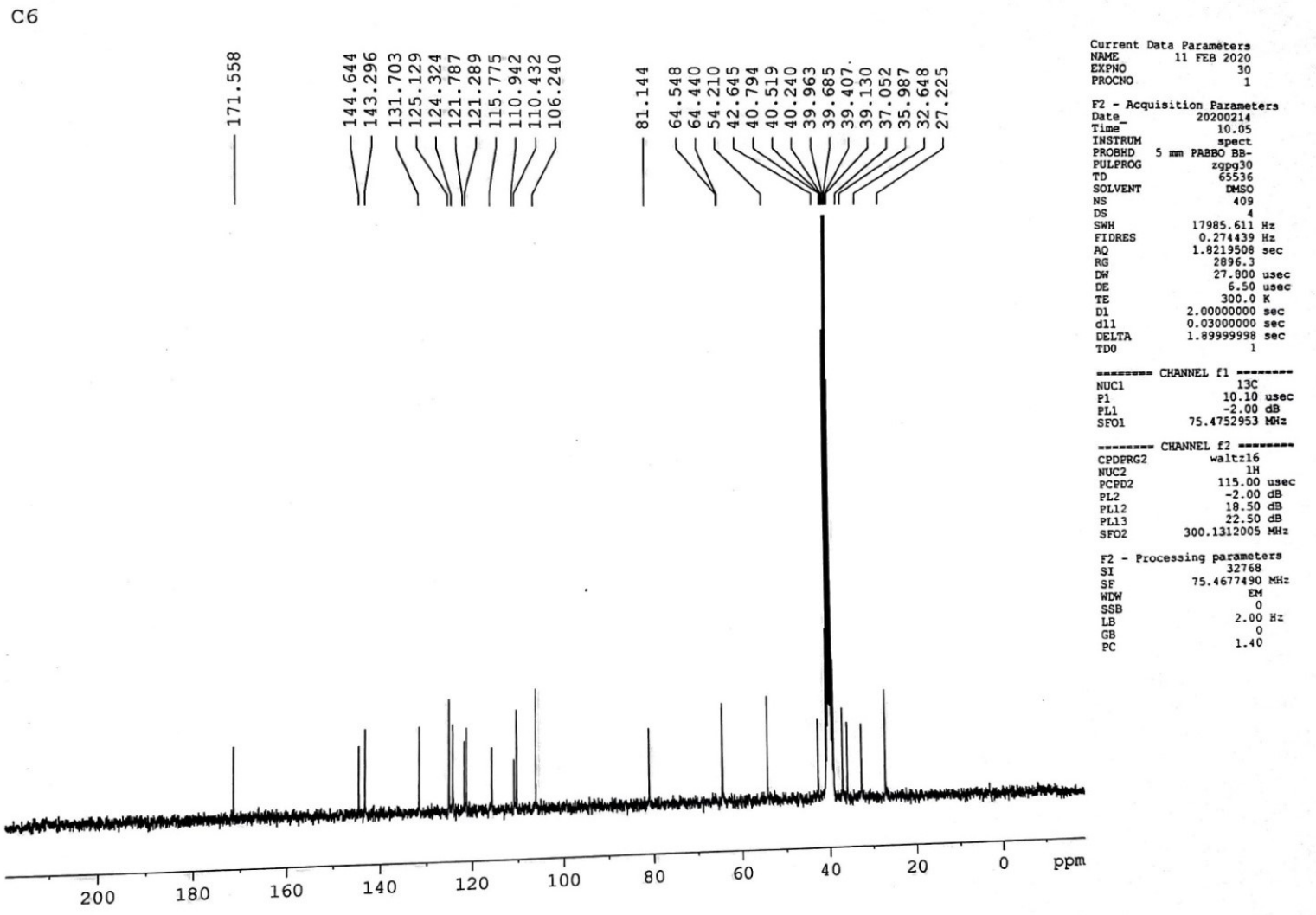

Figure 12:^{13}C NMR **spectrum of (6f)**

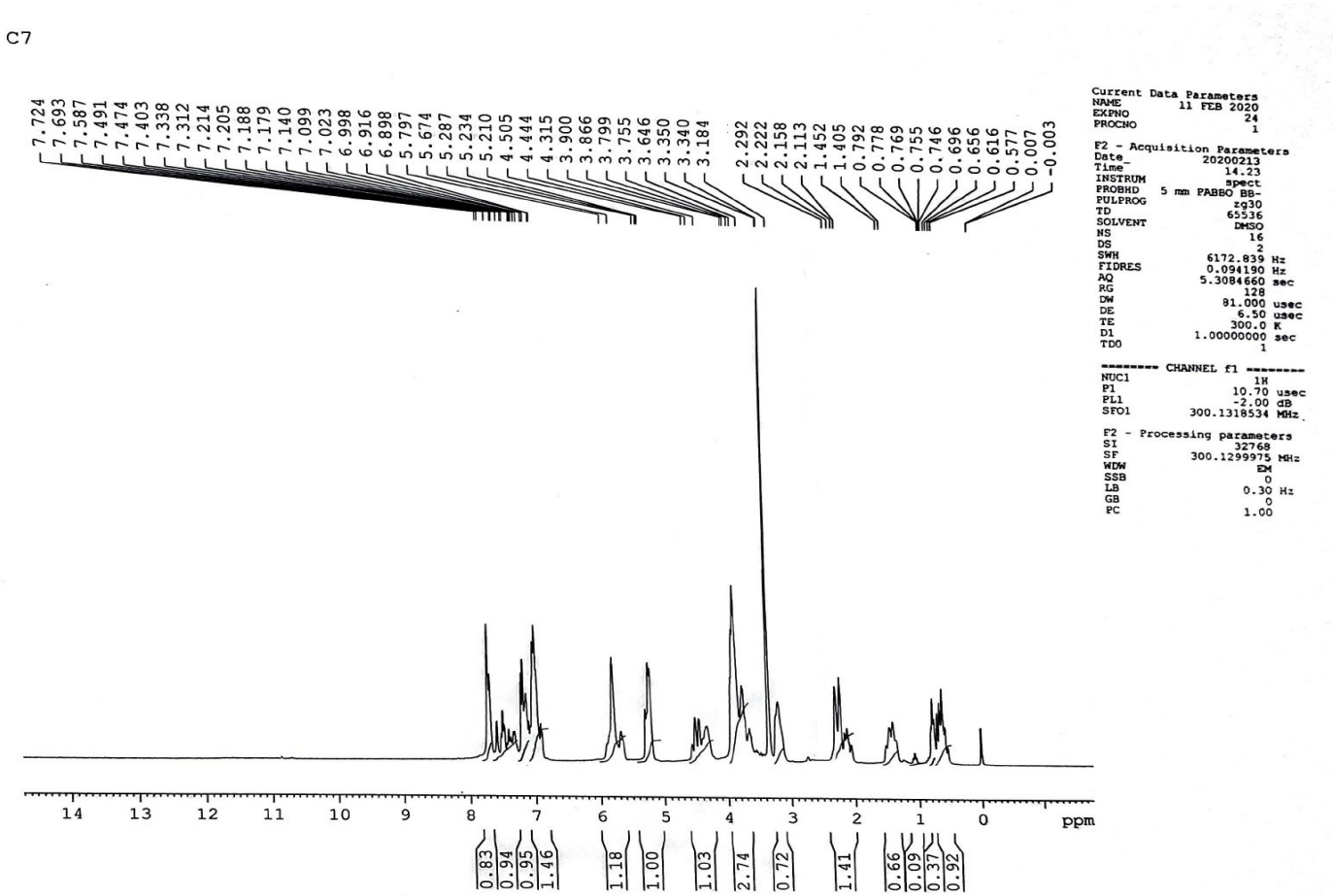

Figure 13: ^{1}H-NMR spectrum of (6g)

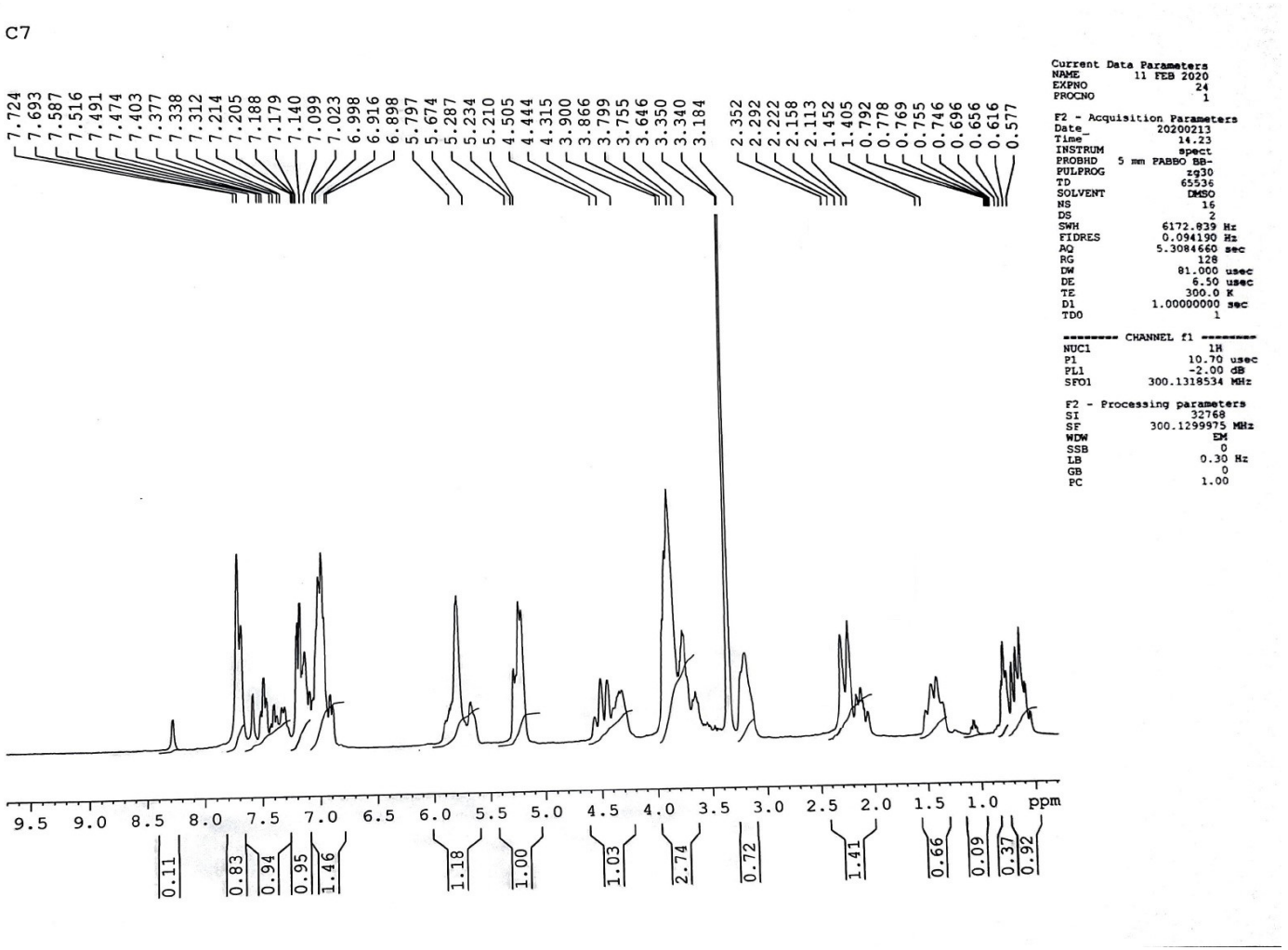

Figure 13A: ^{1}H-NMR spectrum of (6g) Zoom

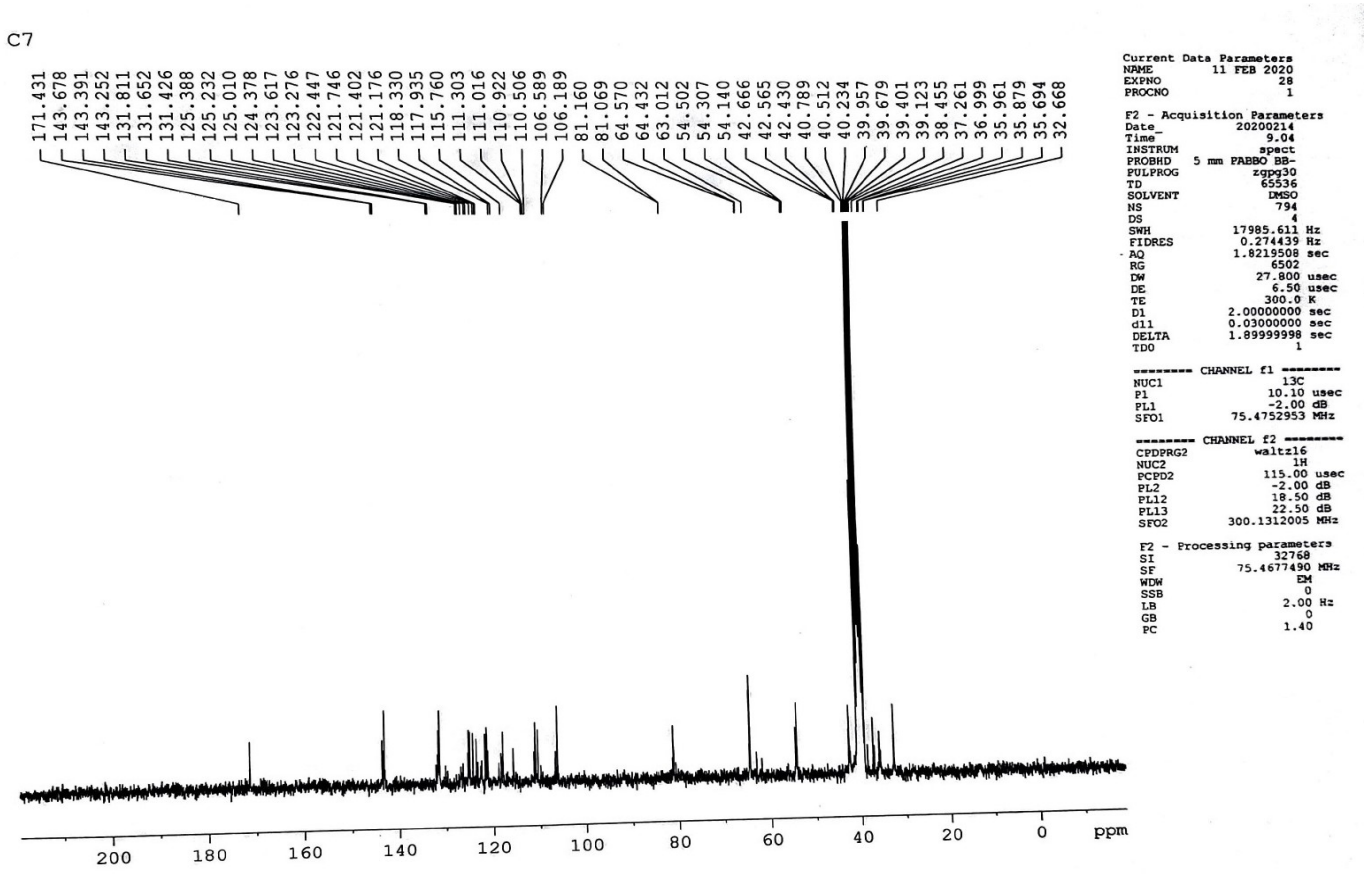

Figure 14:^{13}C NMR **spectrum of (6g)**

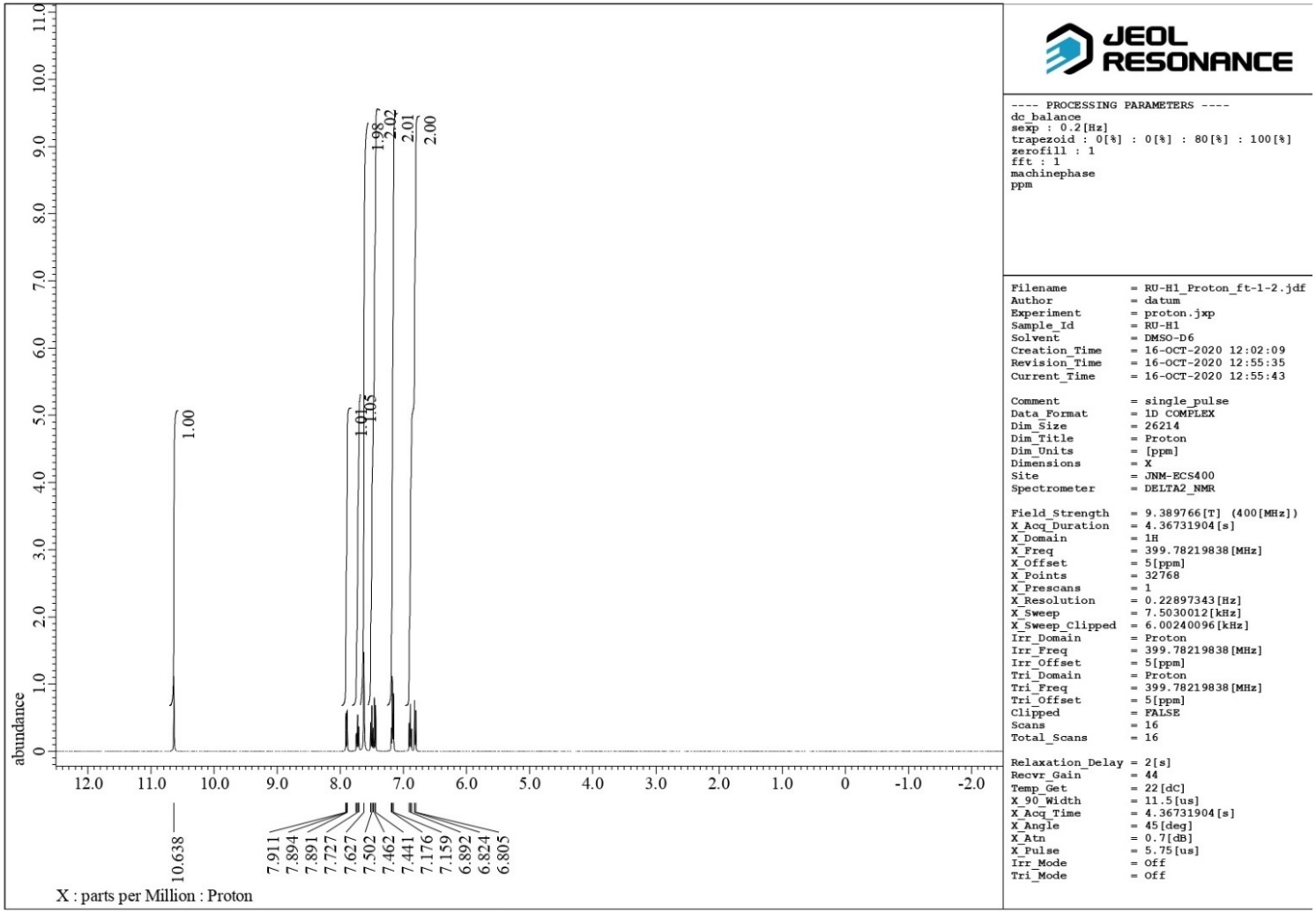

Figure 15: ^{1}H-NMR spectrum of (4a)

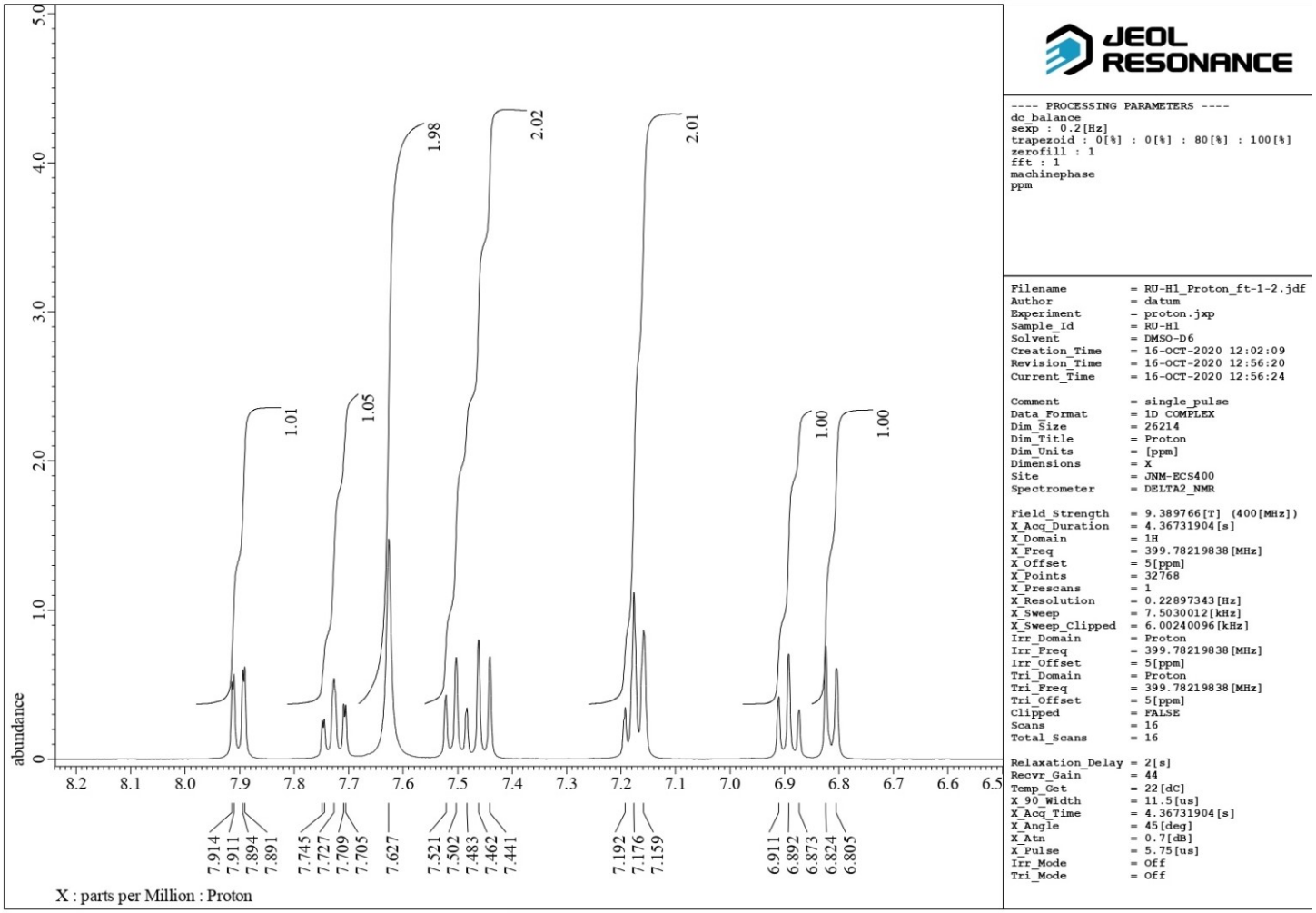

Figure 15A: ^{1}H-NMR spectrum of (4a) zoom

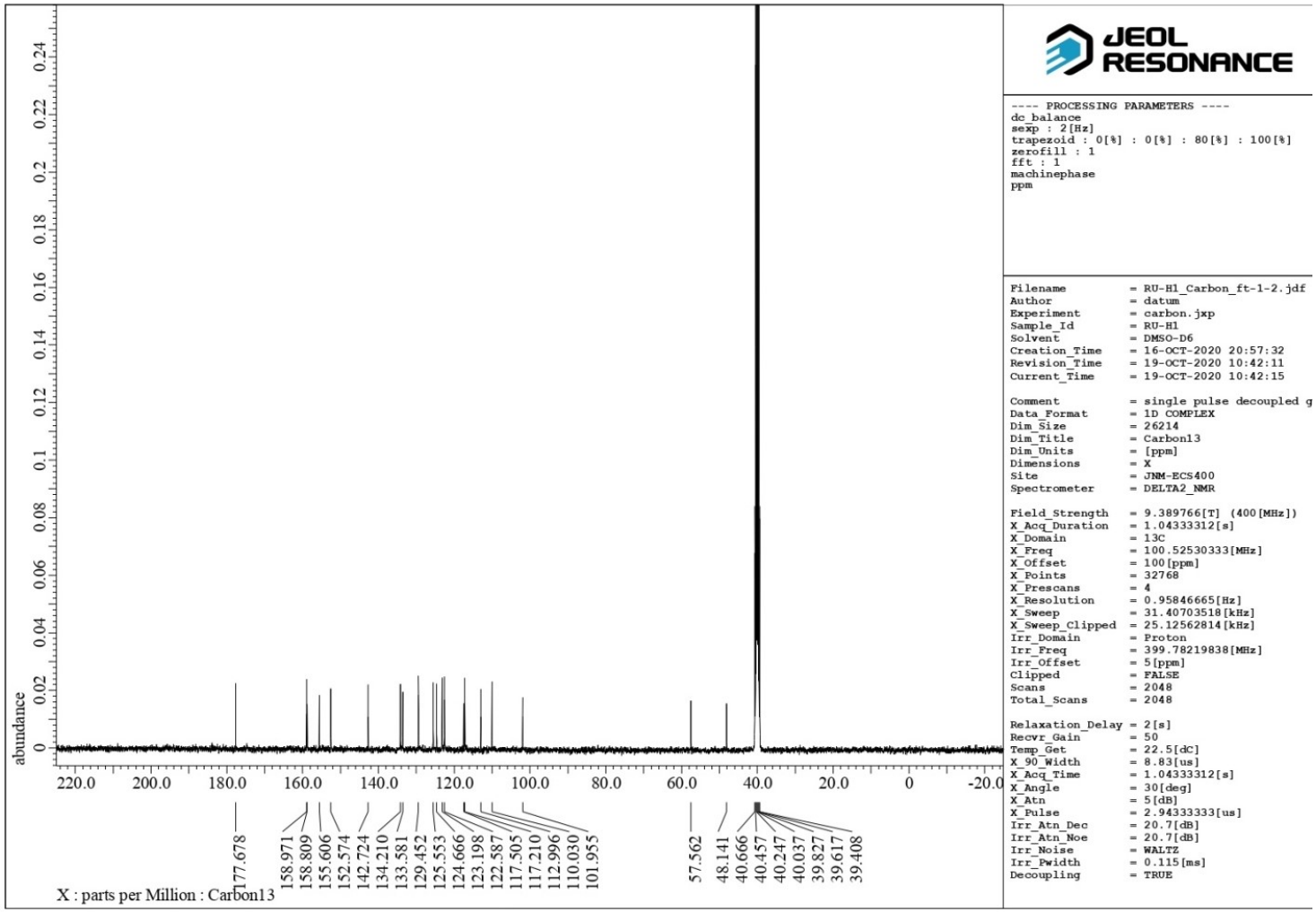

Figure 16: ^{13}C NMR **spectrum of (4a)**

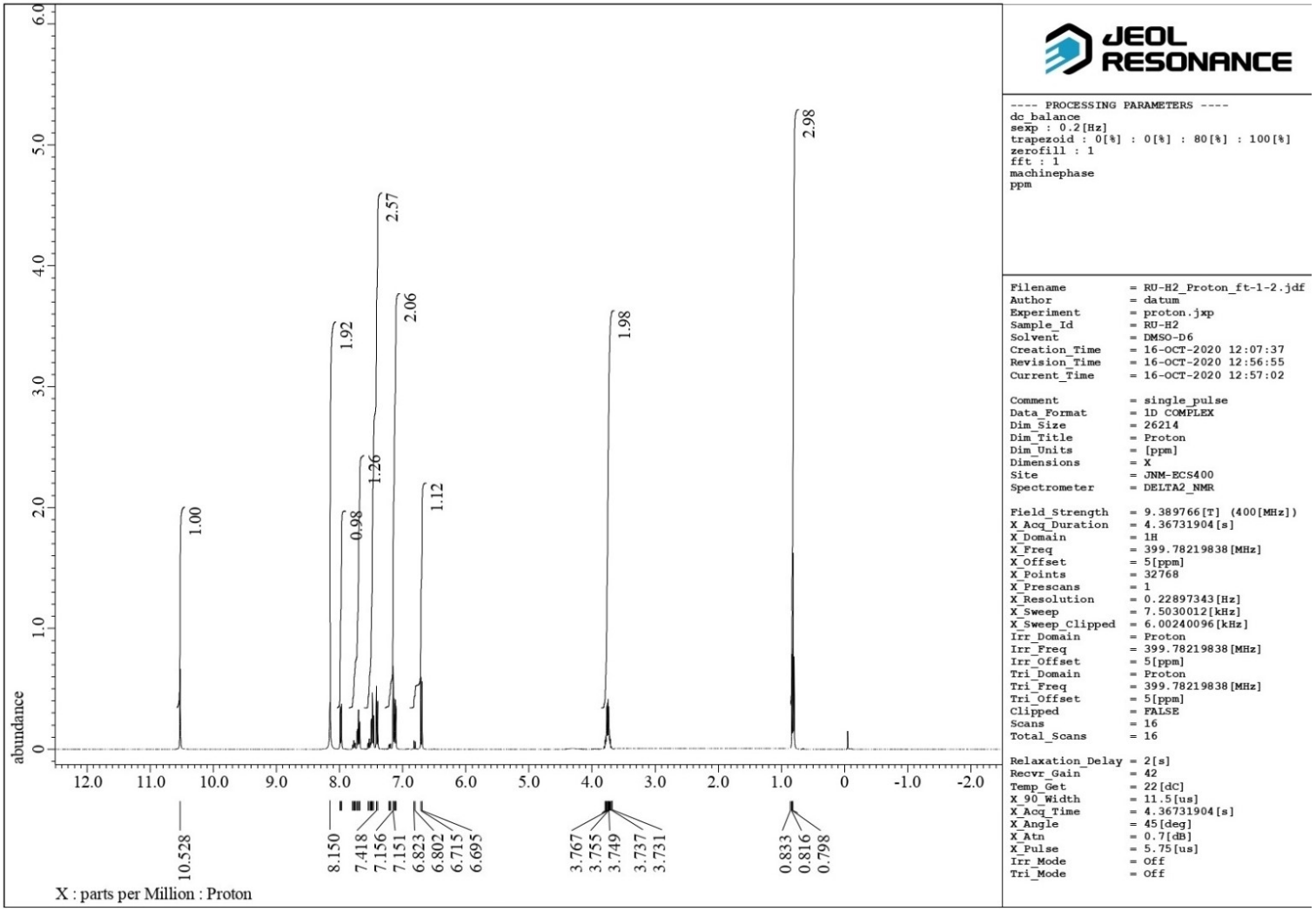

Figure 17: ^{1}H-NMR spectrum of (4b)

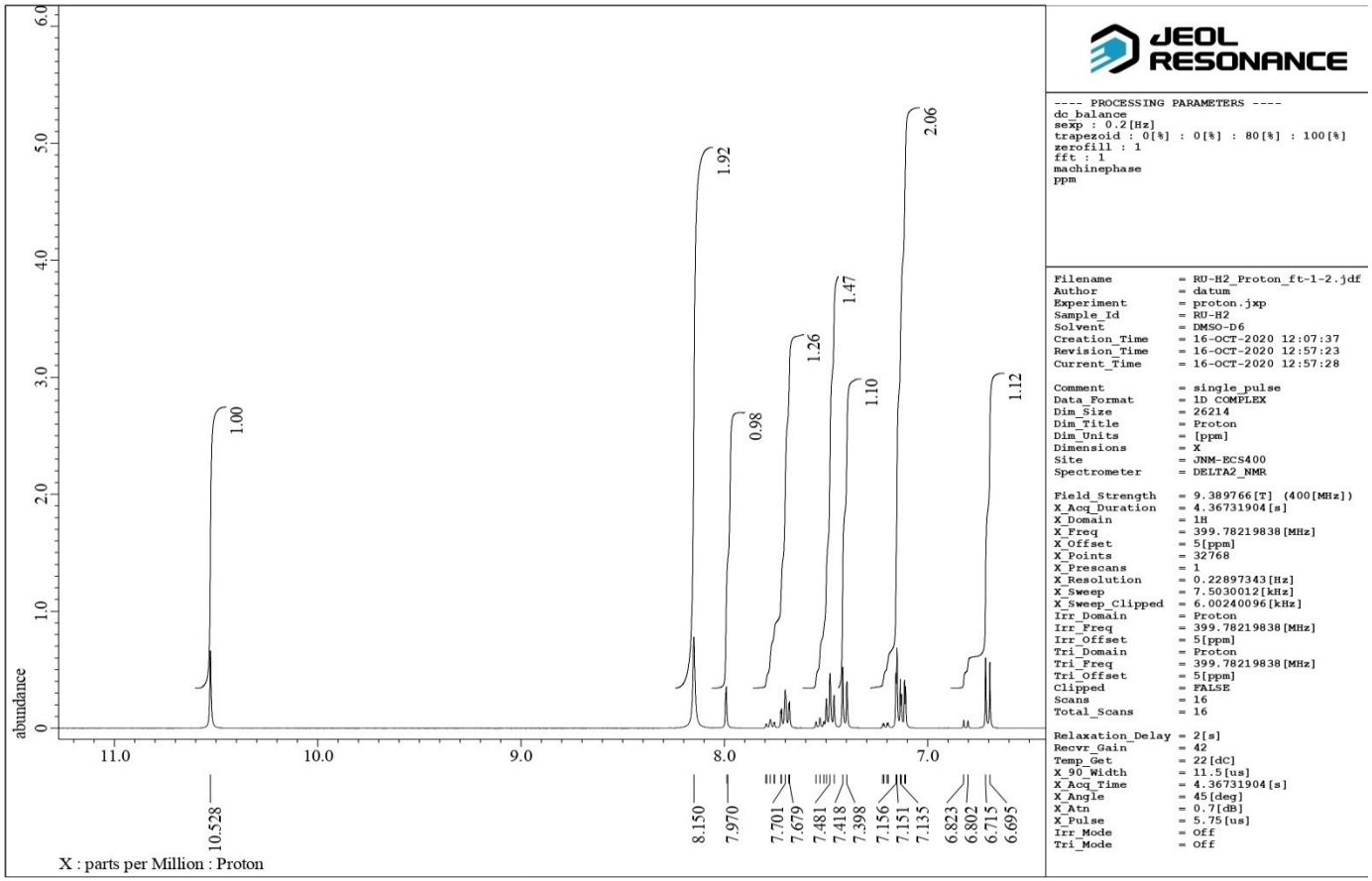

Figure 17A: ^{1}H-NMR spectrum of (4b) zoom

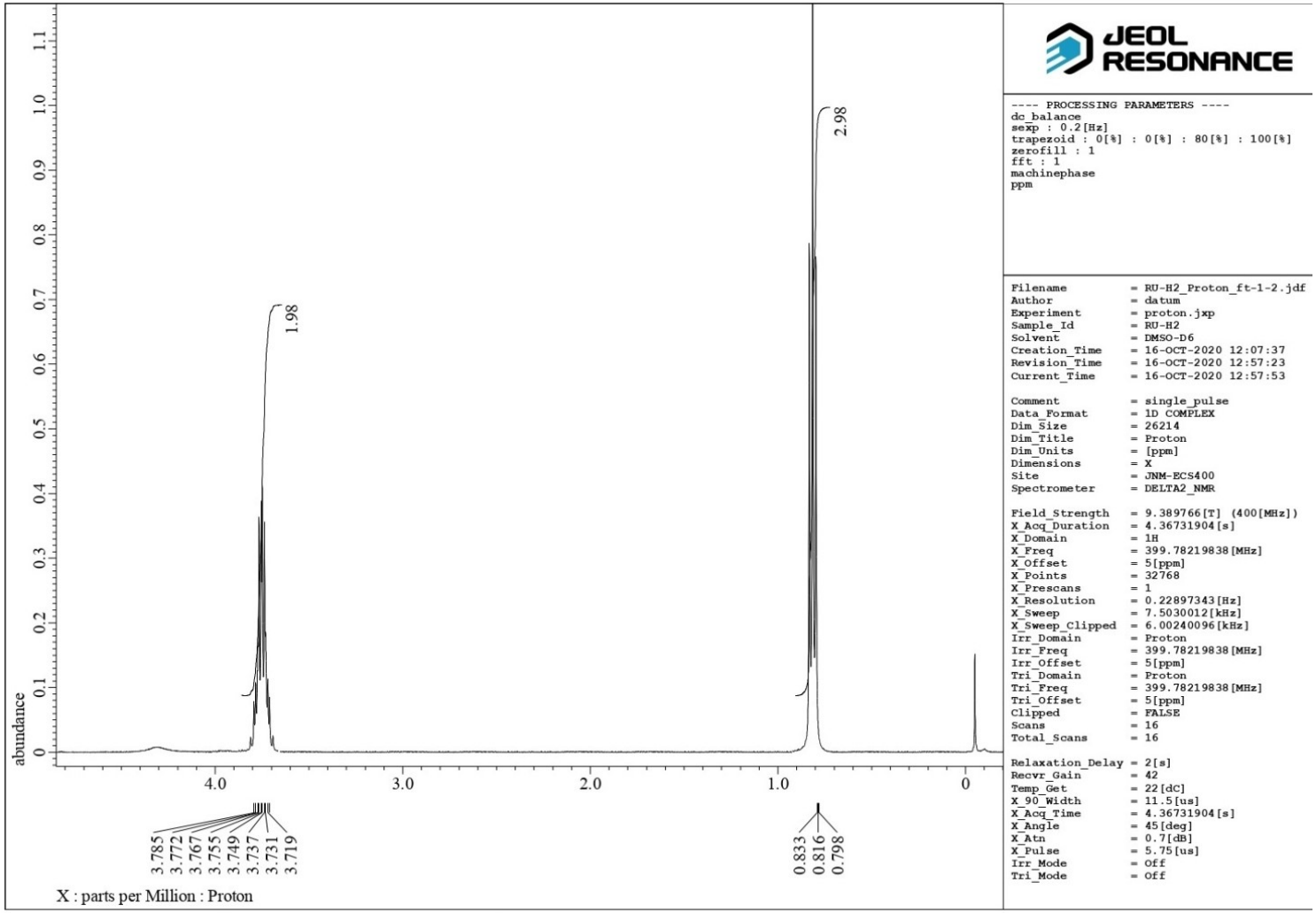

Figure 17B: ^{1}H-NMR spectrum of (4b) zoom

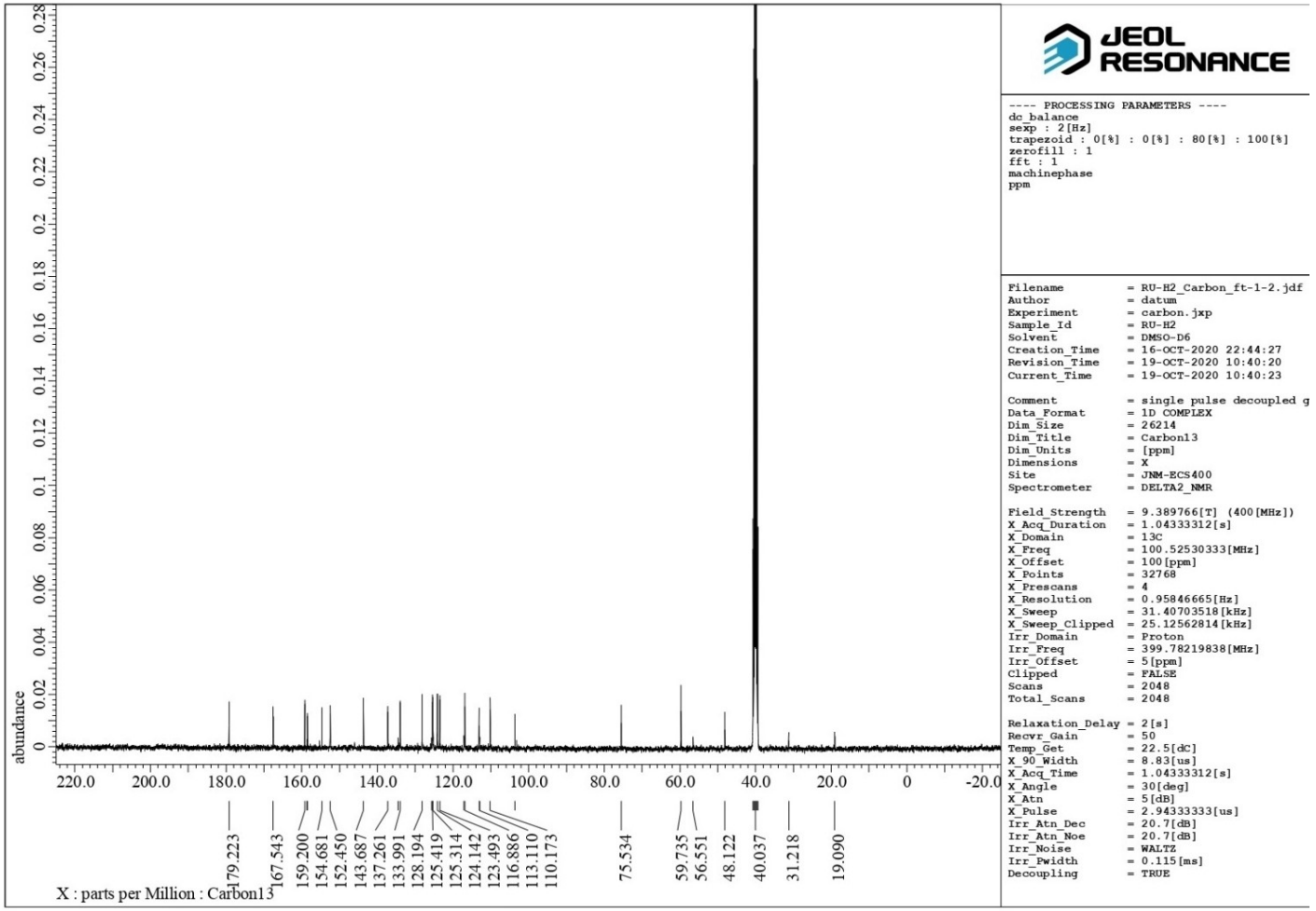

Figure 18: ^{13}C NMR **spectrum of (4b)**

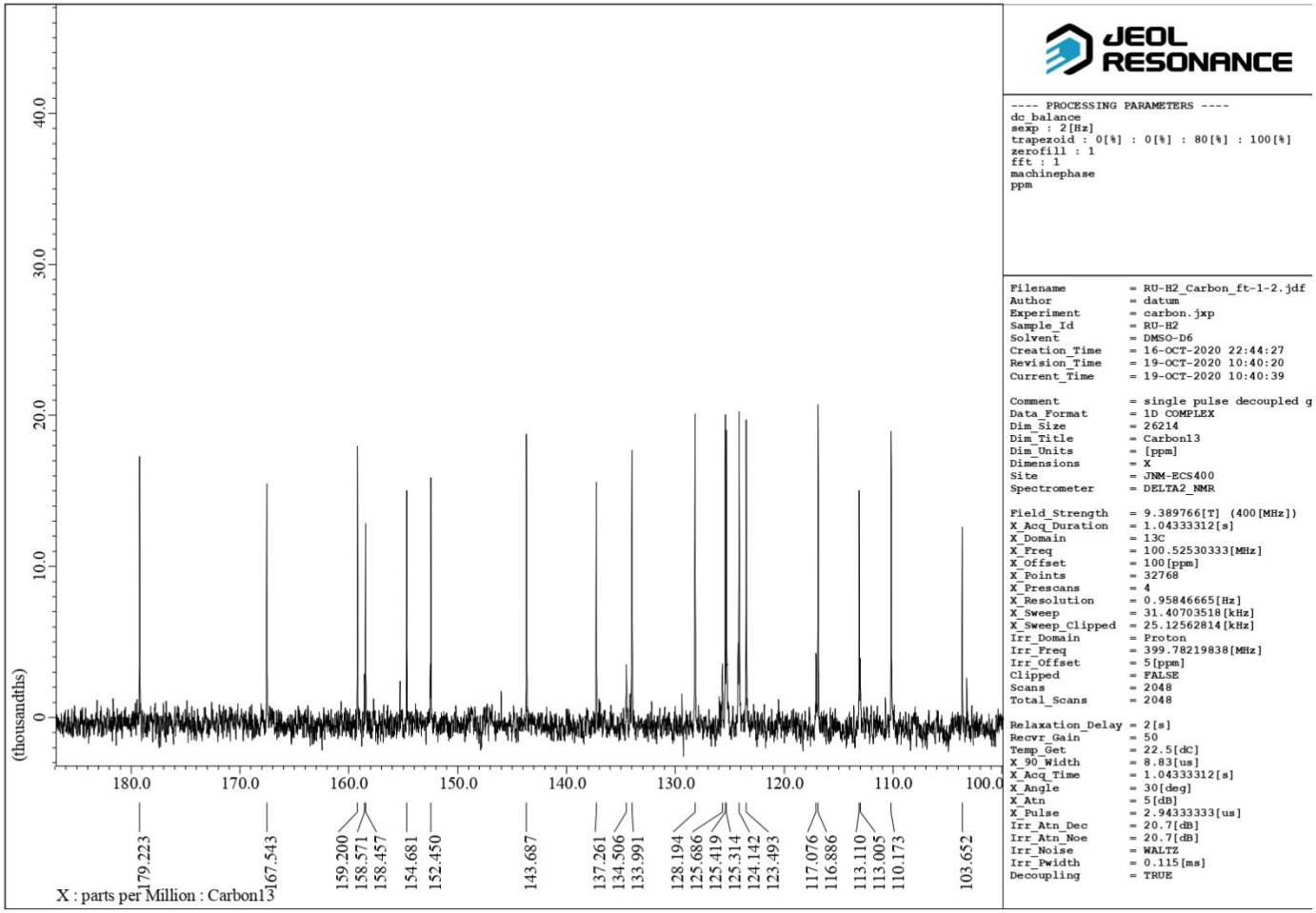

Figure 18A: ^{13}C NMR **spectrum of (4b) Zoom**

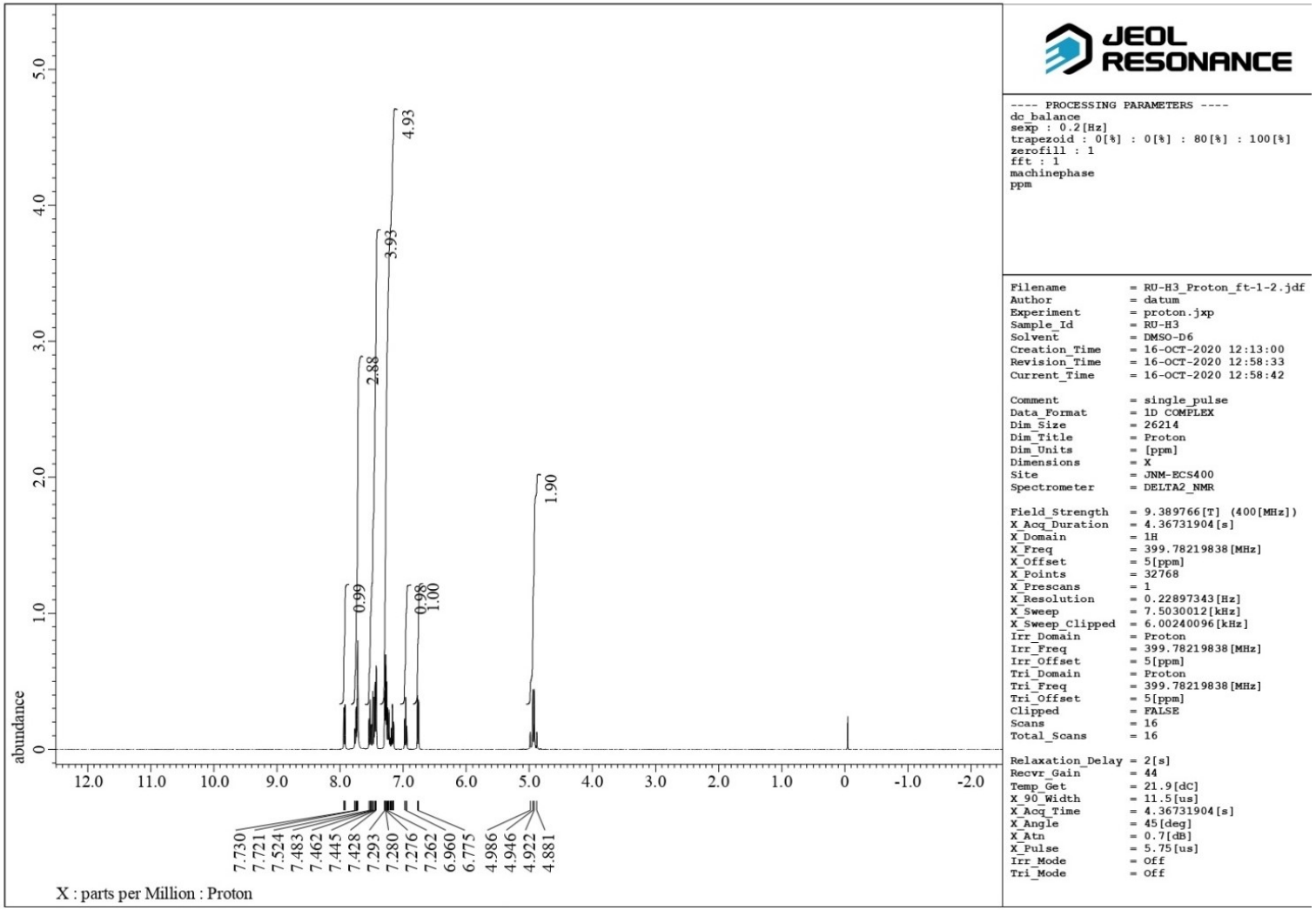

Figure 19: ^{1}H-NMR spectrum of (4c)

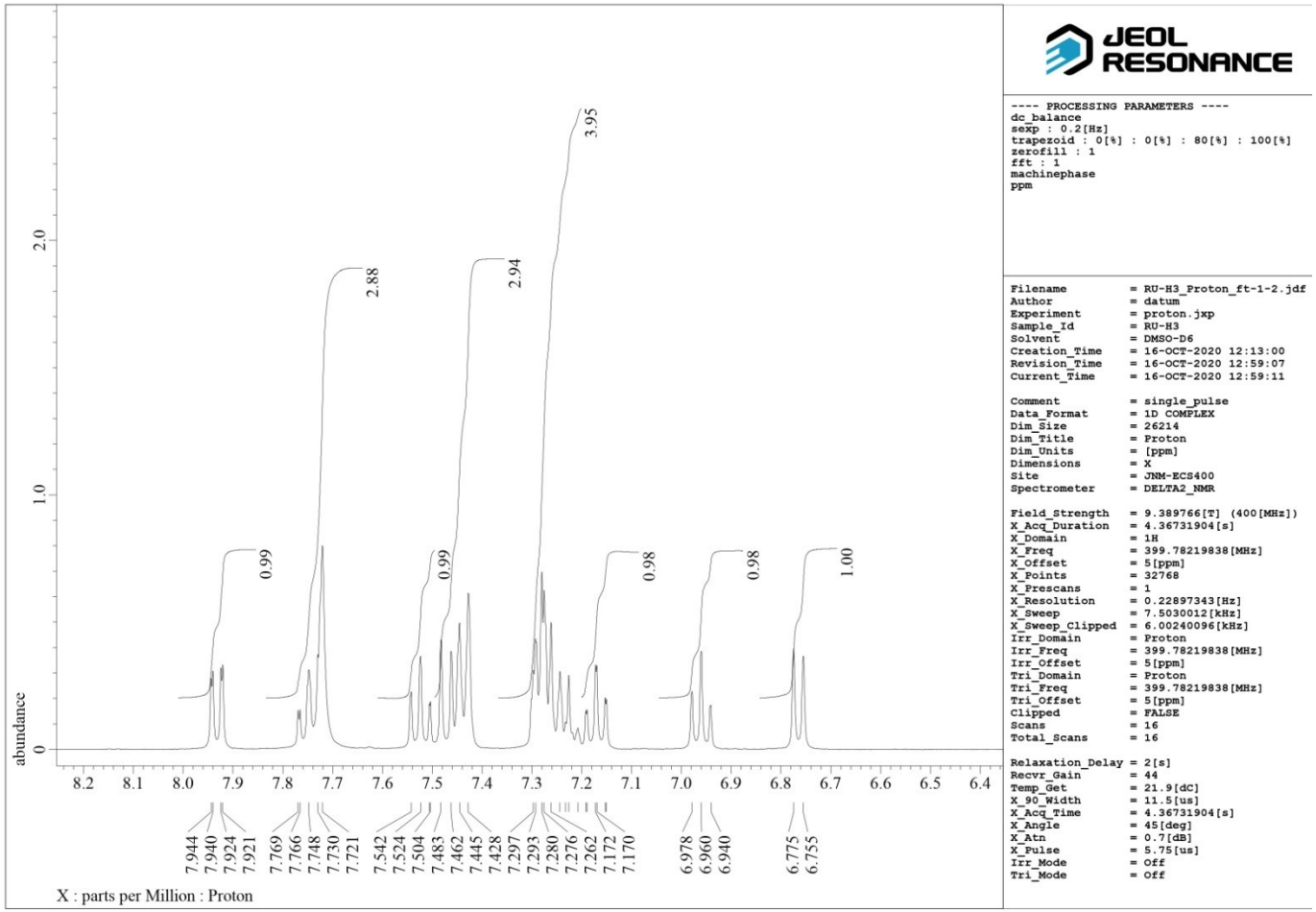

Figure 19A: ^{1}H-NMR spectrum of (4c) Zoom

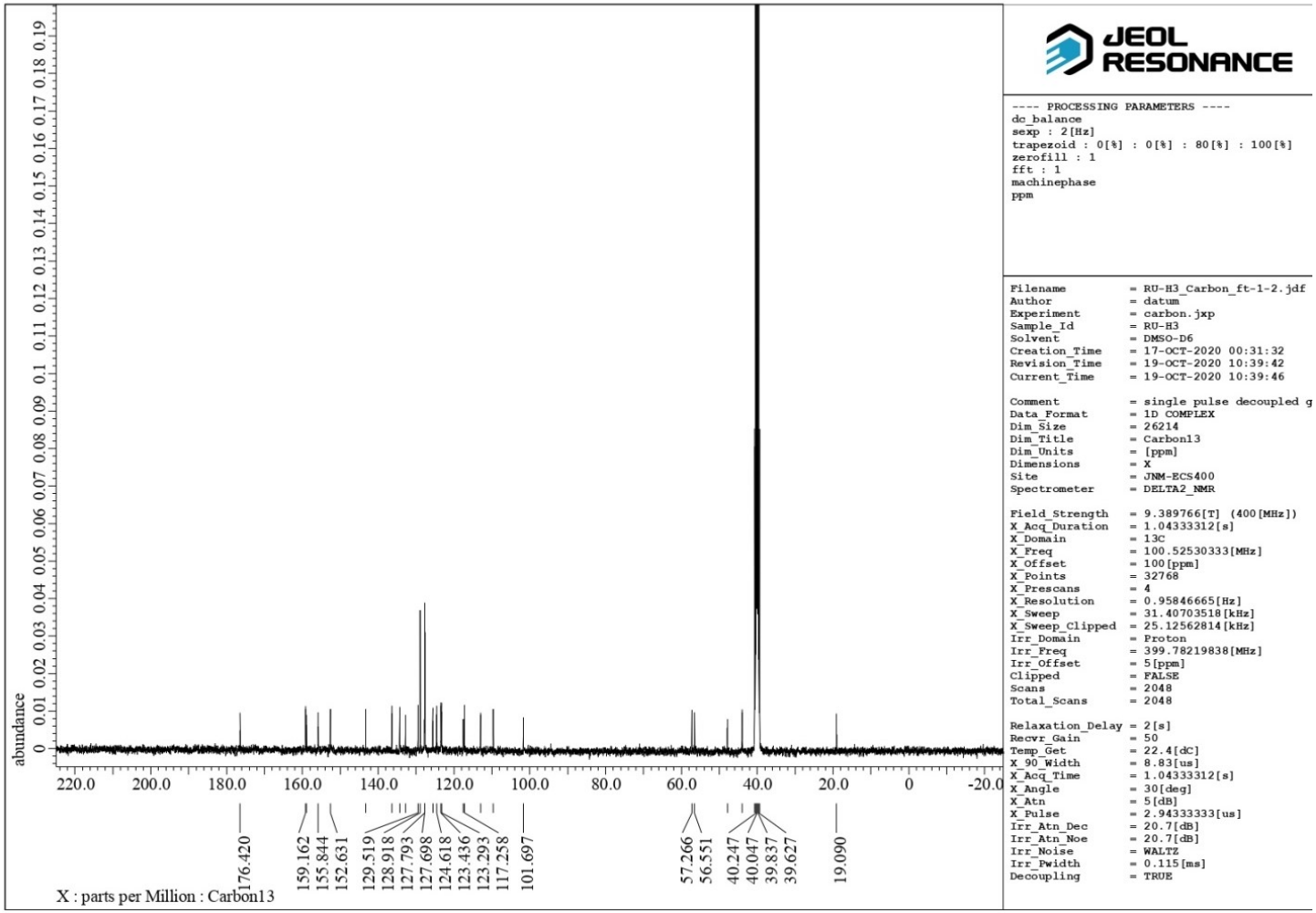

Figure 20: ^{13}C NMR **spectrum of (4c)**

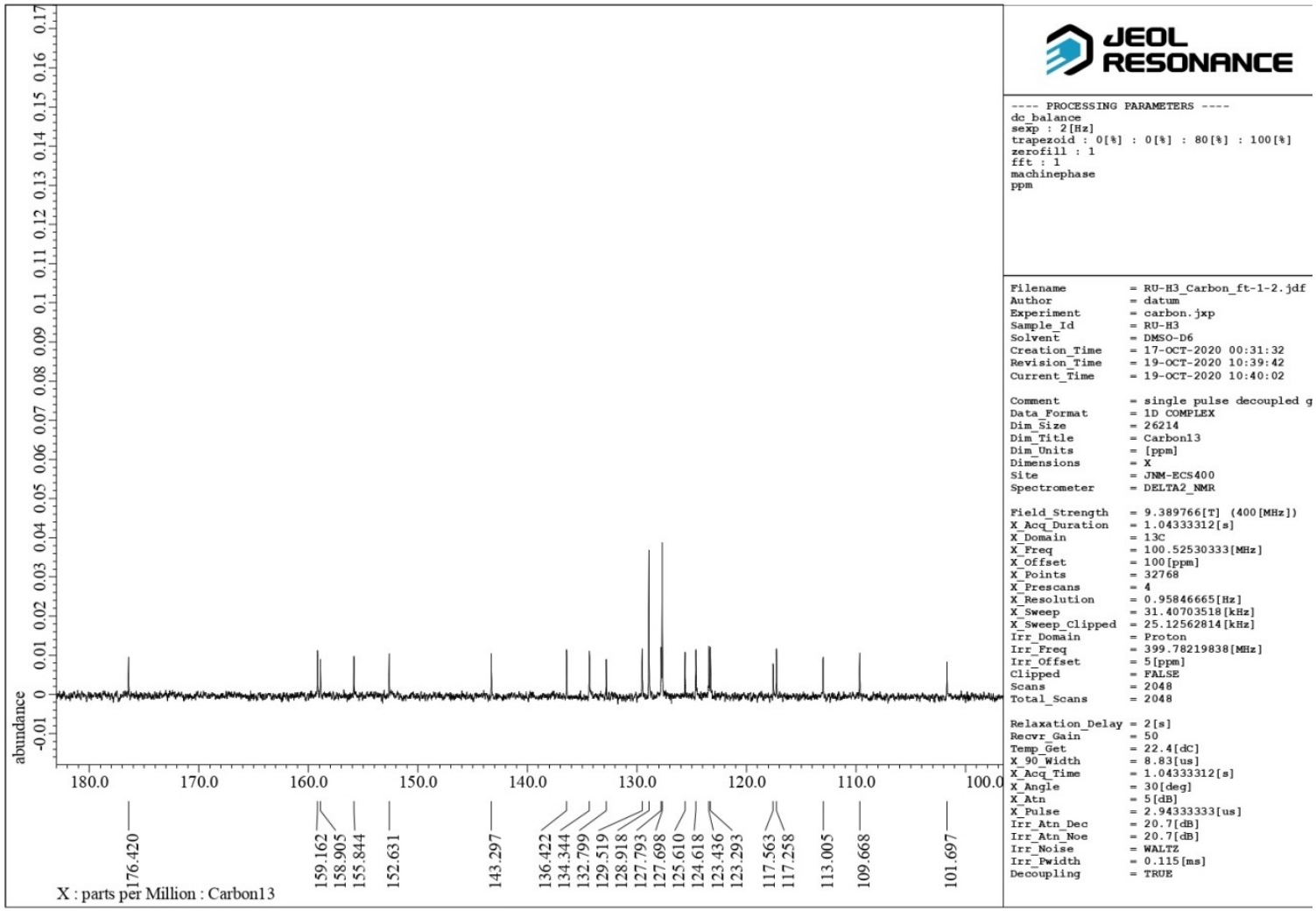

Figure 20A: ^{13}C NMR **spectrum of (4c) zoom**

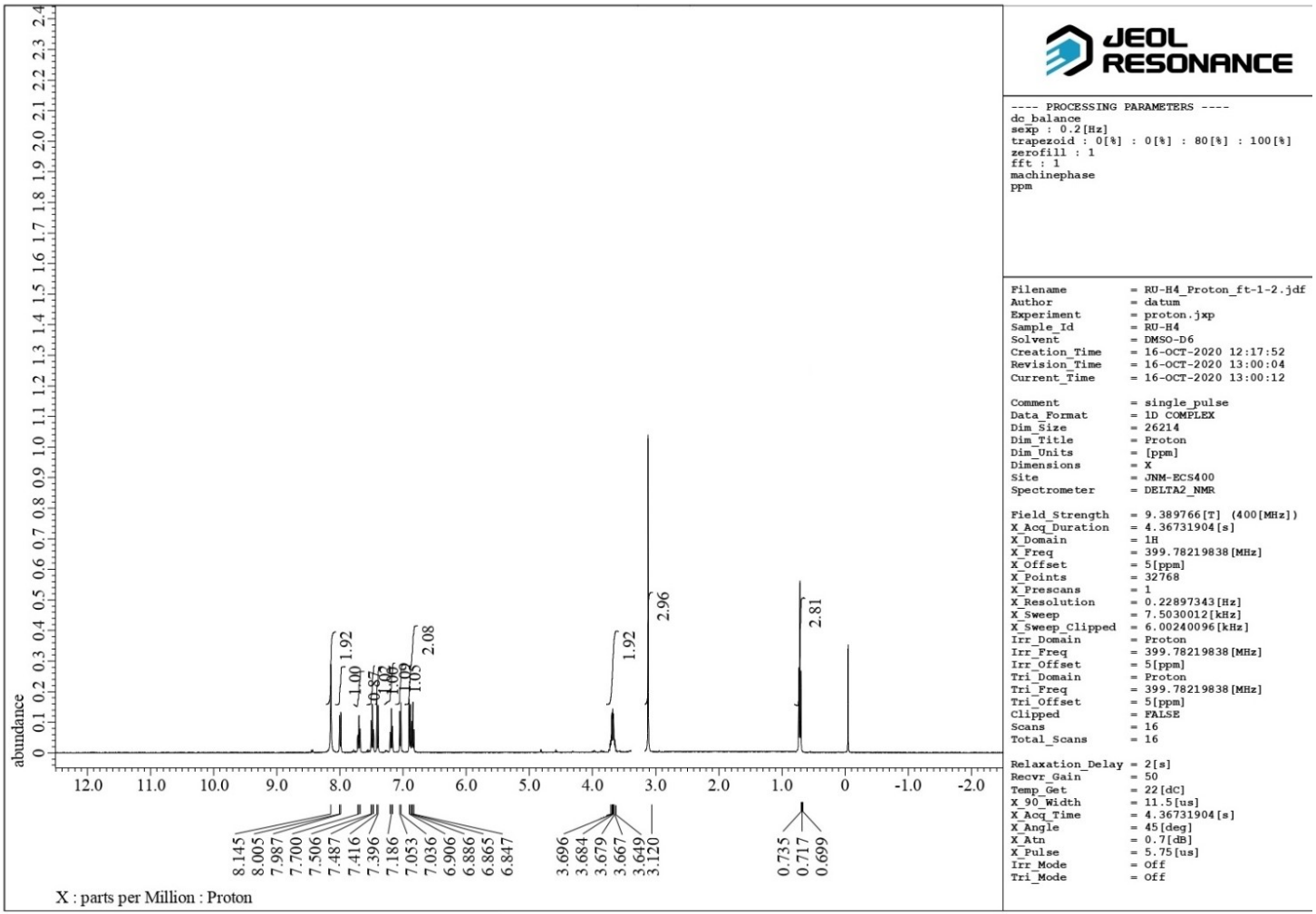

Figure 21: ^{1}H-NMR spectrum of (4d)

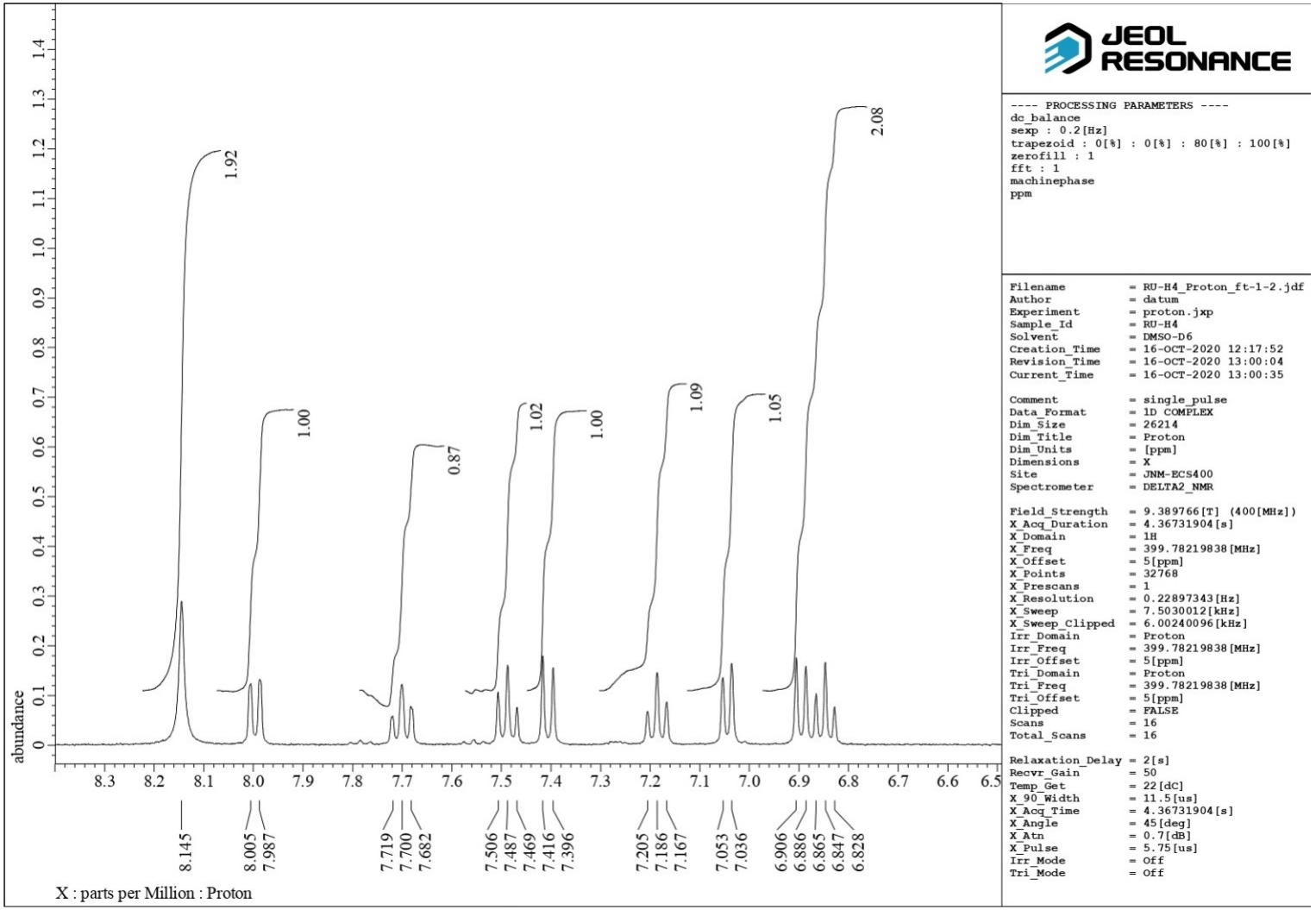

Figure 21A: ^{1}H-NMR spectrum of (4d) zoom

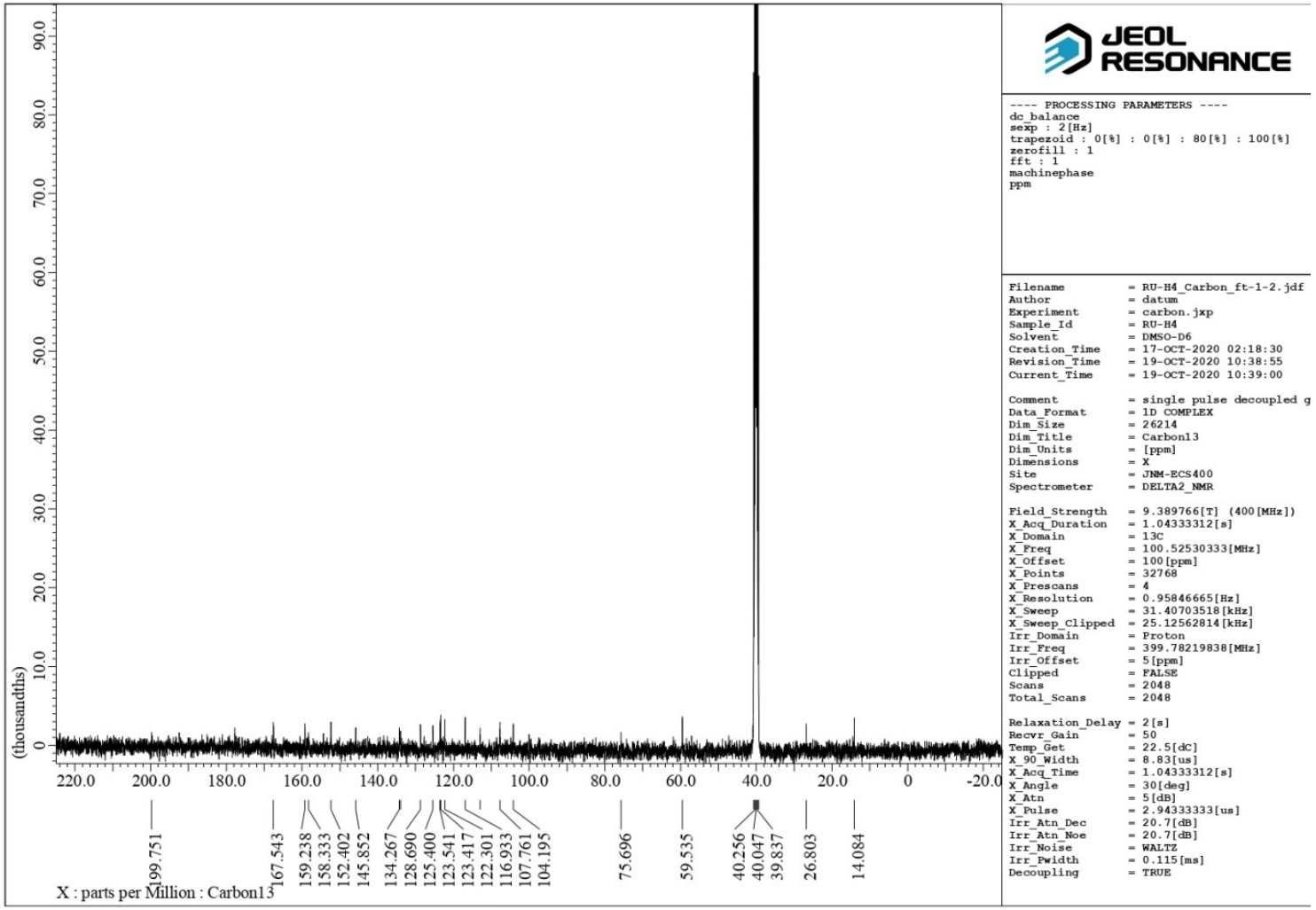

Figure 22: ^{13}C NMR **spectrum of (4d)**

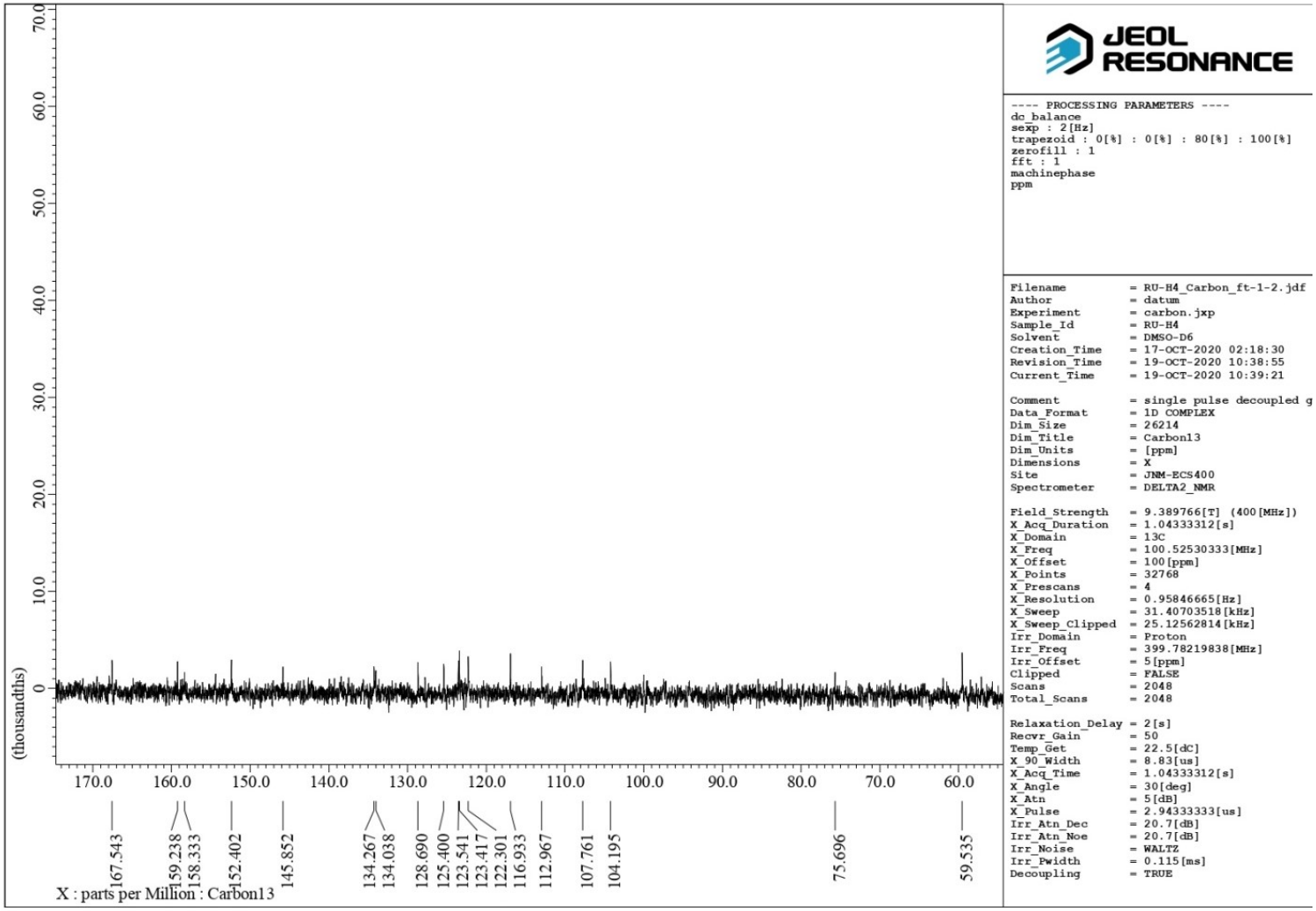

Figure 22A: ^{13}C NMR **spectrum of (4d) zoom**

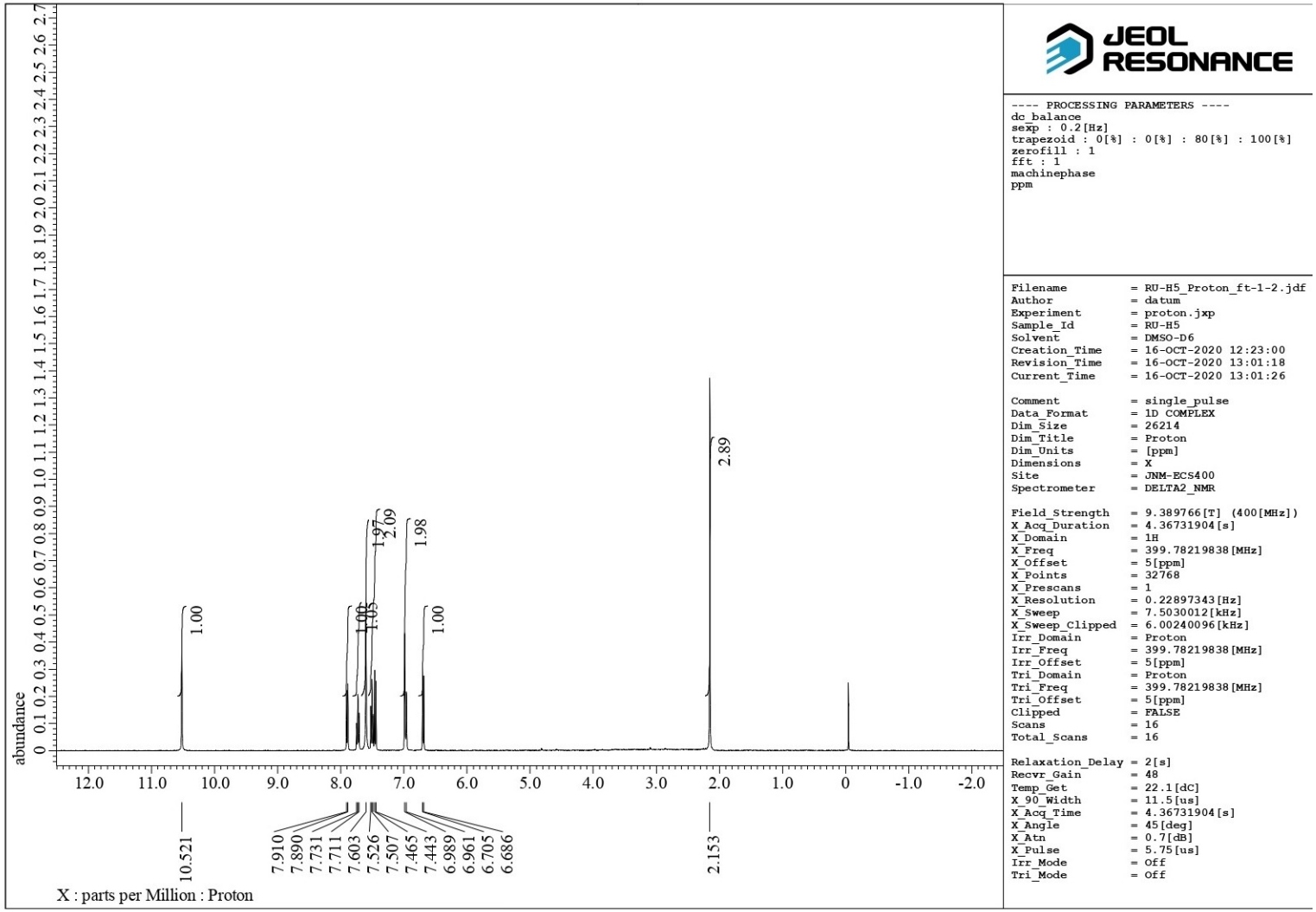

Figure 23: ^{1}H-NMR spectrum of (4e)

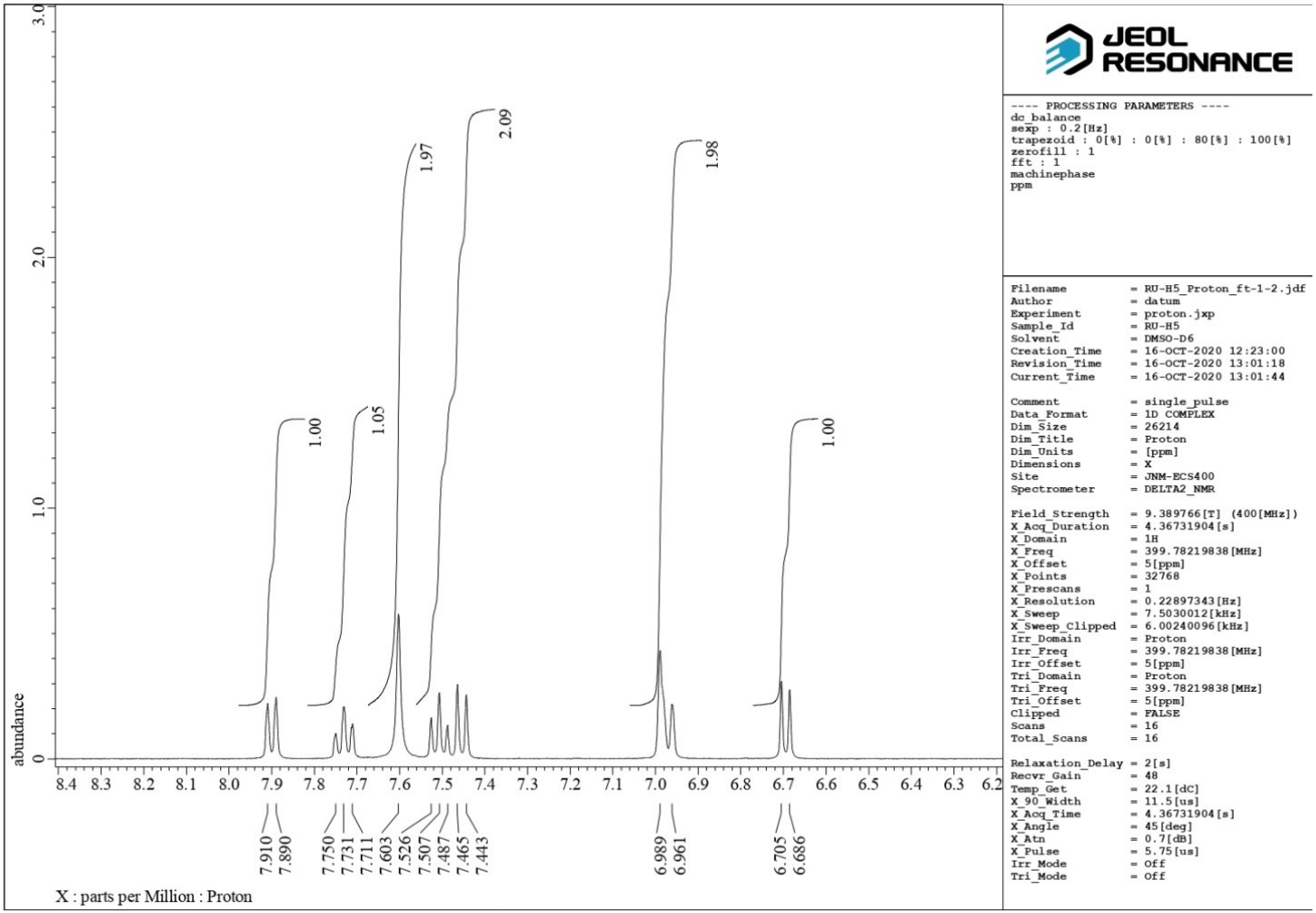

Figure 23A: ^{1}H-NMR spectrum of (4e) zoom

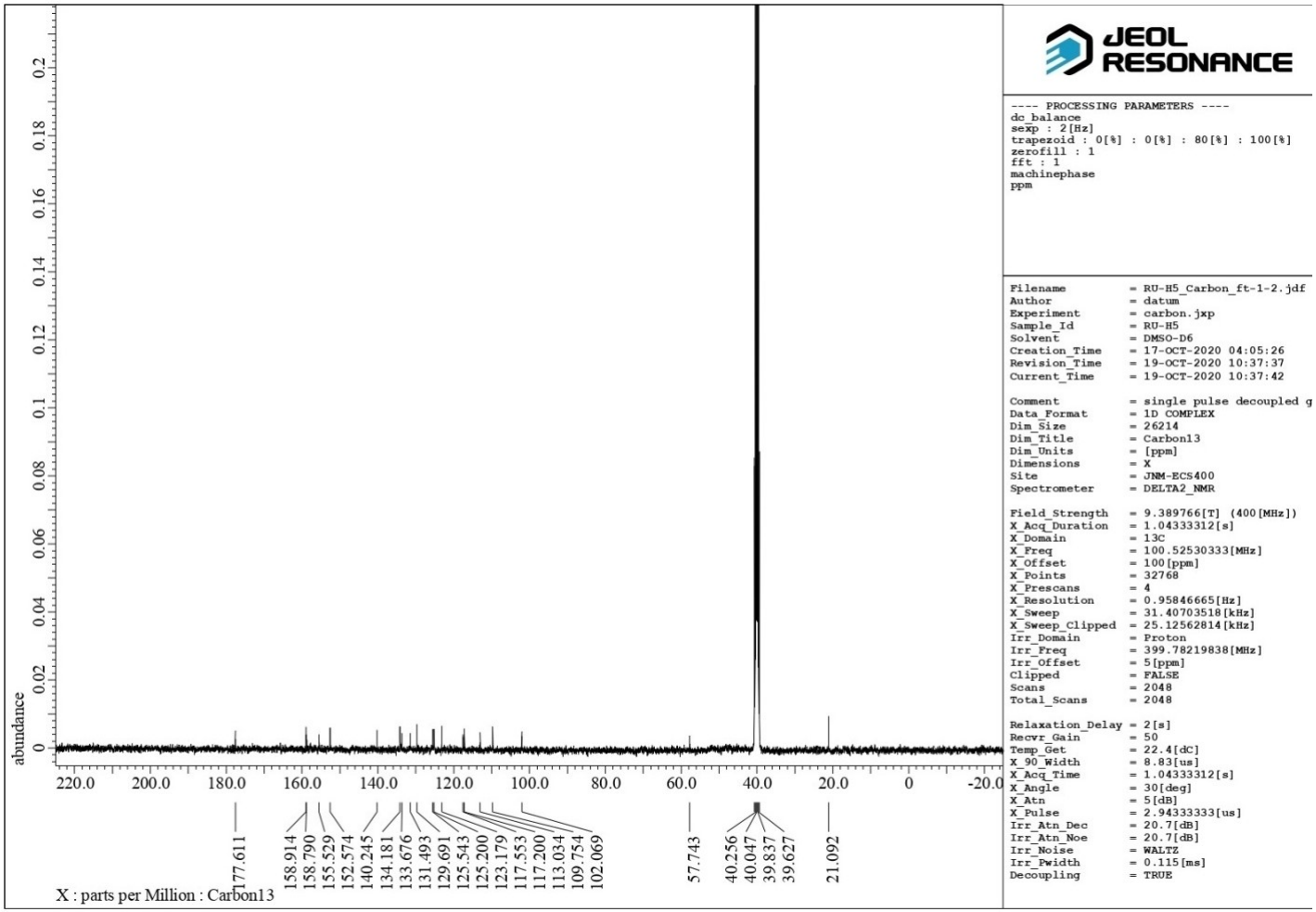

Figure 24: ^{13}C NMR **spectrum of (4e)**

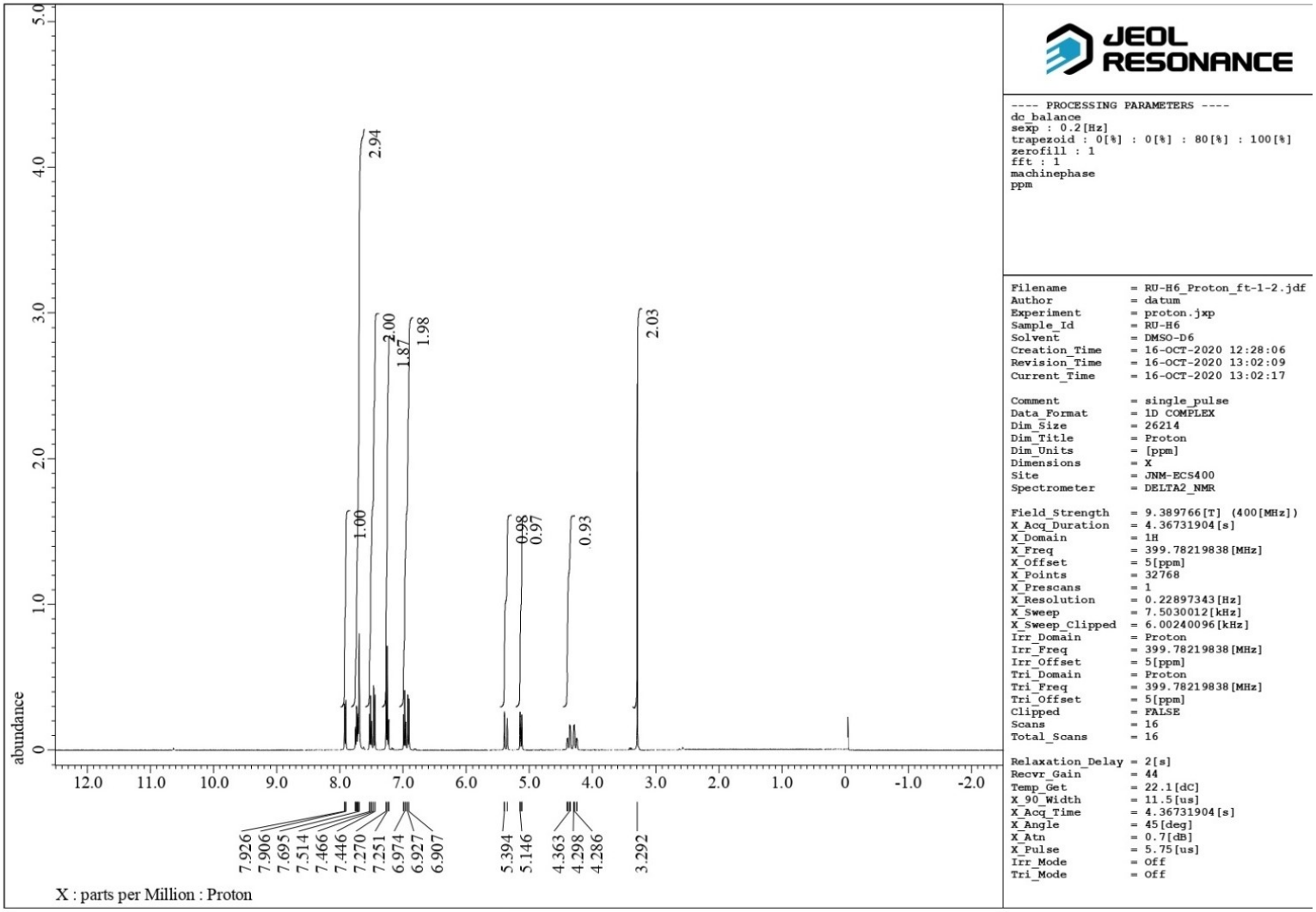

Figure 25: ^{1}H-NMR spectrum of (4f)

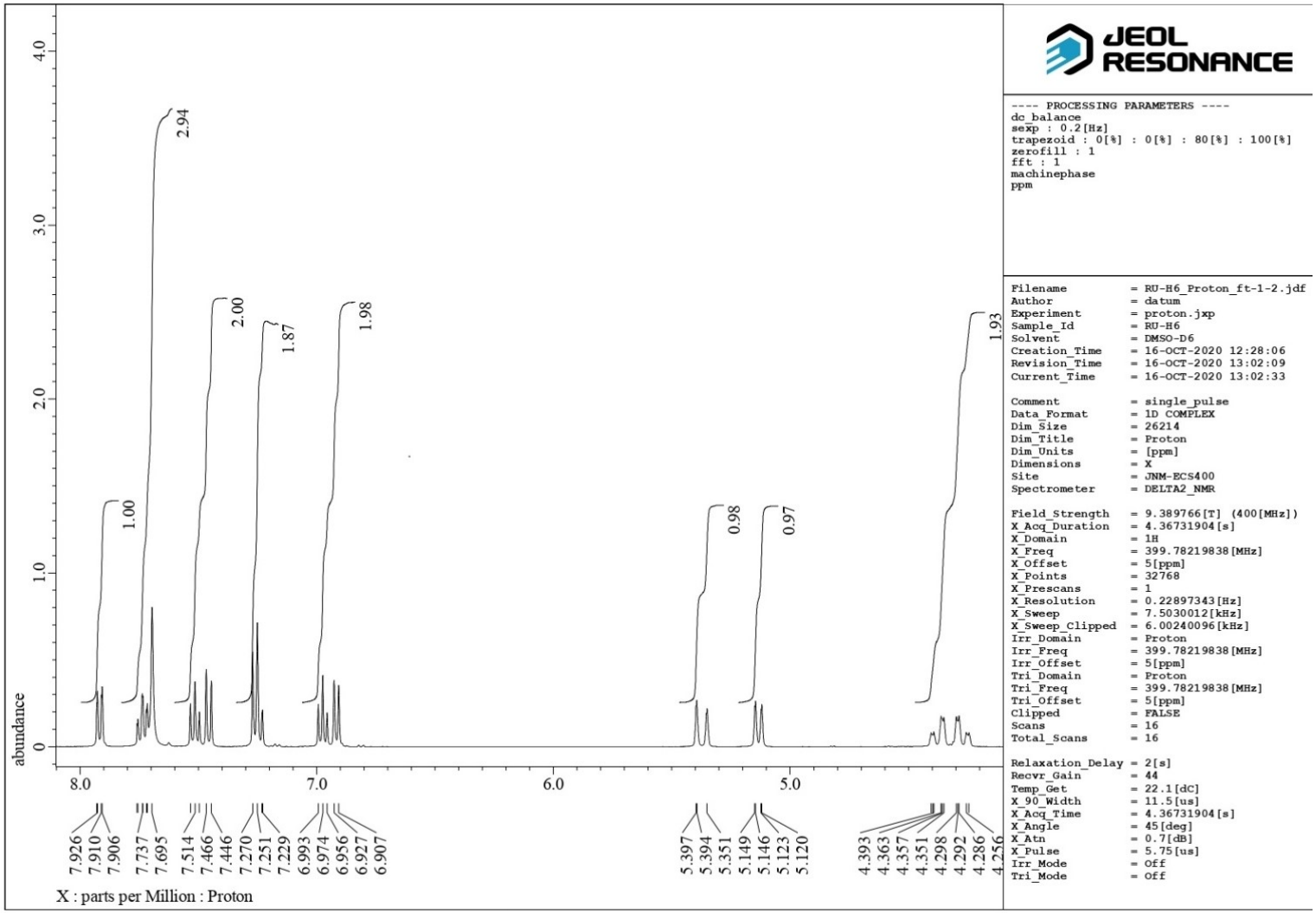

Figure 25A: ^{1}H-NMR spectrum of (4f) zoom

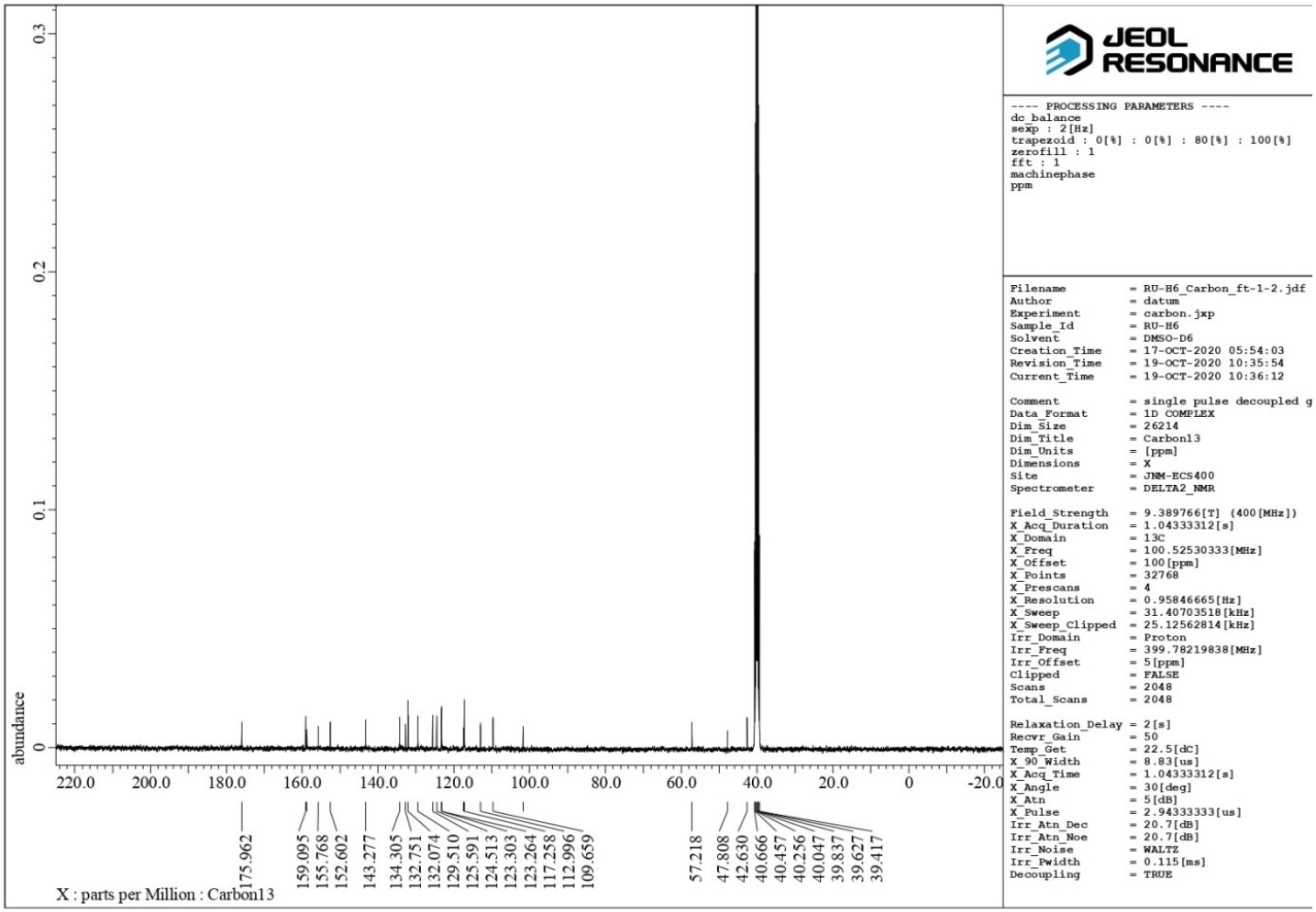

Figure 26: ^{13}C NMR **spectrum of (4f)**

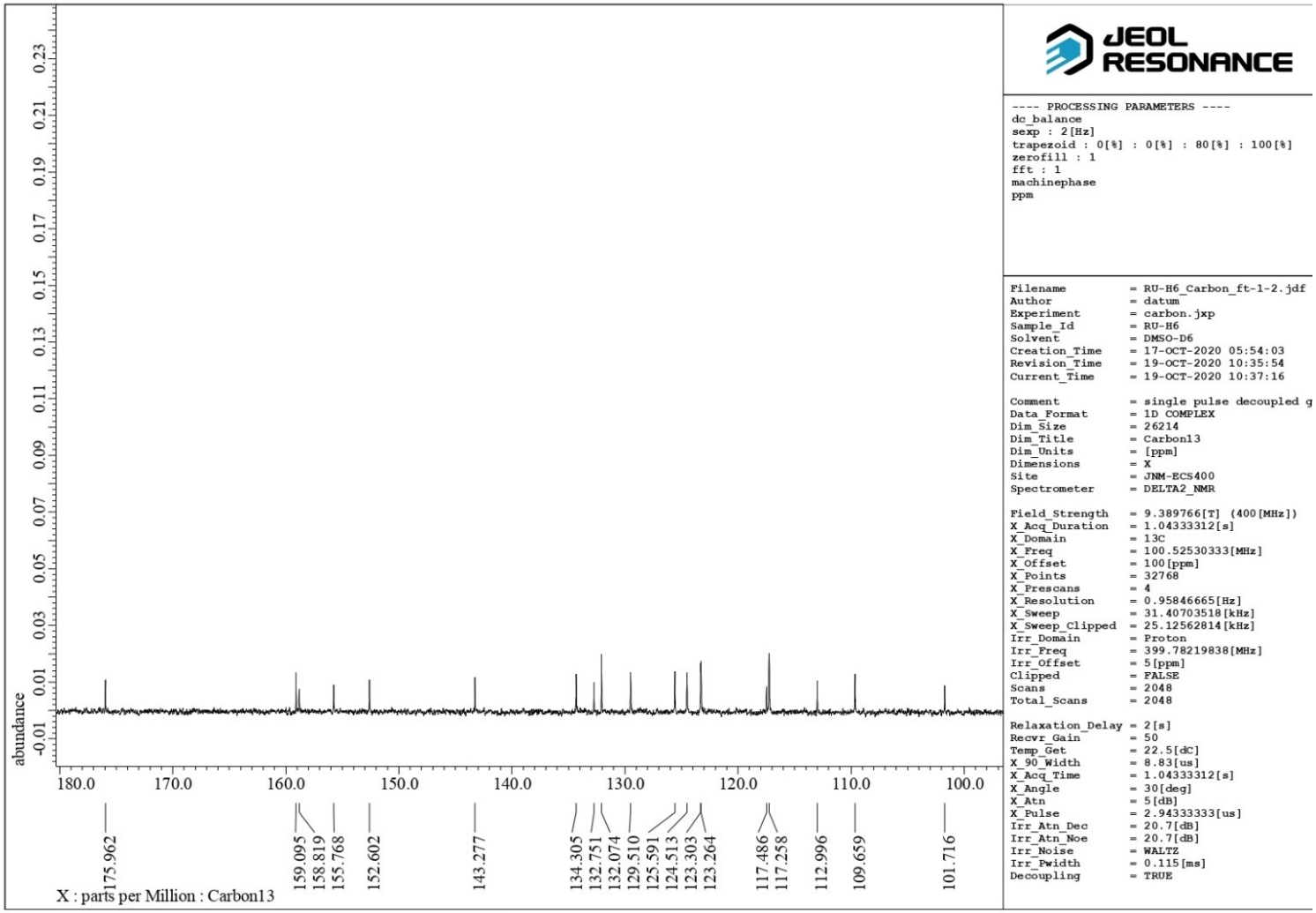

Figure 26A: ^{13}C NMR **spectrum of (4f) zoom**