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Simple Efficient Routes for the Preparation of Pyrazoleamines and Pyrazolopyrimidines: Regioselectivity of Pyrazoleamines Reactions with Bidentate Reagents

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Abstract: Simple and efficient routes for the preparation of 2-amino-5-phenyl-4,5-dihydrofuran-3-carbonitrile (**12**), 2-oxo-5-phenyl-tetrahydrofuran-3-carbonitrile (**13**) and the 3,5-diaminopyrazole derivative **2h** were developed. The results of the reactivity profiles of **12** and **2h** are reported and the previously investigated reaction of pyrazole-3,5-diamine (**2b**) with acrylonitrile to yield compound (**31**), a N-1 acylation product, is currently justified by using X-ray crystallographic analysis. Taken together, the observation of alkenes and alkynes substitution when reacting with 3,5-diaminopyrazole derivative **2h** is explained by the terminal electron withdrawing group. This pattern of substitution is attributed to involvement of sterically unhindered electrophiles primarily at the N-1 position.

Keywords: diamino pyrazoles, reduction, Michael addition, pyrazolopyrimidines, cyclic enamines.

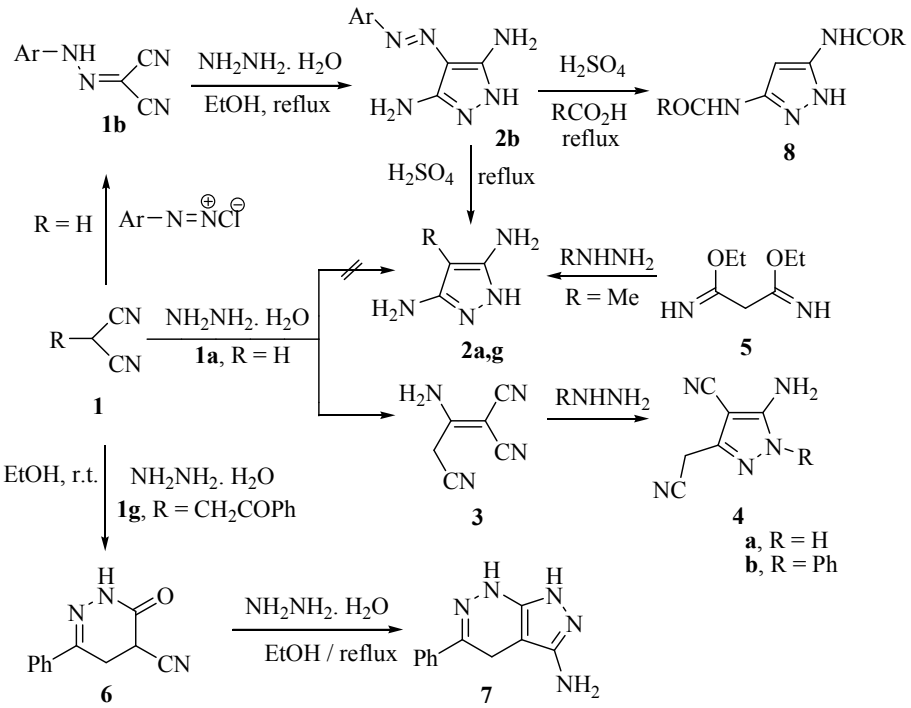
INTRODUCTION

IT was suggested in the early publications[1] that malononitrile (**1a**) reacts with hydrazine monohydrate to yield 3,5-diaminopyrazole (**2a**). Later on, Sato,[2] Taylor, Hartke[3] and Elnagdi *et al.*[4–6] found that the product of this process is actually the dicyano-amino-pyrazole **4**, formed via initial dimerization of malononitrile (**1a**) to yield the enamino-nitrile **3** that subsequently reacts with hydrazine to form **4** (Scheme 1).

3,5-Diaminopyrazole (**2a**) was also prepared through reaction of the bis-imidate **5** with hydrazine hydrate.[7] In addition, it was observed that malononitrile (**1a**) reacts with aromatic diazonium salts to form the corresponding arylhydrazones **1b** that undergo condensations with hydrazine hydrate to yield arylazo-3,5-diaminopyrazoles **2b**.[5] The end products were recognized as patents due to their potential applications as dyes for keratin fibers and antimicrobial agents.[6,8–10] In related studies, mono-substituted malononitriles **1b-f** were shown to be useful for the efficient synthesis of diaminopyrazoles **2b-f**.[11–14] However, the formation of **2g** *via* reaction of phenacyl malononitrile (**1g**) with hydrazine hydrate could not be repeated in our hands.[15–17] Treatment of **1g** with hydrazine hydrate in ethanolic solution as described by Abdelrazek *et al.*[15–17] or in absence of solvent in dry condition as suggested recently[18] has only result in the formation of **6** in 97% yield. What is more, the use of dry conditions was claimed even though hydrazine hydrate already contains one molecule of water.

Elnagdi *et al.* showed that this reaction instead forms **6** or **7** or a mixture of both substances. Moreover, the claim that heating arylazo-3,5-diaminopyrazoles **2b** in the presence of sulfuric acid leads to formation of 3,5-diaminopyrazole (**2a**) has never been validated.[10] Relatedly,,it has been shown repeatedly that reaction of **2b** with H_2SO_4 in acetic acid yields the bis-acetamido-pyrazole **8**.[10,19–22]

In the light of the difficulties encountered in this kind of synthesis, only limited number of studies have been



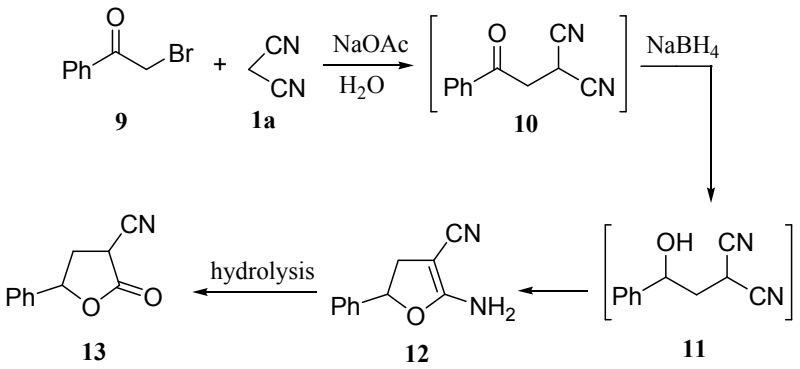
a, R = H; **b**, R = NNHAr; c, R = *i*-Pr ; **d**, R = CH_2-*i*-Bu
e, R = Ph, **f**, R = CH_2Ph; **g**, R = CH_2COPh, **h**, R = CH_2CHOHPh

Scheme 1. Reaction of hydrazine hydrate with derivatives of compound **1**.

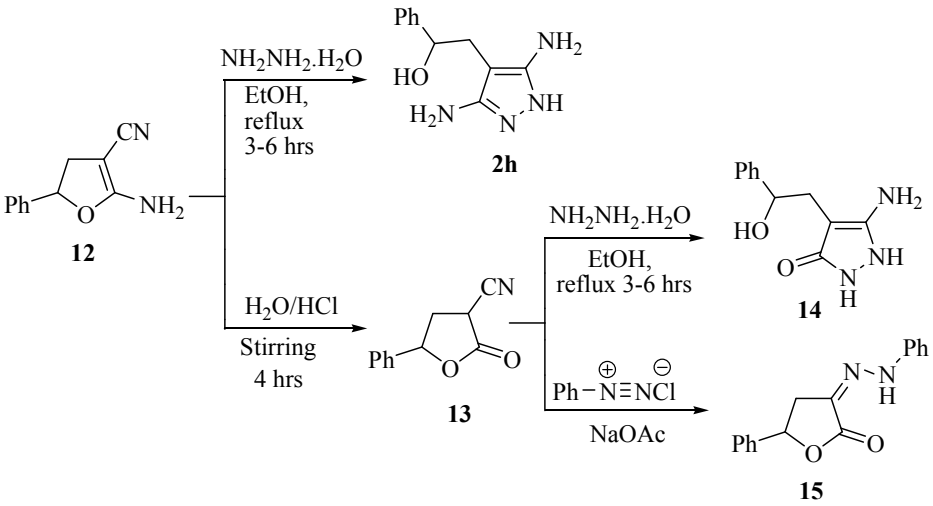
conducted to explore the chemistry of 4-substituted pyrazole-3,5-diamines. For example, Elnagdi *et al.* reported that arylazo-3,5-diaminopyrazoles **2b** reacts with acrylonitrile, ethyl acrylate and phenylisothiocyanate to generate products arising from nucleophilic addition to ring nitrogen,[23] while reactions of electron poor alkenes and alkynes with 3,5-diaminopyrazoles have been suggested to yield products resulting from initial addition to the exocyclic amine moieties,. In this study, we revealed a new and simple route for the preparation of dihydrofuran derivative (**12**). In addition, we described how this substance reacts with hydrazine hydrate to afford the novel 3,5-diaminopyrazole derivative 2h. Finally, we have explored the reactivity profile of **2h** with various electrons withdrawing group substituting the alkenes and alkynes.

RESULTS AND DISCUSSION

In studies targeting the synthesis of diaminopyrazoles, we found that reaction of a mixture of phenacyl bromide (**9**),



Scheme 2. Formation of compounds **12** and **13**.



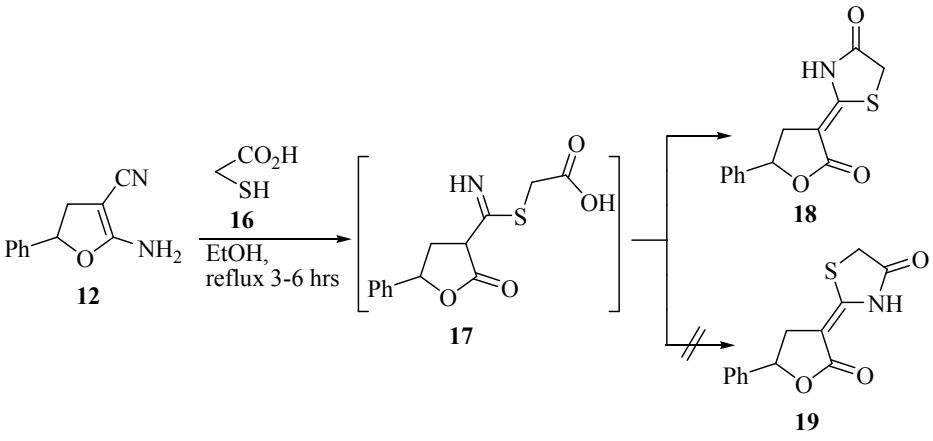
Scheme 3. Formation of compounds **2h**, **14** and **15**.

malononitrile (**1a**) and sodium borohydride in an aqueous solution containing sodium acetate at 0 °C for 1 h produces dihydrofuran derivative (**12**) as the sole isolated product in 85% yield (Scheme 2). However, with a longer reaction time (4 h) and higher temperature (25 °C), tetrahydrofuran derivative (**13**) was formed. It is assumed that both **12** and **13** are formed by pathways in which initial nucleophilic substitution reaction between malononitrile (**1a**) and phenacyl bromide (**9**) occurs in accordance to the previously described manner[19] to yield adduct **10**. In-situ reduction of **10** then produces alcohol **11** that cyclizes to generate **12**. After a while, **12** undergoes hydrolysis to produce lactone **13**, where the structure was assigned by using X-ray crystallographic tools (see supporting information: Figure 1, Tables 1, 2).

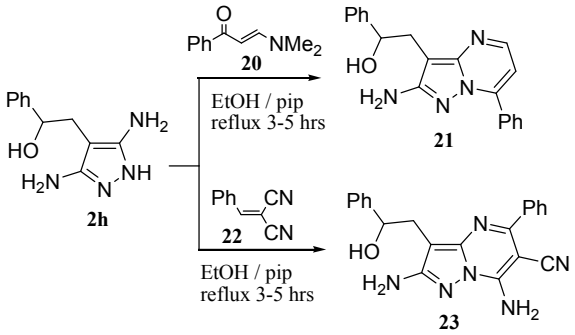
Dihydrofuran derivative (**12**) was observed to react readily with hydrazine hydrate to yield the 3,5-diaminopyrazole derivative **2h** (Scheme 3). In contrast, tetrahydrofuran derivative (**13**) reacts with hydrazine hydrate to yield pyrazolone **14** and with benzenediazonium chloride to form 5-phenyl-3-(2-phenylhydrazono)-dihydrofuran-2(3*H*)-one (**15**). The structures of **2h**, **14**, and **15** were assigned by using X-ray crystallography (see supporting information: Figures 2–4, Tables 3–8).

Furthermore, we found that the thioglycolic acid (**16**) added to dihydrofuran derivative (**12**) produced the *Z*-stereoisomer of 5-phenyl-dihydrofuran-thiazolidin (**18**) rather than its *E*-isomer **19** (Scheme 4), a finding that is confirmed by the X-ray crystallographic analysis (See supporting information: Figure 5, Tables 9,10).

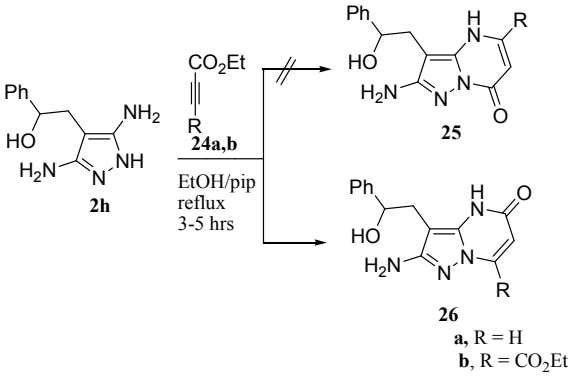
In a similar pattern, **2h** reacted with enaminone **20** to phenylpyrazolo[1,5-*a*]pyrimidine derivative (**21**) (Scheme 5), and the structure was identified using X-ray crystallographic methods (See supporting information:



Scheme 4. Formation of compound **18**.



Scheme 5. Formation of compounds **21** and **23**.



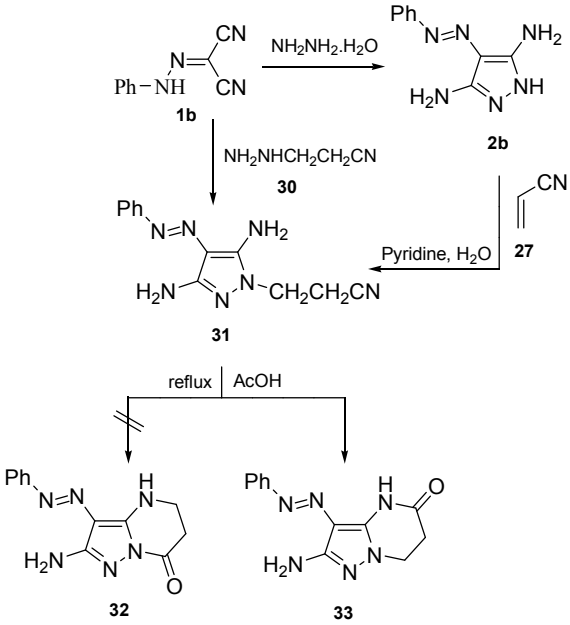
Scheme 6. Formation of compounds **26**.

Figure 6, Tables 11, 12). Additionally, reaction of **2h** with the benzylidine-malononitrile **22** generated phenylpyrazolo[1,5-*a*]pyrimidine **23**.

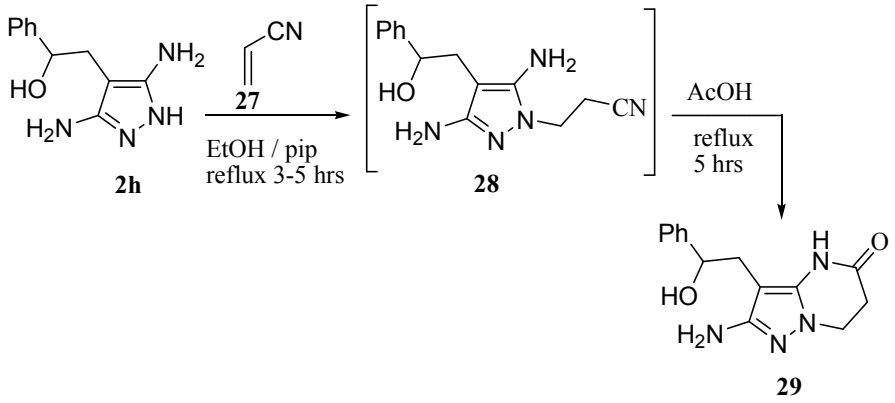
In contrast to the above processes which likely took place via pathways that began with Michael addition of the 5-amino group in **2h** to the electron deficient alkenes **20** and **22**, reaction of **2h** with ethyl propiolate (**24a**) occured by a route involving initial addition of the ring nitrogen of **2h** to the β-position of the alkyne moiety. This pathway lead to formation of pyrazolo[1,5-*a*]pyrimidine (**26a**, R = H), and the structure was assigned by using X-ray crystallographic tools. Similarly, reaction of **2h** with diethyl acetylene dicarboxylate (**24b**, R = CO_2Et) was completed by initial N-1 nitrogen addition to generate **26b** (Scheme 6), a conclusion based on ^{1}H NMR analysis (See supporting information: Figure 7, Tables 13, 14).

Reaction of diaminopyrazole **2h** with acrylonitrile (**27**) occurred by initial Michael addition of the ring N-1 nitrogen to afford dihydropyrazolo[1,5-*a*]pyrimidine (**29**), most likely *via* the intermediate **28** (Scheme 7).

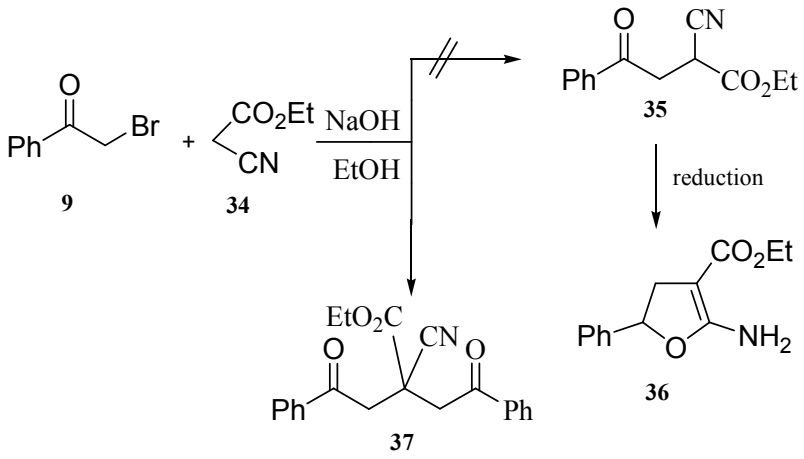
To demonstrate, Elnagdi *et al.* proposed that aminopyrazoles react with sterically unhindered electrophiles preferentially by using ring nitrogen as nucleophilic centers.



Scheme 8. Formation of compounds **31** and **33**.



Scheme 7. Formation of compound **29**.



Scheme 9. Formation of compound **37**.

Forty years ago, Elnagdi *et al.* worked on the reaction of compound (**2b**) with acrylonitrile (**27**) forming the N-1 alkylated product **31** (Scheme 8).[23] This product proved to be identical with that formed by reaction of phenylhydrazono malononitrile (**1b**) with 3-hydrazinylpropanenitrile (**30**).

Moreover, reaction of **31** in refluxing acetic acid produces the fused prymidone **33**. We have repeated these reactions in order to generate samples of **31** and **33** for X-ray crystallographic analysis to prove unambiguously the earlier structural assignments (See supporting information: Figures 8, 9, Tables 15–18).

Finally, it was reported previously that ethyl cyanoacetate (**34**) reacts with phenacyl bromide (**9**) to form compound (**35**),[24] which is transformed to **36** under reduction conditions (Scheme 9). Our attempts to reproduce **35** by following the reported procedure[24] were not successful[25] We have carried out X-ray crystallographic analysis of the end product of this process (See supporting information: Figure 10, Tables 19, 20), and found out that in fact **37** and not **35** was produced, a likely consequence of the greater reactivity of **35** over **34** toward **9** which leads to bis-alkylation to afford **37**. Elnagdi *et al.* suggested earlier that the interaction of **34** with **9** should produce compound (**37**).[26]

CONCLUSIONS

Polyfunctionalized heterocycles have played a key role in the synthesis of many biologically interesting substances over the last decades. For instance, cyclic non-aromatic enaminonitriles and enaminoesters, are well/known for their high yield and wide applications. In the studies described above, we have uncovered a new and efficient route for the preparation of a substituted diamino-pyrazole **2h** that began with the readily obtainable 2-amino-5-phenyl-4,5-dihydrofuran-3-carbonitrile (**12**). Moreover, we have shown that this substance participates in Michael addition reactions via pathways in which both the ring and exocyclic amino nitrogens serve as nucleophiles depending upon the steric requirements of the electrophile. Specifically, the reactions with sterically unhindered electrophiles were undertaken selectively at the ring nitrogen of **2h**. The existence of this dual reactivity profile suggests that caution should be exercised in assigning structures to the products of this type of reactions.

EXPERIMENTAL SECTION

General

Melting points are reported uncorrected and were determined with a Sanyo (Gallaenkamp) instrument. Infrared spectra were recorded using KBr pellets and a Jasco FT–IR 6300 instrument and absorption bands are reported in cm^{-1}. ^1H- and ^{13}C-NMR spectra were determined by using a Bruker DPX instrument at 400 MHz or 600 MHz for ^1H-NMR and 100 MHz for ^{13}C-NMR and either $CDCl_3$ or DMSO-d6 solutions with TMS as internal standards. Chemical shifts are reported in ppm. Mass spectra and accurate mass measurements were made using a GCMS DFS Thermo spectrometer with the EI (70 EV) mode. All reactions were monitored by using TLC with 1:1 ethyl acetate-petroleum ether as eluent and were carried out until starting materials were completely consumed. Single crystals suitable for X-ray diffraction technique were grown by solvent evaporation method. The data were collected at room temperature (296K). In the case of compounds **2h**, **15**, **18**, **26a** and **30**, the crystal data collections were done by Bruker X8 Prospector diffractometer using Cu-K radiation. The reflection frames were then integrated with the Bruker SAINT Software package using a narrow-frame algorithm. Finally, the structure was solved and refined using the Bruker SHELXTL Software Package. The data collections of compounds **13**, **14**, **21**, **33** and **37**

were made on a Rigaku R-AXIS RAPID II diffractometer using filtered Mo-Kα radiation. Crystal clear software package was employed here to generate hkl and p4p files. The structures were then solved by direct methods using "Crystal Structure" crystallographic software package except for refinement, which was performed using SHELXL-97. In all cases, the non-hydrogen atoms were refined an isotropically. In the case of **26a** the molecule has a chiral center at C7. The molecule is not enantiomeric pure and hence the crystal data showed positional disorder for oxygen atom attached to C7. This disorder has been refined successfully after applying PART instruction. The basic crystallographic information of all the crystal samples discussed in this study can be found at www.ccdc.cam.ac.uk. The molecular structure information obtained from single crystal X- diffraction method is in perfect agreement with the predicted synthetic protocol and other characterization techniques like NMR and mass spectroscopy.

General procedure for the syntheses of 12 and 13.

A solution of phenacyl bromide (1.99 g, 0.01 mol) and malononitrile (0.66 g, 0.01 mol) in aqueous sodium acetate solution (1.64 g NaOAc soluble in 25 mL H_2O) was cooled to 0 °C. Sodium borohydride (0.756 g, 0.02 mol) was added and the mixture was stirred for 1 h (followed by TIC). The reaction was quenched by addition to ice-H_2O and 1M HCl and the formed solids were quickly collected by filtration and recrystallized from EtOH to give **12** as colorless crystals. When the reaction mixture was kept at room temperature with stirring for 4 h only **13** was formed and then collected by filtration and recrystallized from EtOH to give colorless crystals.

2-amino-5-phenyl-4,5-dihydrofuran-3-carbonitrile (12)

Yield 85 % (1.5 g); m.p. 135–137 ºC; *Anal*. Calcd. for $C_{11}H_{10}N_2O$ (186.2): C, 70.95; H, 5.41; N, 15.04. Found: C, 70.88; H, 5.36; N, 15.13. EI-HRMS: *m/z* = 186.0 (MH^+); $C_{11}H_{10}N_2O$ requires: *m/z* = 186.2 (MH^+); IR $\tilde{\nu}$/cm^{-1}: 3346, 3243 (NH_2), 2258 (CN); ^{1}H NMR (400 MHz, DMSO-d_6) δ/ppm: 2.68 (dd, 1H, *J* = 8.0 Hz, *J* = 4 Hz, CH), 3.20 (dd, 1H, *J* = 8.0 Hz, *J* = 4 Hz, CH), 5.63 (t, 1H, *J* = 8.0 Hz, CH), 7.12 (br, 2H, NH_2, D_2O exchangeable), 7.33–7.42 (m, 5H, Ph-H); ^{13}C NMR (100 MHz, DMSO-d_6) δ/ppm: 167.7, 140.6, 128.6 (2C), 128.3, 125.7 (2C), 120.0, 82.2, 46.3, 36.6. MS *m/z* (%): 186 (M^+, 100), 169 (45), 143 (60), 115 (65), 106 (15), 89 (10), 77 (20).

2-oxo-5-phenyl-tetrahydrofuran-3-carbonitrile (13)

Yield 73 % (1.3 g); m.p. 121–122 ºC; *Anal*. Calcd. for $C_{11}H_9NO_2$ (187.2): C, 70.58; H, 4.85; N, 7.48. Found: C, 70.35; H, 4.90; N, 7.59. EI-HRMS: *m/z* = 187.0 (MH^+); $C_{11}H_9NO_2$ requires: *m/z* = 187.2 (MH^+); IR $\tilde{\nu}$/cm^{-1}: 2258 (CN), 1769 (CO); ^{1}H NMR (400 MHz, DMSO-d_6) δ/ppm: 2.50–2.65 (m, 1H, CH), 2.98–3.05 (m, 1H, CH), 4.70–4.75 (m, 1H, CH), 5.51–5.55 (m, 1H, CH), 7.39–7.53 (m, 5H, Ph-H); ^{13}C NMR (100 MHz, DMSO-d_6) δ/ppm: 169.1, 129.0, 128.6 (2C), 126.7 (2C), 125.9, 80.6, 40.0, 34.7, 33.3. MS *m/z* (%): 187 (M^+, 100), 143 (75), 105 (70), 77 (35). CCDC 993584 contains the supplementary crystallographic data.

Synthesis of 2-(3,5-diamino-1H-pyrazol-4-yl)-1-phenylethanol (2h)

A mixture of **12** (1.86 g, 0.01 mol) and hydrazine monohydrate (1.00 g, 0.02 mol) in EtOH (25 mL) was stirred at reflux for 3–6 h (completion assessed by TLC). The mixture was cooled and poured into ice-water. The solid was collected by filtration and crystallized from EtOH to give white crystals of **2h**. Yield 82 % (1.7 g); m.p. 178–180 ºC; *Anal*. Calcd. for $C_{11}H_{14}N_4O$ (218.2): C, 60.53; H, 6.47; N, 25.67. Found: C, 60.61; H, 6.45; N, 25.75. EI-HRMS: *m/z* = 218.1 (MH^+); $C_{11}H_{14}N_4O$ requires: *m/z* = 218.2 (MH^+); IR $\tilde{\nu}$/cm^{-1}: 3469 (OH), 3346 (NH), 3289, 3129 (NH_2), 3029, 3030 (NH_2); ^{1}H NMR (400 MHz, DMSO-d_6) δ/ppm: 2.33–2.50 (mm, 2H, CH_2), 4.22 (br, 4H, 2NH_2, D_2O exchangeable), 4.57 (d, 1H, *J* = 4.0 Hz, CH), 5.35 (s, 1H, OH, D_2O exchangeable), 7.19–7.40 (m, 5H, Ph-H), 9.97 (br, 1H, NH, D_2O exchangeable); ^{13}C NMR (100 MHz, DMSO-d_6) δ/ppm: 150.1, 146.8, 128.2, 126.9, 126.2, 86.3, 74.3, 32.9; MS *m/z* (%): 218 (M^+, 60), 200 (5), 111 (100), 96 (15), 77 (15), 70 (5). CCDC 993585 contains the supplementary crystallographic data.

Synthesis of 3-amino-4-(2-hydroxy-2-phenylethyl)-1,2-dihydropyrazol-5-one (14)

A mixture of **13** (1.87 g, 0.01 mol) and hydrazine monohydrate (1.00 g, 0.02 mol) in EtOH (25 mL) was stirred at reflux for 3–6 h (completion assessed by TLC). The mixture was cooled and poured into ice-water. The solid was collected by filtration and crystallized from EtOH to give white crystals of **14**. Yield 75 % (1.6 g); m.p. 205-207 ºC; *Anal.* Calcd. for $C_{11}H_{13}N_3O_2$ (219.2): C, 60.26; H, 5.98; N, 19.17. Found: C, 60.31; H, 5.86; N, 19.02. EI-HRMS: *m/z* = 319.09 (MH^+); $C_{11}H_{13}N_3O_2$ requires: *m/z* = 219.24 (MH^+); IR $\tilde{\nu}$/cm^{-1}: 3383 (OH), 3306, 3217 (NH_2), 3082 (NH), 3059 (NH), 1620 (CO); ^{1}H NMR (600 MHz, DMSO-d_6) δ/ppm: 2.35 (dd, 1H, *J* = 12 Hz, *J* = 6 Hz, CH), 2.49 (dd, 1H, *J* = 12 Hz, *J* = 6 Hz, CH), 4.67–4.69 (m, 1H, CH), 5.82 (br, 2H, NH_2, D_2O exchangeable), 6.90 (br, 1H, OH, D_2O exchangeable), 7.17–7.38 (m, 5H, Ph-H), 8.97 (br, 2H, 2NH, D_2O exchangeable); ^{13}C NMR (150 MHz, DMSO-d_6) δ/ppm: 173.0, 158.8, 146.4, 128.1 (2C), 126.7, 126.1 (2C), 84.2, 74.0, 32.7. MS: *m/z* (%) 219 (M^+, 10), 201 (100), 172 (10), 130 (10), 112 (50), 99 (30), 77 (40). CCDC 993586 contains the supplementary crystallographic data.

Synthesis of 5-phenyl-3-(2-phenylhydrazono)-dihydrofuran-2(3H)-one (15)

A cold solution of benzenediazonium chloride (0.01 mol) was prepared by adding a solution of sodium nitrite (0.7 g

in 10 mL H_2O) to a cold solution of aniline hydrochloride (0.93 g, 0.01 mol of aniline in 5 mL concentrated HCl) with stirring at room temperature. The resulting solution was then added to a cold solution of **13** (1.87 g, 0.01 mol) in ethanol (50 mL) containing sodium acetate (2 g). The mixture was stirred for 1 h and then filtered. The solid was crystallized from EtOH to give **15** as yellow crystals, yield 78 % (2.0 g); m.p. 162–164 °C; *Anal.* Calcd. for $C_{16}H_{14}N_2O_2$ (266.3): C, 72.17; H, 5.30; N, 10.52. Found: C, 72.13; H, 5.44; N, 10.51. EI-HRMS: *m/z* = 266.1 (MH^+); $C_{16}H_{14}N_2O_2$ requires: *m/z* = 266.3 (MH^+); IR $\tilde{\nu}$/cm^{-1}: 3267 (NH), 1747 (CO); ^{1}H NMR (400 MHz, DMSO-d_6) δ/ppm: 2.85 (dd, 1H, *J* = 12 Hz, *J* = 8, CH), 3.51 (dd, 1H, *J* = 12 Hz, *J* = 8, CH), 5.76–5.79 (m, 1H, CH), 6.92-7.44 (m, 10H, Ph-H), 10.24 (s, 1H, NH, D_2O exchangeable); ^{13}C NMR (100 MHz, DMSO-d_6) δ/ppm: 166.7, 143.8, 140.54, 130.10, 129.24 (2C), 128.8 (2C), 128.51, 125.83 (2C), 121.51, 113.72 (2C), 76.36, 33.47. MS *m/z* (%): 266 (M^+, 100), 246 (10), 236 (10), 189 (15), 171 (75), 145 (10), 105 (25), 92 (55), 77 (60). CCDC 993587 contains the supplementary crystallographic data.

Synthesis of (2-(2-oxo-5-phenyl-dihydrofuran-3(2H)-ylidene)thiazolidin-4-one (18)

A mixture of **12** (1.86 g, 0.01 mol) and thioglycolic acid (16) (0.92 g, 0.01 mol) in EtOH (25 mL) was stirred at reflux for 3–6 h (completion assessed by TLC). The mixture was cooled and poured into ice-water. The solid was collected by filtration and crystallized from AcOH to give yellow crystals of **18**. Yield 80 % (2.0 g); m.p. 190–192 ºC; *Anal*. Calcd. for $C_{13}H_{11}NO_3S$ (261.3): C, 59.76; H, 4.24; N, 5.36; S, 12.27. Found: C, 59.71; H, 4.20; N, 5.28; S, 12.40. EI-HRMS: *m/z* = 261.0 (MH^+); $C_{13}H_{11}NO_3S$ requires: *m/z* = 261.3 (MH^+); IR $\tilde{\nu}$/cm^{-1}: 3197 (NH), 1744 (CO), 1722 (CO); ^{1}H NMR (400 MHz, DMSO-d_6) δ/ppm: 2.75–2.80 (m, 1H, CH), 3.37–3.43 (m, 1H, CH), 3.88 (s, 2H, CH_2), 5.58 (dd, 1H, *J* = 4 Hz, *J* = 8, CH), 7.32-7.43 (m, 5H, Ph-H), 11.5 (br, 1H, NH, D_2O exchangeable); ^{13}C NMR (100 MHz, DMSO-d_6) δ/ppm: 175.0, 170.8, 149.7, 141.0, 128.7 (2C), 128.2, 125.6 (2C), 93.2, 77.4, 35.3, 32.3. MS *m/z* (%): 261 (M^+, 40), 155 (55), 127 (100), 115 (20), 85 (10), 77 (15), 54 (20). CCDC 993588 contains the supplementary crystallographic data.

Synthesis of 2-(2-amino-7-phenylpyrazolo[1,5-a]pyrimidin-3-yl)-1-phenylethanol (21)

A mixture of **2h** (2.18 g, 0.01 mol) and enaminone **20** (1.75 g, 0.01 mol) in EtOH (25 mL) in presence of piperidine (1 mL) was stirred at reflux for 3–5 h. (completion assessed by TLC). The mixture was cooled and poured into ice-water. The solid was collected by filtration and crystallized from AcOH to give yellow crystals of **21**. Yield 84 % (2.7 g); m.p. 186–188 ºC; *Anal*. Calcd for $C_{20}H_{18}N_4O$ (330.3): C, 72.71; H, 5.49; N, 16.96. Found: C, 72.72; H, 5.47; N, 16.81. EI-HRMS: *m/z* = 330.1 (MH^+); $C_{20}H_{18}N_4O$ requires: *m/z* = 330.3 (MH^+); IR $\tilde{\nu}$/cm^{-1}: 3483 (OH), 3387, 3284 (NH_2); ^{1}H NMR (400 MHz, DMSO-d_6) δ/ppm: 2.87–2.99 (m, 2H, CH_2), 4.89–4.93 (m, 1H, CH), 5.55 (d, 1H, OH, D_2O exchangeable), 5.60 (s, 2H, NH_2, D_2O exchangeable), 6.77 (d, 1H, *J* = 4, CH), 7.19–8.24 (m, 10H, Ph-H), 8.24 (d, 1H, *J* = 4, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ/ppm: 159.8, 148.1, 147.2, 145.8, 143.5, 131.4, 130.4, 129.0 (2C), 128.3 (2C), 127.8 (2C), 126.6, 125.8 (2C), 104.0, 90.1, 72.7, 32.1. MS *m/z* (%): 330 (M^+, 10), 312 (5), 223 (100), 208 (25), 181 (20), 155 (10), 129 (5), 103 (25), 77 (10). CCDC 993589 contains the supplementary crystallographic data.

Synthesis of 2,7-diamino-3-(2-hydroxy-2-phenylethyl)-5-phenylpyrazolo[1,5-a]pyrimidine-6-carbonitrile (23)

A mixture of **2h** (2.18 g, 0.01 mol) and benzylidenemalononitrile **22** (1.54 g, 0.01 mol) in EtOH (25 mL) in presence of piperidine (1 mL) was stirred at reflux for 3–5 h (completion assessed by TLC). The mixture was cooled and poured into ice-water. The solid was collected by filtration and crystallized from dioxane to give yellow crystals of **23**. Yield 68 % (2.5 g); m.p. 200–202 ºC; *Anal*. Calcd. for $C_{21}H_{18}N_6O$ (370.1): C, 68.09; H, 4.90; N, 22.69. Found: C, 68.22; H, 5.12; N, 22.75. EI-HRMS: *m/z* = 370.1 (MH^+); $C_{21}H_{18}N_6O$ requires: *m/z* = 370.4 (MH^+); IR $\tilde{\nu}$/cm^{-1}: 3439 (OH), 3290, 3184 (NH_2), 3131, 3081 (NH_2); ^{1}H NMR (400 MHz, DMSO-d_6) δ/ppm: 2.82-2.92 (m, 2H, CH_2), 4.92 (br, 1H, CH), 5.65 (br, 1H, OH, D_2O exchangeable), 5.69 (br, 2H, NH_2, D_2O exchangeable), 7.17–7.74 (m, 10H, Ph-H), 8.14 (br, NH_2, D_2O exchangeable); ^{13}C NMR (100 MHz, DMSO-d_6) δ/ppm: 160.7, 157.0, 148.6, 145.4, 137.7, 129.6, 128.3 (2C), 128.1 (2C), 127.7 (2C), 126.6, 125.9 (2C), 117.2, 93.9, 72.3, 69.6, 31.9, 21.0. MS *m/z* (%): 370 (M^+, 5), 352 (10), 265 (5), 264 (25), 263 (100), 248 (10), 77 (5).

General procedure for the Syntheses of 26a and 26b

Mixtures of **2h** (2.18 g, 0.01 mol) and ethyl propiolate or diethylacetylene dicarboxylate (**24a,b**) (0.01 mol) in EtOH (25 mL) in presence of piperidine (1 mL) were stirred at reflux for 3–5 h (completion assessed by TLC). The mixtures were cooled and poured into ice-water. The solids were collected by filtration and crystallized from EtOH to give yellow crystals of **26a** or dark red crystals of **26b**.

2-Amino-3-(2-hydroxy-2-phenylethyl)pyrazolo[1,5-a]pyrimidin-5(4H)-one (26a)

Yield 80 % (2.1 g); m.p. 268-270 ºC; *Anal*. Calcd. for $C_{14}H_{14}N_4O_2$ (270.2): C, 62.21; H, 5.22; N, 20.73. Found: C, 62.25; H, 5.34; N, 20.82. EI-HRMS: *m/z* = 270.1 (MH^+); $C_{14}H_{14}N_4O_2$ requires: *m/z* = 270.2 (MH^+); IR $\tilde{\nu}$/cm^{-1}: 3413 (OH), 3309, 3206 (NH_2), 3124 (NH), 1678 (CO); ^{1}H NMR (400 MHz, DMSO-d_6) δ/ppm: 2.50–2.74 (m, 2H, CH_2), 4.66 (d, 1H, *J* = 8.0 CH), 5.27 (br, 2H, NH_2, D_2O exchangeable), 5.46–5.48 (d, 2H, *J* = 8.0, CH, OH, D_2O exchangeable), 7.20–7.46 (m,

5H, Ph-H), 8.02 (d, *J* = 8.0 Hz, 1H, CH), 11.41 (s, 1H, NH, D_2O exchangeable); ^{13}C NMR (100 MHz, DMSO-d_6) δ/ppm: 160.3, 158.8, 145.6, 138.7, 137.9, 127.7 (2C), 126.6, 125.9 (2C), 99.5, 86.4, 72.7, 30.7. MS *m/z* (%): 270 (M^+, 10), 163 (100), 148 (10), 122 (10), 107 (5), 85 (15), 79 (10). CCDC 993590 contains the supplementary crystallographic data.

Ethyl 2-amino-3-(2-hydroxy-2-phenylethyl)-5-oxo-4,5-dihydropyrazolo-[1,5-a]-pyrimidine-7-carboxylate (26b)

Yield 69 % (2.3 g); m.p. 258–260 ºC; *Anal*. Calcd. for $C_{17}H_{18}N_4O_4$ (342.3): C, 59.64; H, 5.30; N, 16.37. Found: C, 59.69; H, 5.45; N, 16.51. EI-HRMS: *m/z* = 324.1 (MH^+); $C_{17}H_{18}N_4O_4$ requires: *m/z* = 342.3 (MH^+); IR $\tilde{\nu}$/cm^{-1}: 3431 (OH), 3350, 3284 (NH_2), 3107 (NH), 1725 (CO), 1670 (CO); ^{1}H NMR (400 MHz, DMSO-d_6) δ/ppm: 1.31 (t, 3H, *J* = 8.0 Hz, CH_3), 2.50–2.75 (m, 2H, CH_2), 4.34 (q, 2H, *J* = 8.0 Hz, CH_2), 4.66–4.68 (m, 1H, CH), 5.46–5.50 (m, 3H, OH, NH_2, D_2O exchangeable), 5.78 (s, 1H, CH), 7.20–7.47 (m, 5H, Ph-H), 11.70 (s, 1H, NH, D_2O exchangeable); ^{13}C NMR (100 MHz, DMSO-d_6) δ/ppm: 160.3, 159.6, 159.1, 145.5, 139.8, 139.1, 127.7 (2C), 126.7, 125.9 (2C), 99.0, 87.1, 72.4, 62.5, 30.6, 13.8. MS *m/z* (%): 342 (M^+, 10), 235 (100), 220 (25), 194 (15), 162 (5), 111 (10), 96 (35), 79 (15).

Synthesis of 2-(2,5-diamino-6,7-dihydropyrazolo[1,5-a]pyrimidin-3-yl)-1-phenylethanol (29)

A mixture of **2h** (2.18 g, 0.01 mol) and acrylonitrile **27** (0.53 g, 0.01 mol) in EtOH (25 mL) in presence of piperidine (3 mL) was stirred at reflux for 3-5 h (completion assessed by TLC). The mixture was cooled and poured into ice-water. The solid was collected by filtration and crystallized from EtOH to give white crystals of 29. Yield 77 % (2.0 g); m.p. 110–112 ºC; *Anal*. Calcd. for $C_{14}H_{17}N_5O$ (271.3): C, 61.98; H, 6.32; N, 25.81. Found: C, 61.86; H, 6.35; N, 25.69. EI-HRMS: *m/z* = 271.14 (MH^+); $C_{14}H_{17}N_5O$ requires: *m/z* = 271.32 (MH^+); IR $\tilde{\nu}$/cm^{-1}: 2406 (OH), 3387, 3326 (NH_2), 3323, 3220 (NH_2); ^{1}H NMR (400 MHz, DMSO-d_6) δ/ppm: 2.34-2.45 (m, 2H, CH_2), 2.75 (t, 2H, *J* = 6.0 Hz, CH_2), 3.89 (t, 2H, *J* = 6.0 Hz, CH_2), 4.18 (br, 2H, NH_2, D_2O exchangeable), 4.45 (m, 1H, CH), 4.79 (br, 2H, NH_2, D_2O exchangeable), 5.30 (d, 1H, OH, D_2O exchangeable), 7.20-7.39 (m, 5H, Ph-H); ^{13}C NMR (100 MHz, DMSO-d_6) δ/ppm: 153.4, 146.3, 128.2, 127.7 (2C), 126.4, 125.7 (2C), 118.9, 86.6, 73.7, 41.4, 32.6, 17.3. MS *m/z* (%): 271 (M^+, 10), 164 (100), 123 (15), 111 (35), 79 (5).

Synthesis of 3-(3,5-Diamino-4-phenylazo-pyrazol-1-yl)-propionitrile (31)

A mixture of diaminopyrazole derivative **2b** (2.02 g, 0.01 mol), which prepared via literature procedures,[22] and acrylonitrile **27** (0.53 g, 0.01 mol) in pyridine (25 mL) as a solvent was stirred at reflux for 3–5 h (completion assessed by TLC). The mixture was cooled and poured into ice-water. The solid was collected by filtration and crystallized from EtOH to give dark yellow crystals of **31**. Yield 85 % (2.1 g); m.p. 195-197 ºC; *Anal*. Calcd. for $C_{12}H_{13}N_7$ (255.2): C, 56.46; H, 5.13; N, 38.41. Found: C, 56.43; H, 4.98; N, 38.45. EI-HRMS: *m/z* = 255.12 (MH^+); $C_{12}H_{13}N_7$ requires: *m/z* = 255.2 (MH^+); IR $\tilde{\nu}$/cm^{-1}: 3390, 3383 (NH_2), 3345, 3230 (NH_2), 2224 (CN); ^{1}H NMR (600 MHz, DMSO-d_6) δ/ppm: 2.92 (t, 2H, *J* = 6.0 Hz, CH_2), 4.09 (t, 2H, *J* = 6.0 Hz, CH_2), 5.39 (br, 1H, NH_2 proton, D_2O exchangeable), 6.06 (br, 1H, NH_2 proton, D_2O exchangeable), 6.72 (br, 1H, NH_2 proton, D_2O exchangeable), 7.21–7.72 (m, 6H, Ph-H, NH_2 proton D_2O exchangeable); ^{13}C NMR (100 MHz, DMSO-d_6) δ/ppm: 153.4, 128.6, 126.7, 120.4, 118.5, 113.7, 41.5, 16.7. MS *m/z* (%): 271 (M^+, 10), 164 (100), 123 (15), 111 (35), 79 (5). CCDC 1041079 contains the supplementary crystallographic data.

Synthesis of 2-amino-3-(phenyldiazenyl)-6,7-dihydropyrazolo[1,5-a]pyrimidin-5(4H)-one (33)

A mixture of **31** (2.55 g, 0.01 mol) in acetic acid (25 mL) was stirred at reflux for 3–5 h (completion assessed by TLC). The mixture was cooled and poured into ice-water. The solid was collected by filtration and crystallized from dimethylformamide to give yellow crystals of **33**. Yield 80 % (2.0 g); m.p. 320-322 ºC; *Anal*. Calcd. for $C_{12}H_{12}N_6O$ (256.2): C, 56.24; H, 4.72; N, 32.79. Found: C, 56.10; H, 4.54; N, 32.95. EI-HRMS: *m/z* = 256.10 (MH^+); $C_{12}H_{12}N_6O$ requires: *m/z* = 256.2 (MH^+); IR $\tilde{\nu}$/cm^{-1}: 3385, 3376 (NH_2),3220 (NH), 1702 (CO); ^{1}H NMR (400 MHz, DMSO-d_6) δ/ppm: 2.88 (t, 2H, *J* = 6.0 Hz, CH_2), 4.06 (t, 2H, *J* = 6.0 Hz, CH_2), 6.09 (br, 2H, NH_2, D_2O exchangeable), 7.29-7.83 (m, 5H, Ph-H), 11.35 (br, 1H, NH, D_2O exchangeable); ^{13}C NMR (100 MHz, DMSO-d_6) δ/ppm: 166.5, 162.2, 152.9, 146.9, 128.8 (2C), 128.1, 121.3 (2C), 113.5, 42.4, 30.4. MS *m/z* (%): 255 (M^{-1}, 100), 215 (10), 178 (50), 125 (5), 84 (10), 77 (15), 68 (30). CCDC 1041241 contains the supplementary crystallographic data.

Ethyl 2-cyano-4-oxo-2-(2-oxo-2-phenylethyl)-4-phenylbutanoate (37)

A solution of phenacyl bromide (1.99 g, 0.01 mol) and ethylcyanoacetate (0.56 g, 0.005 mol) in aqueous sodium acetate solution (1.64 g NaOAc soluble in 25 mL H_2O) was cooled to 0 °C. Sodium borohydride (0.756 g, 0.02 mol) was added and the mixture was stirred for 1 h (followed by TIC). The reaction was quenched by addition to ice-H_2O and 1M HCl and the formed solids were quickly collected by filtration and recrystallized from EtOH to give **37** as colorless crystals.

Yield 75 % (2.6 g); m.p. 140–142 ºC; *Anal*. Calcd. for $C_{21}H_{19}N_1O_4$ (349.1): C, 72.19; H, 5.48; N, 4.01. Found: C, 72.44; H, 5.52; N, 4.25. EI-HRMS: *m/z* = 349.1 (MH^+); $C_{21}H_{19}N_1O_4$ requires: *m/z* = 349.1 (MH^+); IR $\tilde{\nu}$/cm^{-1}: 2250 (CN), 1722 (CO), 1690 (CO); ^{1}H NMR (400 MHz, DMSO-d_6) δ/ppm: 1.22 (t, 3H, *J* = 8 Hz, CH_3), 4.01 (m, 4H, 2CH_2), 4.19 (q, 2H, *J* = 8 Hz, CH_2), 7.56-8.02 (m, 5H, Ph-H); ^{13}C NMR (100

MHz, DMSO-d_6) δ/ppm: 195.2 (2C), 168.0, 135.4 (2C), 133.9 (2C), 128.8 (4C), 128.0 (4C), 118.7, 62.3, 43.8 (2C), 41.4, 13.6. MS *m/z* (%): 349 (M^+, 10), 276 (10), 244 (15), 184 (10), 172 (5), 120 (10), 105 (100), 77 (35). CCDC 1447290 contains the supplementary crystallographic data.

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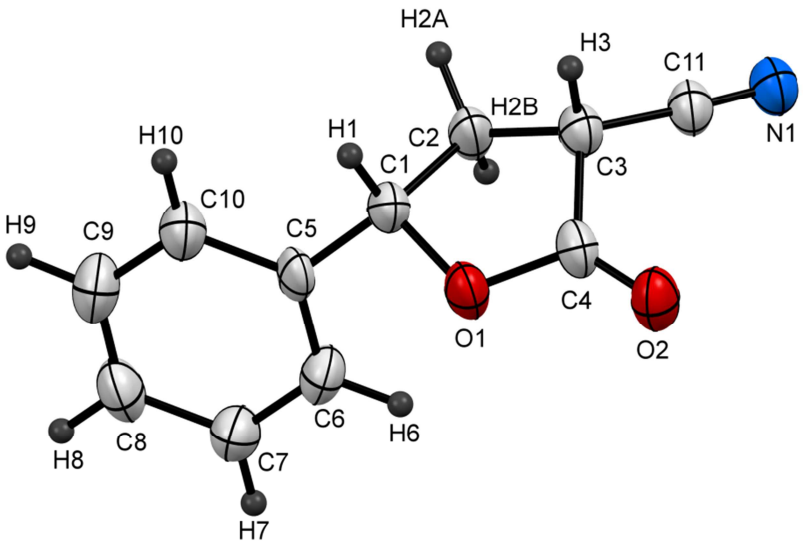


Figure 1. Plot of X-ray crystal structure data for **13**.

Table 1: Bond lengths of compound **13**

Atom	Distance (Å)	Atom	Distance (Å)
O1-C1	1.484(6)	O1-C4	1.348(6)
O2-C4	1.205(6)	N1-C11	1.133(6)
C1-C2	1.521(7)	C1-C5	1.506(6)
C2-C3	1.529(6)	C3-C4	1.522(7)
C3-C11	1.471(6)	C5-C6	1.390(7)
C5-C10	1.383(7)	C6-C7	1.391(6)
C7-C8	1.395(7)	C8-C9	1.379(8)
C9-C10	1.387(7)		

Table 2: Bond angles of compound **13**

Atom	Angles (°)	Atom	Angles (°)
C1-O1-C4	110.0(4)	O1-C1-C2	104.4(4)
O1-C1-C5	109.6(4)	C2-C1-C5	116.1(4)
C1-C2-C3	101.6(4)	C2-C3-C4	102.6(4)
C2-C3-C11	115.2(4)	C4--C3-C11	113.6(4)
O1-C4-O2	122.0(5)	O1-C4-C3	109.5(4)
O2-C4-C3	128.4(4)	C1-C5-C6	121.3(4)
C1-C5-C10	119.2(4)	C6-C5-C10	119.4(4)
C5-C6-C7	120.1(5)	C6-C7-C8	119.9(5)
C7-C8-C9	119.8(5)	C8-C9-C10	120.0(5)
C5-C10-C9	120.8(5)	N1-C11-C3	177.4(6)

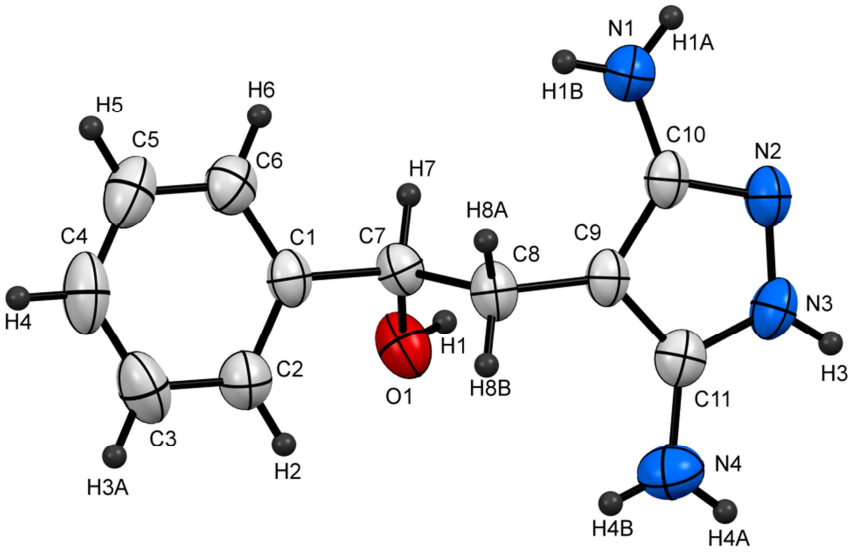


Figure 2. Plot of X-ray crystal structure data for **2h**.

Table 3: Bond lengths of compound **2h**

Atom	Distance (Å)	Atom	Distance (Å)
O1-C7	1.419(2)	O1-H1	0.82
C9-C11	1.377(2)	C9-C10	1.409(2)
C9-C8	1.497(2)	N1-C10	1.378(2)
N1-H1A	0.86	N1-H1B	0.86
N2-C10	1.332(2)	N2-N3	1.373(2)
N3-C11	1.334(2)	N3-H3	0.86
N4-C11	1.386(2)	N4-H4A	0.86
N4-H4B	0.86	C8-C7	1.529(2)
C8-H8A	0.97	C8-H8B	0.97
C7-C1	1.511(2)	C7-H7	0.98
C1-C6	1.377(3)	C1-C2	1.389(3)
C6-C5	1.381(3)	C6-H6	0.93
C5-C4	1.375(4)	C5-H5	0.93
C4-C3	1.382(3)	C4-H4	0.93
C2-C3	1.385(3)	C2-H2	0.93
C3-H3A	0.93		

Table 4: Bond angles of compound **2h**

Atom	Angles (°)	Atom	Angles (°)
C7-O1-H1	109.5	C11-C9-C10	103.68(14)
C11-C9-C8	128.61(16)	C10-C9-C8	127.61(15)
C10-N1-H1A	120.0	C10-N1-H1B	120.0
H1A-N1-H1B	120.0	C10-N2-N3	103.46(14)
C11-N3-N2	112.31(14)	C11-N3-H3	123.8
N2-N3-H3	123.8	C11-N4-H4A	120.0
C11-N4-H4B	120.0	H4A-N4-H4B	120.0
N3-C11-C9	107.97(16)	N3-C11-N4	120.46(17)

C9-C11-N4	131.57(17)	C9-C8-C7	114.33(14)
C9-C8-H8A	108.7	C7-C8-H8A	108.7
C9-C8-H8B	108.7	C7-C8-H8B	108.7
H8A-C8-H8B	107.6	O1-C7-C1	108.64(13)
O1-C7-C8	111.33(14)	C1-C7-C8	110.74(13)
O1-C7-H7	108.7	C1-C7-H7	108.7
C8-C7-H7	108.7	C6-C1-C2	118.69(16)
C6-C1-C7	120.53(15)	C2-C1-C7	120.78(16)
C1-C6-C5	120.81(19)	C1-C6-H6	119.6
C5-C6-H6	119.6	C4-C5-C6	120.6(2)
C4-C5-H5	119.7	C6-C5-H5	119.7
C5-C4-C3	119.19(18)	C5-C4-H4	120.4
C3-C4-H4	120.4	C3-C2-C1	120.40(18)
C3-C2-H2	119.8	C1-C2-H2	119.8
C4-C3-C2	120.3(2)	C4-C3-H3A	119.8
C2-C3-H3A	119.8	N2-C10-N1	119.90(15)
N2-C10-C9	112.57(15)	N1-C10-C9	127.39(15)

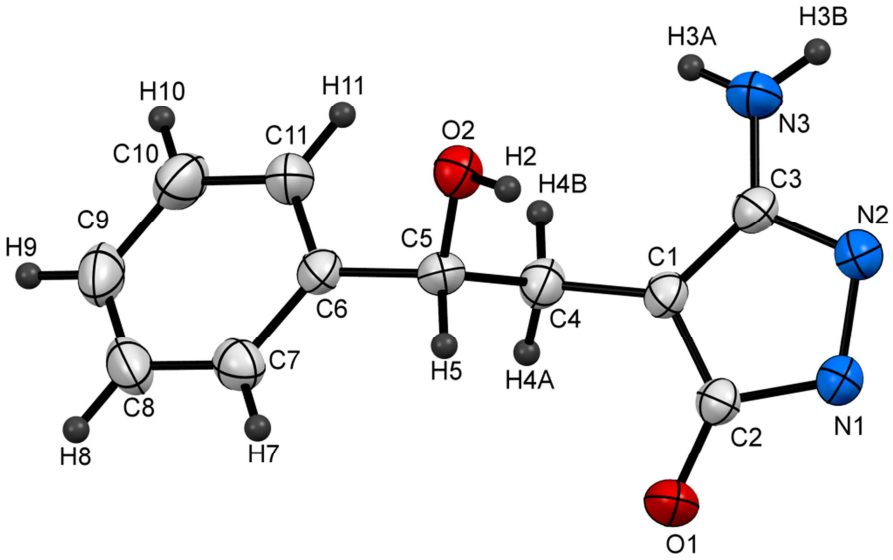


Figure 3. Plot of X-ray crystal structure data for **14**.

Table 5: Bond lengths of compound **14**

Atom	Distance (Å)	Atom	Distance (Å)
O1-C2	1.259(3)	O2-C5	1.436(3)
N1-N2	1.426(3)	N1-C2	1.398(4)
N2-C3	1.385(4)	N3-C3	1.350(4)
C1-C2	1.410(4)	C1-C3	1.372(4)
C1-C4	1.492(4)	C4-C5	1.529(4)
C5-C6	1.517(4)	C6-C7	1.386(4)
C6-C11	1.391(4)	C7-C8	1.391(4)
C8-C9	1.374(5)	C9-C10	1.377(5)
C10-C11	1.391(5)		

Table 6: Bond angles of compound **14**

Atom	Angles (°)	Atom	Angles (°)
N2-N1-C2	106.8(2)	N1-N2-C3	106.1(2)
C2-C1-C3	106.2(3)	C2-C1-C4	125.6(3)
C3-C1-C4	127.8(3)	O1-C2-N1	121.4(3)
O1-C2-C1	129.7(3)	N1-C2-C1	108.9(2)
N2-C3-N3	119.1(3)	N2-C3-C1	111.1(3)
N3-C3-C1	129.8(3)	C1-C4-C5	115.4(3)
O2-C5-C4	111.5(2)	O2-C5-C6	112.0(2)
C4-C5-C6	110.8(2)	C5-C6-C7	120.5(3)
C5-C6-C11	120.5(3)	C7-C6-C11	118.9(3)
C6-C7-C8	120.5(3)	C7-C8-C9	120.1(3)
C8-C9-C10	119.9(3)	C9-C10-C11	120.4(3)
C6-C11-C10	120.1(3)		

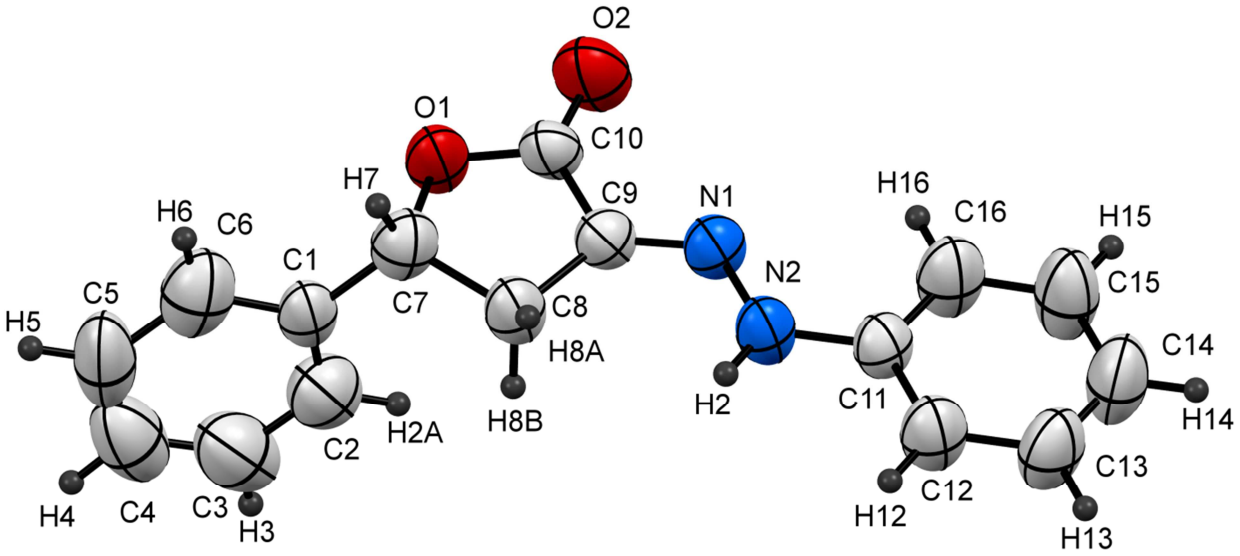


Figure 4. Plot of X-ray crystal structure data for **15**.

Table 7: Bond lengths of compound **15**

Atom	Distance (Å)	Atom	Distance (Å)
N1-C9	1.284(5)	N1-N2	1.348(4)
O1-C10	1.342(5)	O1-C7	1.476(5)
N2-C11	1.391(5)	N2-H2	0.86
O2-C10	1.254(4)	C14-C13	1.349(7)
C14-C15	1.362(7)	C14-H14	0.93
C13-C12	1.391(6)	C13-H13	0.93
C12-C11	1.377(5)	C12-H12	0.93
C11-C16	1.373(6)	C9-C10	1.463(5)
C9-C8	1.490(5)	C8-C7	1.540(5)
C8-H8A	0.97	C8-H8B	0.97
C7-C1	1.520(6)	C7-H7	0.98
C1-C2	1.343(7)	C1-C6	1.396(6)
C6-C5	1.442(8)	C6-H6	0.93
C5-C4	1.358(9)	C5-H5	0.93
C4-C3	1.342(9)	C4-H4	0.93
C3-C2	1.349(7)	C3-H3	0.93
C2-H2A	0.93	C16-C15	1.376(6)
C16-H16	0.93	C15-H15	0.93

Table 8: Bond angles of compound **15**

Atom	Angles (^{o})	Atom	Angles (^{o})
C9-N1-N2	119.4(3)	C10-O1-C7	112.0(3)
N1-N2-C11	119.3(3)	N1-N2-H2	120.4
C11-N2-H2	120.4	C13-C14-C15	118.8(4)
C13-C14-H14	120.6	C15-C14-H14	120.6
C14-C13-C12	121.5(4)	C14-C13-H13	119.2
C12-C13-H13	119.2	C11-C12-C13	119.5(4)
C11-C12-H12	120.2	C13-C12-H12	120.2
C16-C11-C12	118.6(4)	C16-C11-N2	122.5(3)
C12-C11-N2	118.9(3)	N1-C9-C10	119.0(3)
N1-C9-C8	131.9(3)	C10-C9-C8	109.0(3)
C9-C8-C7	103.4(3)	C9-C8-H8A	111.1
C7-C8-H8A	111.1	C9-C8-H8B	111.1
C7-C8-H8B	111.1	H8A-C8-H8B	109.0
O1-C7-C1	106.4(3)	O1-C7-C8	104.8(3)
C1-C7-C8	116.0(3)	O1-C7-H7	109.8
C1-C7-H7	109.8	C8-C7-H7	109.8
C2-C1-C6	120.1(5)	C2-C1-C7	122.6(4)
C6-C1-C7	117.4(4)	C1-C6-C5	117.9(6)
C1-C6-H6	121.0	C5-C6-H6	121.0
C4-C5-C6	118.3(6)	C4-C5-H5	120.9
C6-C5-H5	120.9	C3-C4-C5	121.3(6)
C3-C4-H4	119.3	C5-C4-H4	119.3

O2-C10-O1	119.4(3)	O2-C10-C9	131.5(4)
O1-C10-C9	109.0(3)	C4-C3-C2	121.2(7)
C4-C3-H3	119.4	C2-C3-H3	119.4
C1-C2-C3	121.2(6)	C1-C2-H2A	119.4
C3-C2-H2A	119.4	C11-C16-C15	120.7(4)
C11-C16-H16	119.7	C15-C16-H16	119.7
C14-C15-C16	120.9(4)	C14-C15-H15	119.5
C16-C15-H15	119.5		

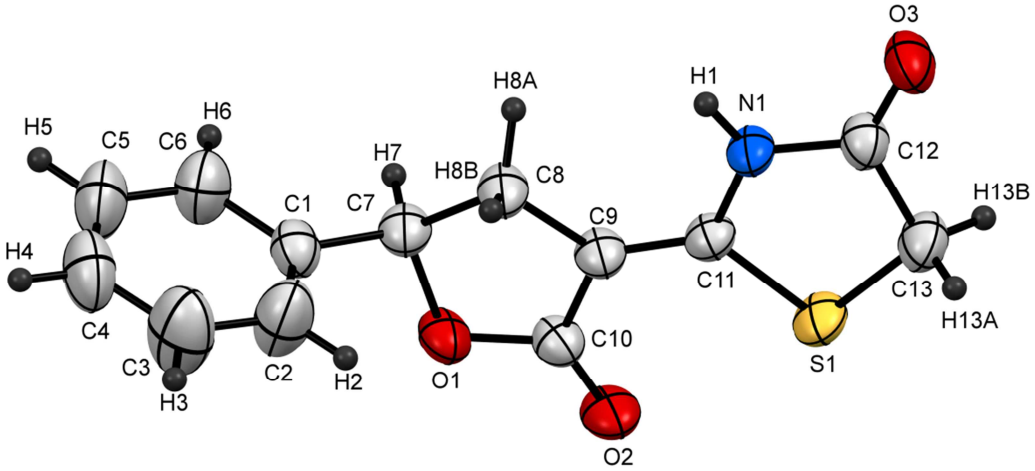


Figure 5. Plot of X-ray crystal structure data for **18**.

Table 9: Bond lengths of compound **18**

Atom	**Distance (Å)**	**Atom**	**Distance (Å)**
S1-C11	1.754(3)	S1-C13	1.805(3)
O3-C12	1.213(4)	O2-C10	1.223(4)
O1-C10	1.358(4)	O1-C7	1.483(4)
C3-C4	1.375(7)	C3-C2	1.388(7)
C3-H3	0.93	C12-N1	1.371(4)
C12-C13	1.508(5)	N1-C11	1.377(4)
N1-H1	0.86	C11-C9	1.344(4)
C9-C10	1.441(4)	C9-C8	1.499(4)
C8-C7	1.534(4)	C8-H8A	0.97
C8-H8B	0.97	C7-C1	1.495(4)
C7-H7	0.98	C1-C2	1.347(6)
C1-C6	1.392(5)	C2-H2	0.93
C4-C5	1.348(8)	C4-H4	0.93
C13-H13A	0.97	C13-H13B	0.97
C6-C5	1.377(6)	C6-H6	0.93
C5-H5	0.93		

Table 10: Bond angles of compound **18**

Atom	Angles (°)	Atom	Angles (°)
C11-S1-C13	92.19(14)	C10-O1-C7	109.7(2)
C4-C3-C2	120.3(4)	C4-C3-H3	119.9
C2-C3-H3	119.9	O3-C12-N1	123.4(3)
O3-C12-C13	125.9(3)	N1-C12-C13	110.7(3)
C12-N1-C11	117.9(3)	C12-N1-H1	121.0
C11-N1-H1	121.0	C9-C11-N1	123.4(3)
C9-C11-S1	125.9(2)	N1-C11-S1	110.69(19)
C11-C9-C10	123.3(3)	C11-C9-C8	127.9(3)
C10-C9-C8	108.8(2)	C9-C8-C7	102.4(2)
C9-C8-H8A	111.3	C7-C8-H8A	111.3
C9-C8-H8B	111.3	C7-C8-H8B	111.3
H8A-C8-H8B	109.2	O1-C7-C1	109.9(2)
O1-C7-C8	104.8(2)	C1-C7-C8	116.4(3)
O1-C7-H7	108.5	C1-C7-H7	108.5
C8-C7-H7	108.5	C2-C1-C6	118.2(3)
C2-C1-C7	123.0(3)	C6-C1-C7	118.6(3)
C1-C2-C3	121.2(4)	C1-C2-H2	119.4
C3-C2-H2	119.4	C5-C4-C3	118.7(4)
C5-C4-H4	120.7	C3-C4-H4	120.7
C12-C13-S1	107.3(2)	C12-C13-H13A	110.3
S1-C13-H13A	110.3	C12-C13-H13B	110.3
S1-C13-H13B	110.3	H13A-C13-H13B	108.5
O2-C10-O1	121.1(3)	O2-C10-C9	129.0(3)
O1-C10-C9	109.9(3)	C5-C6-C1	120.2(4)
C5-C6-H6	119.9	C1-C6-H6	119.9
C4-C5-C6	121.4(4)	C4-C5-H5	119.3
C6-C5-H5	119.3		

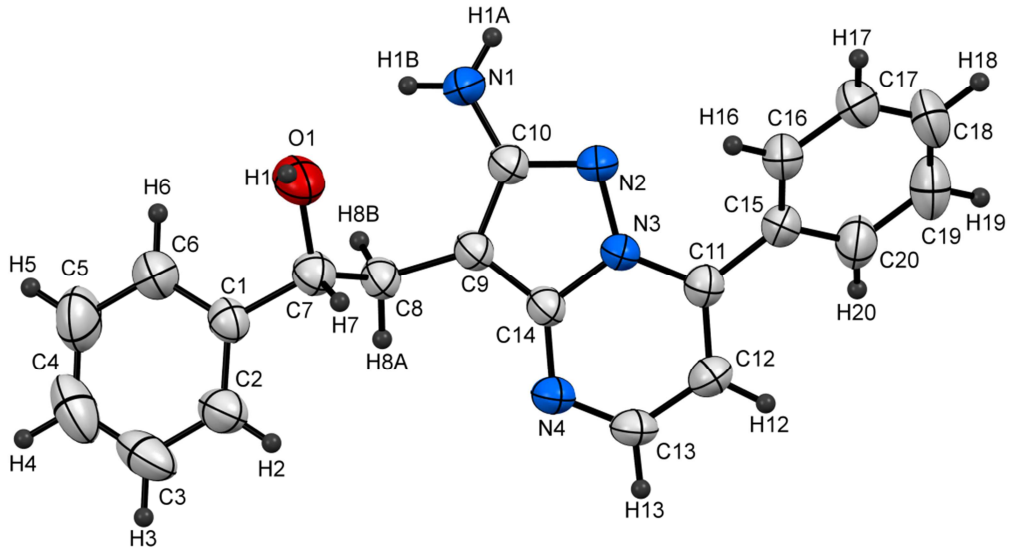


Figure 6. Plot of X-ray crystal structure data for **21**.

Table 11: Bond lengths of compound **21**

Atom	Distance (Å)	Atom	Distance (Å)
O1-C7	1.449(3)	N1-C10	1.353(3)
N2-N3	1.372(3)	N2-C10	1.359(3)
N3-C11	1.361(3)	N3-C14	1.404(3)
N4-C13	1.312(3)	N4-C14	1.350(3)
C1-C2	1.379(4)	C1-C6	1.380(4)
C1-C7	1.512(4)	C2-C3	1.380(5)
C3-C4	1.365(5)	C4-C5	1.363(6)
C5-C6	1.380(5)	C7-C8	1.522(4)
C8-C9	1.504(4)	C9-C10	1.410(4)
C9-C14	1.379(3)	C11-C12	1.373(4)
C11-C15	1.482(4)	C12-C13	1.398(4)
C15-C16	1.378(4)	C15-C20	1.385(4)
C16-C17	1.387(4)	C17-C18	1.368(5)
C18-C19	1.364(6)	C19-C20	1.389(5)

Table 12: Bond angles of compound **21**

Atom	Angles (°)	Atom	Angles (°)
C7-O1-H1	109.5	C10-N1-H1A	120.0
C10-N1-H1B	120.0	H1A-N1-H1B	120.0
C1-C2-H2	119.5	C3-C2-H2	119.5
C2-C3-H3	120.2	C4-C3-H3	120.2
C3-C4-H4	119.6	C5-C4-H4	119.6
C4-C5-H5	120.4	C6-C5-H5	120.4
C1-C6-H6	119.2	C5-C6-H6	119.2
O1-C7-H7	109.4	C1-C7-H7	109.4
C8-C7-H7	109.4	C7-C8-H8A	108.4
C7-C8-H8B	108.4	C9-C8-H8A	108.4
C9-C8-H8B	108.4	H8A-C8-H8B	107.5
C11-C12-H12	119.9	C13-C12-H12	119.9
N4-C13-H13	117.8	C12-C13-H13	117.8
C15-C16-H16	119.6	C17-C16-H16	119.6
C16-C17-H17	120.2	C18-C17-H17	120.2
C17-C18-H18	119.8	C19-C18-H18	119.8
C18-C19-H19	119.8	C20-C19-H19	119.8
C15-C20-H20	120.0	C19-C20-H20	120.1

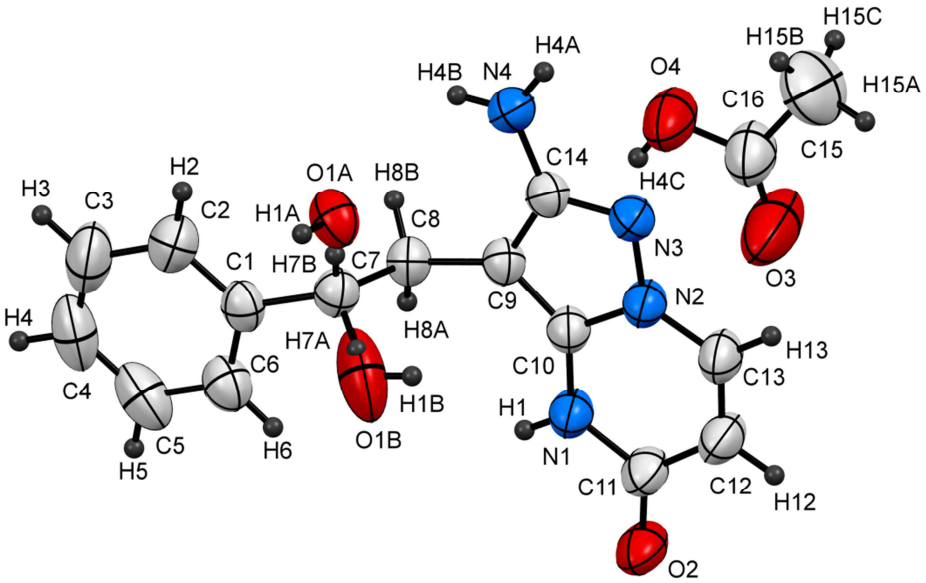


Figure 7. Plot of X-ray crystal structure data for **26a**.

Table 13: Bond lengths of compound **26a**

Atom	Distance (Å)	Atom	Distance (Å)
C1-C2	1.380(3)	C1-C6	1.387(3)
C1-C7	1.511(3)	C8-C9	1.498(3)
C8-C7	1.532(3)	C8-H8A	0.97
C8-H8B	0.97	C7-O1A	1.454(3)
C7-O1B	1.556(8)	C7-H7A	0.98
C7-H7B	0.98	O1A-H7B	0.5461
O1A-H1A	0.82	O1B-H1B	0.82
O2-C11	1.243(3)	N3-C14	1.335(3)
N3-N2	1.377(2)	O4-C16	1.281(3)
O4-H4C	0.82	O3-C16	1.171(4)
N1-C10	1.372(3)	N1-C11	1.372(3)
N1-H1	0.86	C9-C10	1.370(3)
C9-C14	1.412(3)	N2-C13	1.353(3)
N2-C10	1.370(3)	C12-C13	1.349(3)
C12-C11	1.440(3)	C12-H12	0.93
C2-C3	1.398(4)	C2-H2	0.93
C3-C4	1.354(5)	C3-H3	0.93
C4-C5	1.378(5)	C4-H4	0.93
C5-C6	1.380(4)	C5-H5	0.93
C6-H6	0.93	C14-N4	1.373(3)
C13-H13	0.93	N4-H4A	0.86
N4-H4B	0.86	C16-C15	1.5289(19)
C15-H15A	0.96	C15-H15B	0.96
C15-H15C	0.96		

Table 14: Bond angles of compound **26a**

Atom	Angles (°)	Atom	Angles (°)
C2-C1-C6	118.4(2)	C2-C1-C7	122.0(2)
C6-C1-C7	119.6(2)	C9-C8-C7	112.42(17)
C9-C8-H8A	109.1	C7-C8-H8A	109.1
C9-C8-H8B	109.1	C7-C8-H8B	109.1
H8A-C8-H8B	107.9	O1A-C7-C1	111.20(18)
O1A-C7-C8	104.19(16)	C1-C7-C8	112.25(17)
O1A-C7-O1B	125.6(4)	C1-C7-O1B	102.1(3)
C8-C7-O1B	101.1(4)	O1A-C7-H7A	109.7
C1-C7-H7A	109.7	C8-C7-H7A	109.7
O1B-C7-H7A	16.1	O1A-C7-H7B	13.0
C1-C7-H7B	113.4	C8-C7-H7B	113.4
O1B-C7-H7B	113.4	H7A-C7-H7B	97.4
C7-O1A-H7B	23.8	C7-O1A-H1A	109.5
H7B-O1A-H1A	89.2	C7-O1B-H1B	109.5
C14-N3-N2	103.86(16)	C16-O4-H4C	109.5
C10-N1-C11	123.19(18)	C10-N1-H1	118.4
C11-N1-H1	118.4	C10-C9-C14	103.55(17)
C10-C9-C8	127.60(18)	C14-C9-C8	128.82(17)
C13-N2-C10	123.09(18)	C13-N2-N3	126.00(18)
C10-N2-N3	110.91(16)	C13-C12-C11	121.2(2)
C13-C12-H12	119.4	C11-C12-H12	119.4
O2-C11-N1	120.2(2)	O2-C11-C12	123.8(2)
N1-C11-C12	115.96(19)	C9-C10-N2	108.44(17)
C9-C10-N1	134.16(19)	N2-C10-N1	117.40(17)
C1-C2-C3	120.0(3)	C1-C2-H2	120.0
C3-C2-H2	120.0	C4-C3-C2	120.9(3)
C4-C3-H3	119.5	C2-C3-H3	119.5
C3-C4-C5	119.6(3)	C3-C4-H4	120.2
C5-C4-H4	120.2	C6-C5-C4	120.2(3)
C6-C5-H5	119.9	C4-C5-H5	119.9
C5-C6-C1	120.9(3)	C5-C6-H6	119.6
C1-C6-H6	119.6	N3-C14-N4	120.84(18)
N3-C14-C9	113.23(17)	N4-C14-C9	125.88(19)
C12-C13-N2	119.1(2)	C12-C13-H13	120.4
N2-C13-H13	120.4	C14-N4-H4A	120.0
C14-N4-H4B	120.0	H4A-N4-H4B	120.0
O3-C16-O4	123.6(3)	O3-C16-C15	123.2(3)
O4-C16-C15	113.1(3)	C16-C15-H15A	109.5
C16-C15-H15B	109.5	H15A-C15-H15B	109.5
C16-C15-H15C	109.5	H15A-C15-H15C	109.5
H15B-C15-H15C	109.5		

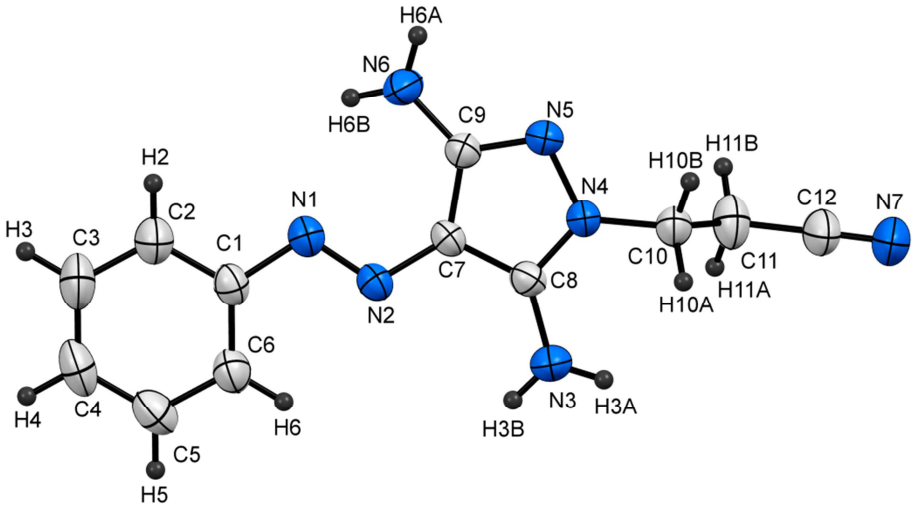


Figure 8. Plot of X-ray crystal structure data for **30**.

Table 15: Bond lengths of compound **30**

Atom	Distance (Å)	Atom	Distance (Å)
N1-N2	1.275(2)	N1-C1	1.422(2)
N2-C7	1.371(2)	C7-C8	1.392(3)
C7-C9	1.434(2)	N4-C8	1.336(2)
N4-N5	1.401(2)	N4-C10	1.442(2)
C9-N5	1.318(3)	C9-N6	1.355(2)
N3-C8	1.374(2)	N3-H3A	0.86
N3-H3B	0.86	C4-C5	1.371(3)
C4-C3	1.378(4)	C4-H4	0.93
C5-C6	1.387(3)	C5-H5	0.93
C6-C1	1.387(3)	C6-H6	0.93
C1-C2	1.379(3)	C10-C11	1.520(3)
C10-H10A	0.97	C10-H10B	0.97
C11-C12	1.455(3)	C11-H11A	0.97
C11-H11B	0.97	C12-N7	1.142(3)
N6-H6A	0.86	N6-H6B	0.86
C2-C3	1.388(3)	C2-H2	0.93
C3-H3	0.93		

Table 16: Bond angles of compound **30**

Atom	Angles (°)	Atom	Angles (°)
N2-N1-C1	113.43(16)	N1-N2-C7	115.24(16)
N2-C7-C8	122.91(16)	N2-C7-C9	132.26(17)
C8-C7-C9	104.67(15)	C8-N4-N5	112.19(15)
C8-N4-C10	129.34(15)	N5-N4-C10	118.46(15)
N5-C9-N6	122.46(17)	N5-C9-C7	111.44(16)
N6-C9-C7	126.09(17)	C9-N5-N4	104.58(14)
C8-N3-H3A	120.0	C8-N3-H3B	120.0

H3A-N3-H3B	120.0	C5-C4-C3	119.7(2)
C5-C4-H4	120.2	C3-C4-H4	120.2
C4-C5-C6	120.7(2)	C4-C5-H5	119.7
C6-C5-H5	119.7	C5-C6-C1	119.8(2)
C5-C6-H6	120.1	C1-C6-H6	120.1
C2-C1-C6	119.36(19)	C2-C1-N1	116.14(18)
C6-C1-N1	124.50(19)	N4-C8-N3	123.37(17)
N4-C8-C7	107.11(15)	N3-C8-C7	129.46(17)
N4-C10-C11	112.02(17)	N4-C10-H10A	109.2
C11-C10-H10A	109.2	N4-C10-H10B	109.2
C11-C10-H10B	109.2	H10A-C10-H10B	107.9
C12-C11-C10	110.10(19)	C12-C11-H11A	109.6
C10-C11-H11A	109.6	C12-C11-H11B	109.6
C10-C11-H11B	109.6	H11A-C11-H11B	108.2
N7-C12-C11	177.0(3)	C9-N6-H6A	120.0
C9-N6-H6B	120.0	H6A-N6-H6B	120.0
C1-C2-C3	120.4(2)	C1-C2-H2	119.8
C3-C2-H2	119.8	C4-C3-C2	120.1(2)
C4-C3-H3	120.0	C2-C3-H3	120.0

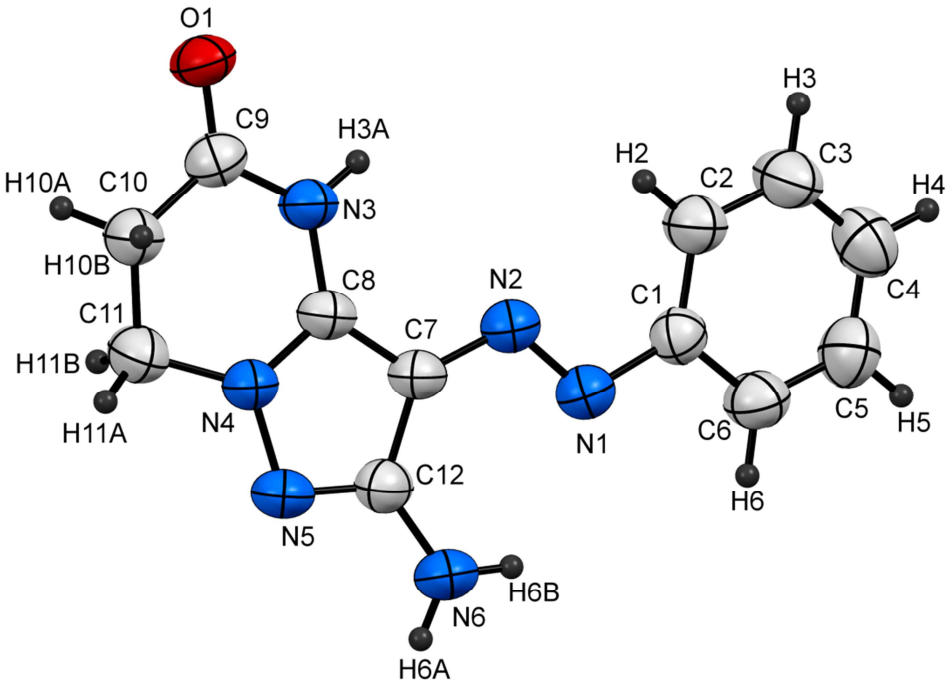


Figure 9. Plot of X-ray crystal structure data for **33**.

Table 17: Bond lengths of compound **33**

Atom	Distance (Å)	Atom	Distance (Å)
O1-C9	1.228(4)	N1-N2	1.285(3)
N1-C1	1.423(4)	N2-C7	1.368(4)
N3-C8	1.373(4)	N3-C9	1.356(4)
N4-N5	1.405(3)	N4-C8	1.329(4)
N4-C11	1.438(4)	N5-C12	1.326(4)
N6-C12	1.358(4)	C1-C2	1.381(4)
C1-C6	1.385(4)	C2-C3	1.379(5)
C3-C4	1.372(5)	C4-C5	1.365(5)
C5-C6	1.380(5)	C7-C8	1.392(4)
C7-C12	1.433(4)	C9-C10	1.495(4)
C10-C11	1.515(4)		

Table 18: Bond angles of compound **33**

Atom	Angles (°)	Atom	Angles (°)
N2-N1-C1	112.3(3)	N1-N2-C7	115.5(3)
C8-N3-C9	122.6(3)	N5-N4-C8	111.9(2)
N5-N4-C11	122.5(2)	C8-N4-C11	123.4(3)
N4-N5-C12	104.1(2)	N1-C1-C2	124.5(3)
N1-C1-C6	116.2(3)	C2-C1-C6	119.3(3)
C1-C2-C3	119.6(3)	C2-C3-C4	121.1(3)
C3-C4-C5	119.3(3)	C4-C5-C6	120.6(3)
C1-C6-C5	120.1(3)	N2-C7-C8	122.5(3)
N2-C7-C12	133.6(2)	C8-C7-C12	103.8(3)
N3-C8-N4	121.1(2)	N3-C8-C7	130.7(3)
N4-C8-C7	108.2(3)	O1-C9-N3	121.6(3)
O1-C9-C10	121.6(3)	N3-C9-C10	116.8(3)
C9-C10-C11	117.1(2)	N4-C11-C10	109.3(2)
N5-C12-N6	122.7(3)	N5-C12-C7	112.0(2)
N6-C12-C7	125.4(3)		

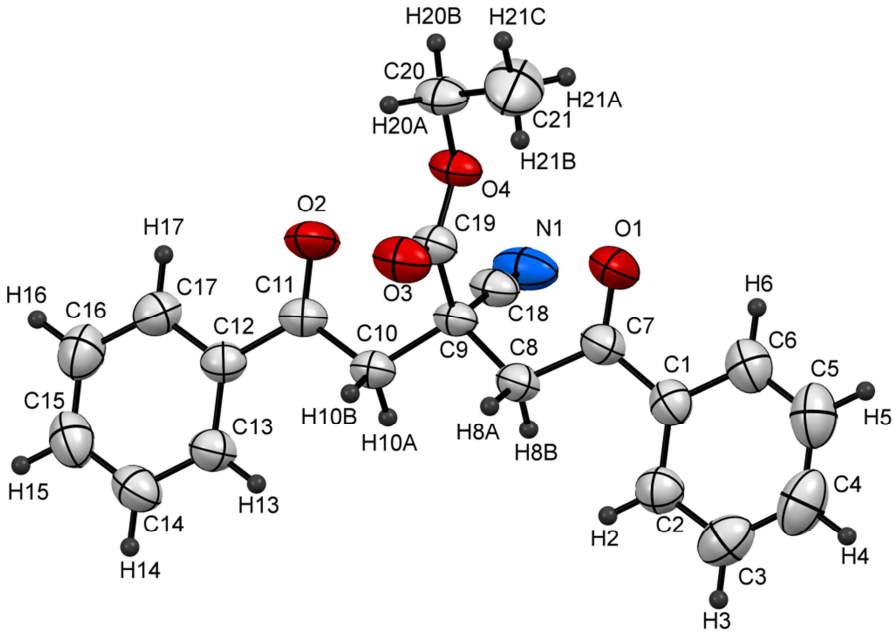


Figure 10. Plot of X-ray crystal structure data for **37**.

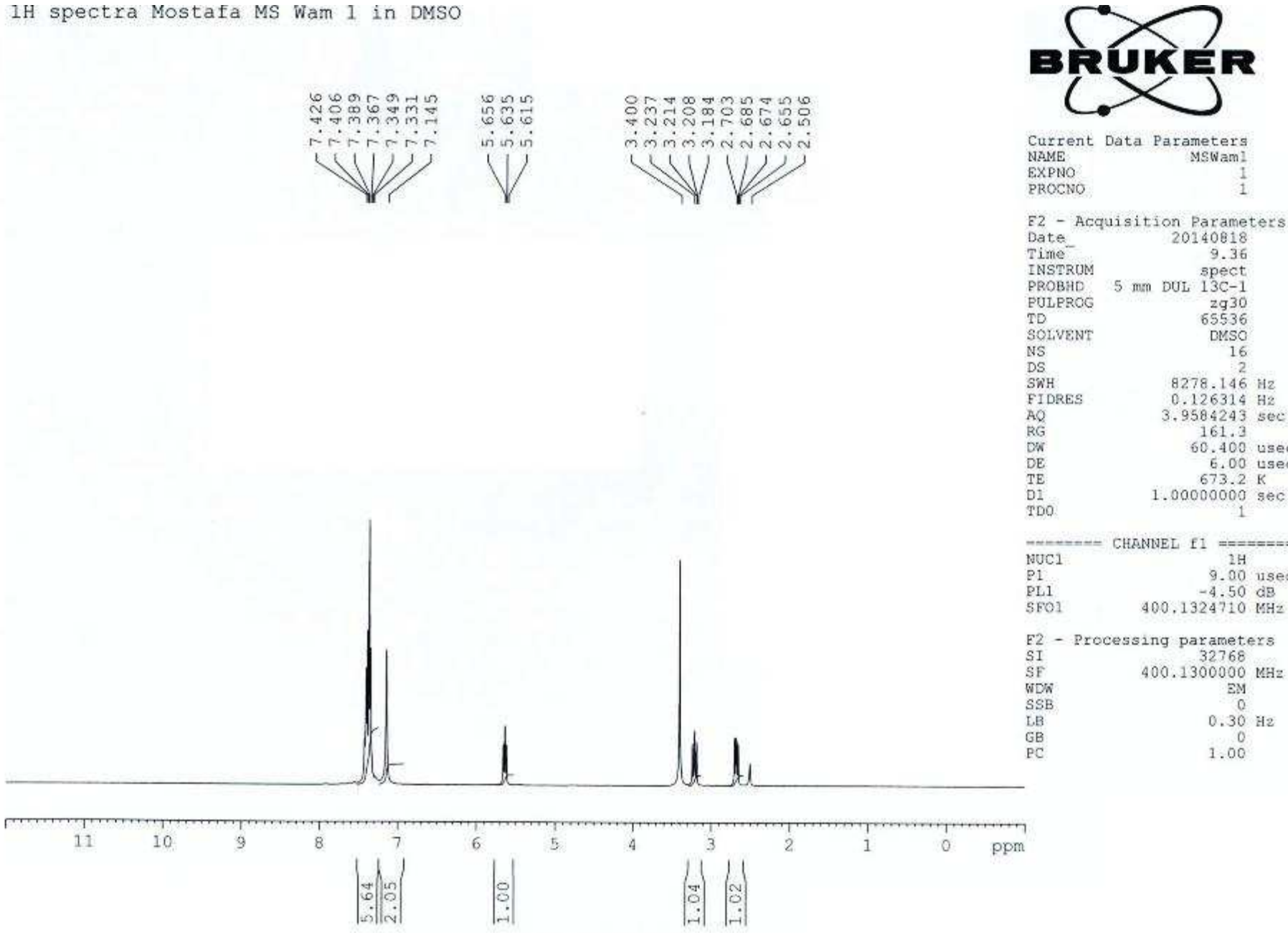
Table 19: Bond lengths of compound **37**

Atom	Distance (Å)	Atom	Distance (Å)
O1-C7	1.219(3)	O2-C11	1.215(3)
O3-C19	1.200(2)	O4-C19	1.322(3)
O4-C20	1.462(2)	N1-C18	1.138(3)
C1-C2	1.386(3)	C1-C6	1.393(3)
C1-C7	1.486(3)	C2-C3	1.387(3)
C3-C4	1.381(4)	C4-C5	1.373(4)
C5-C6	1.366(4)	C7-C8	1.507(3)
C8-C9	1.543(3)	C9-C10	1.548(3)
C9-C18	1.476(3)	C9-C19	1.537(3)
C10-C11	1.512(3)	C11-C12	1.492(3)
C12-C13	1.394(3)	C12-C17	1.388(3)
C13-C14	1.380(3)	C14-C15	1.376(3)
C15-C16	1.374(3)	C16-C17	1.379(3)
C20-C21	1.475(3)		

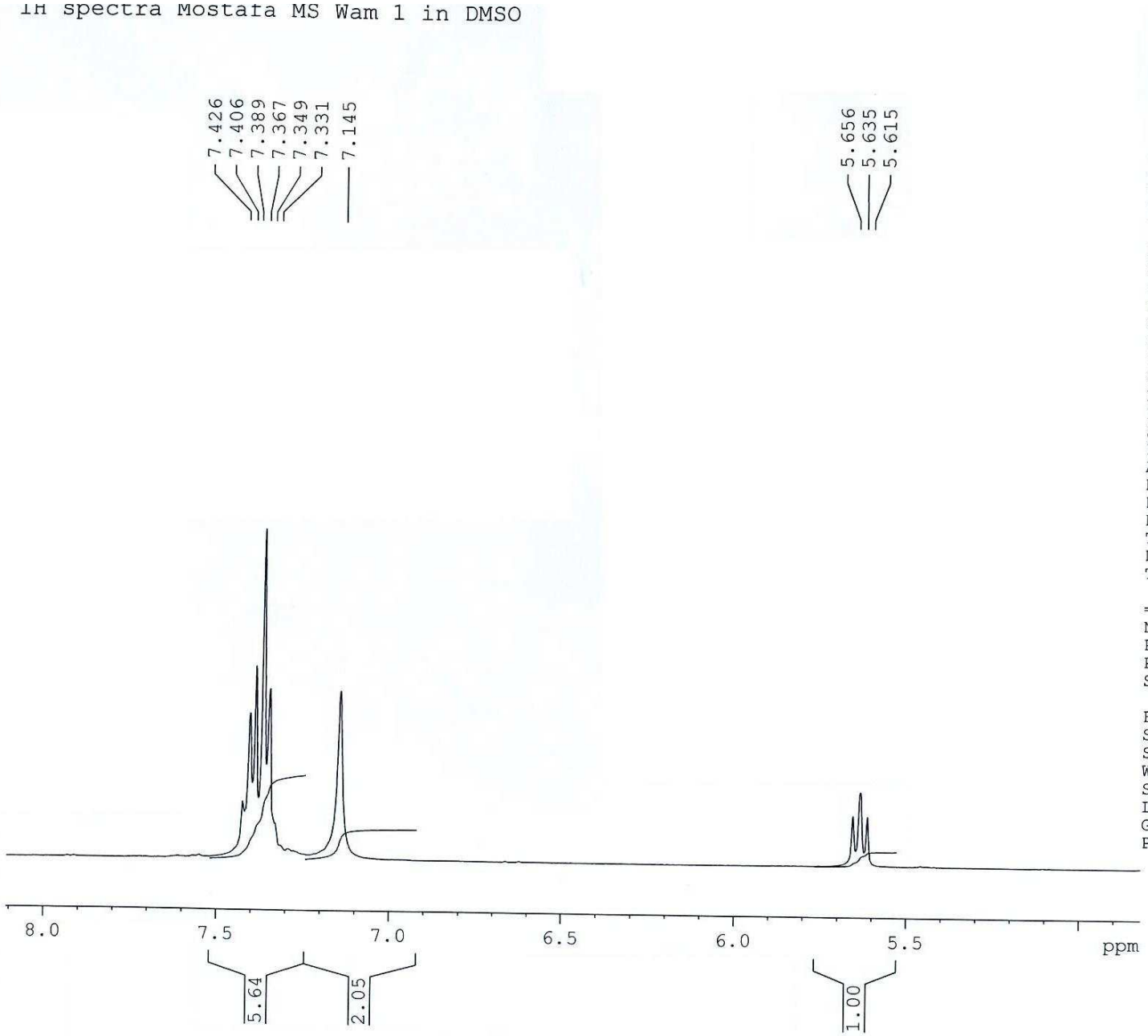
Table 20: Bond angles of compound **37**

Atom	Angles (°)	Atom	Angles (°)
C19-O4-C20	116.18(12)	C2-C1-C6	119.07(17)
C2-C-C7	123.06(16)	C6-C1-C7	117.87(16)
C1-C2-C3	120.16(18)	C2-C3-C4	119.6(2)
C3-C4-C5	120.3(3)	C4-C5-C6	120.3(3)
C1-C6-C5	120.5(2)	O1-C7-C1	120.95(17)
O1-C7-C8	119.91(17)	C1-C7-C8	119.13(15)

C7-C8-C9	114.94(14)	C8-C9-C10	106.57(13)
C8-C9-C18	109.35(13)	C8-C9-C19	109.64(13)
C10-C9-C18	109.32(14)	C10-C9-C19	109.93(13)
C18-C9-C19	111.87(13)	C9-C10-C11	114.53(14)
O2-C11-C10	120.24(16)	O2-C11-C12	121.39(16)
C10-C11-C12	118.36(15)	C11-C12-C13	122.39(16)
C11-C12-C17	118.39(16)	C13-C12-C17	119.20(17)
C12-C13-C14	119.87(17)	C13-C14-C15	120.34(19)
C14-C15-C16	120.1(2)	C15-C16-C17	120.19(19)
C12-C17-C16	120.26(18)	N1-C18-C9	175.77(17)
O3-C19-O4	125.42(15)	O3-C19-C9	120.18(15)
O4-C19-C9	114.40(13)	O4-C20-C21	111.04(15)



^{1}H NMR for compound **12**



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PROCNO	1

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DS	2
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FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	161.3
DW	60.400 usec
DE	6.00 usec
TE	673.2 K
D1	1.00000000 sec
TD0	1

======== CHANNEL f1 ========

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PL1	-4.50 dB
SFO1	400.1324710 MHz

F2 - Processing parameters

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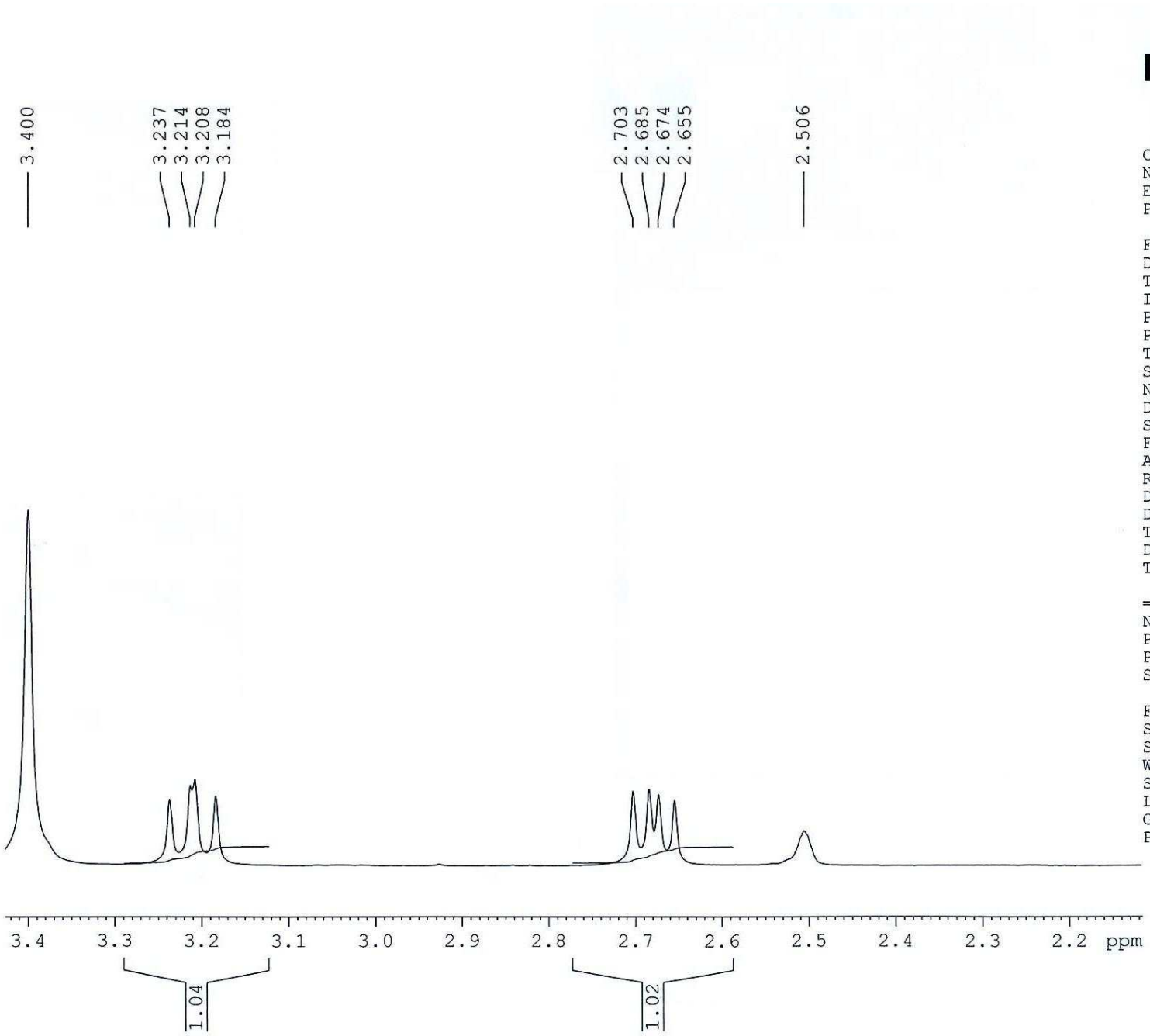
^{1}H NMR for compound **12**



BRUKER

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Current Data Parameters
NAME                  MSWam1
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
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PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                 3.9584243 sec
RG                     161.3
DW                    60.400 usec
DE                     6.00 usec
TE                    673.2 K
D1               1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.00 usec
PL1                   -4.50 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
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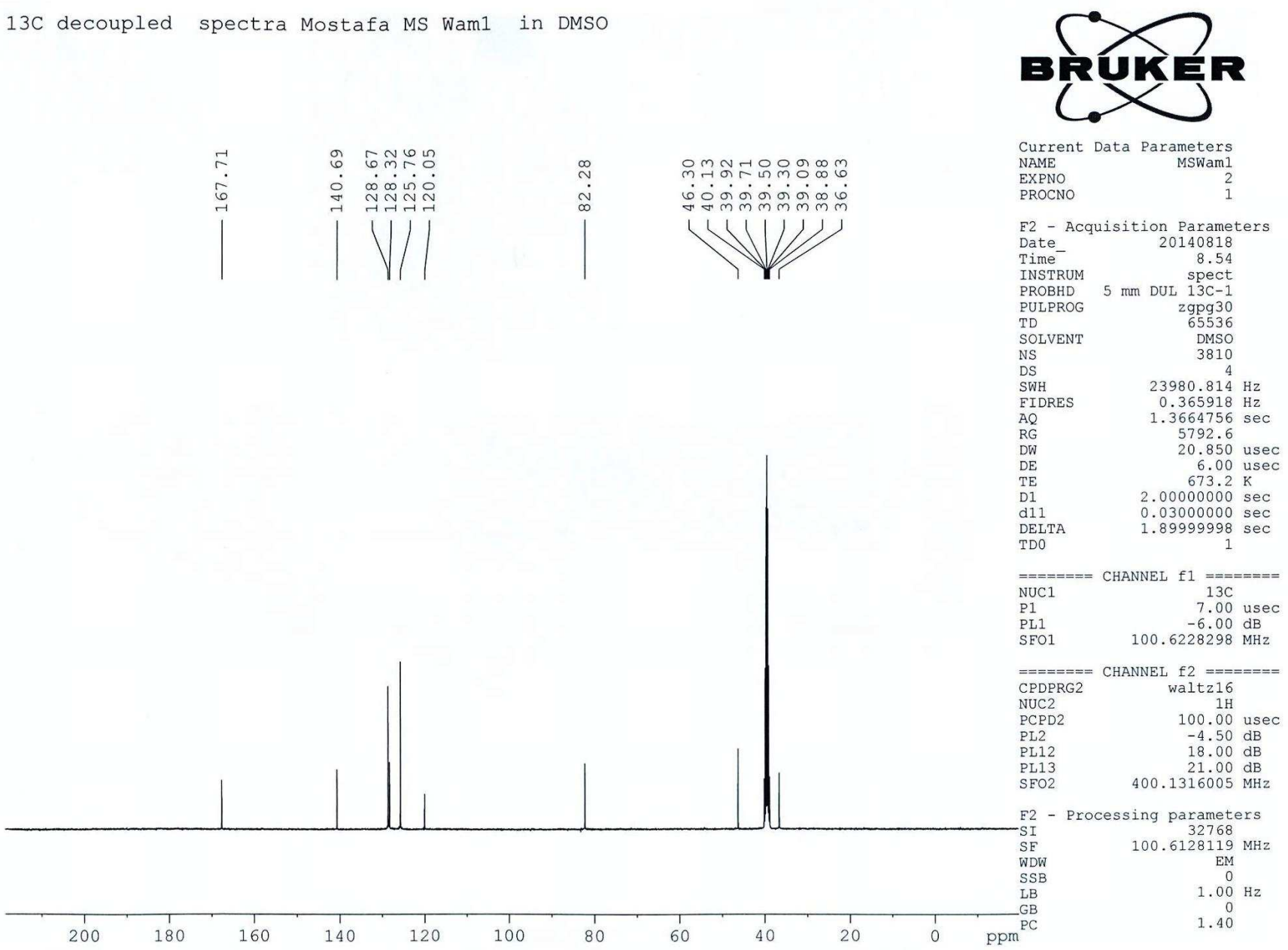
^{1}H NMR for compound **12**



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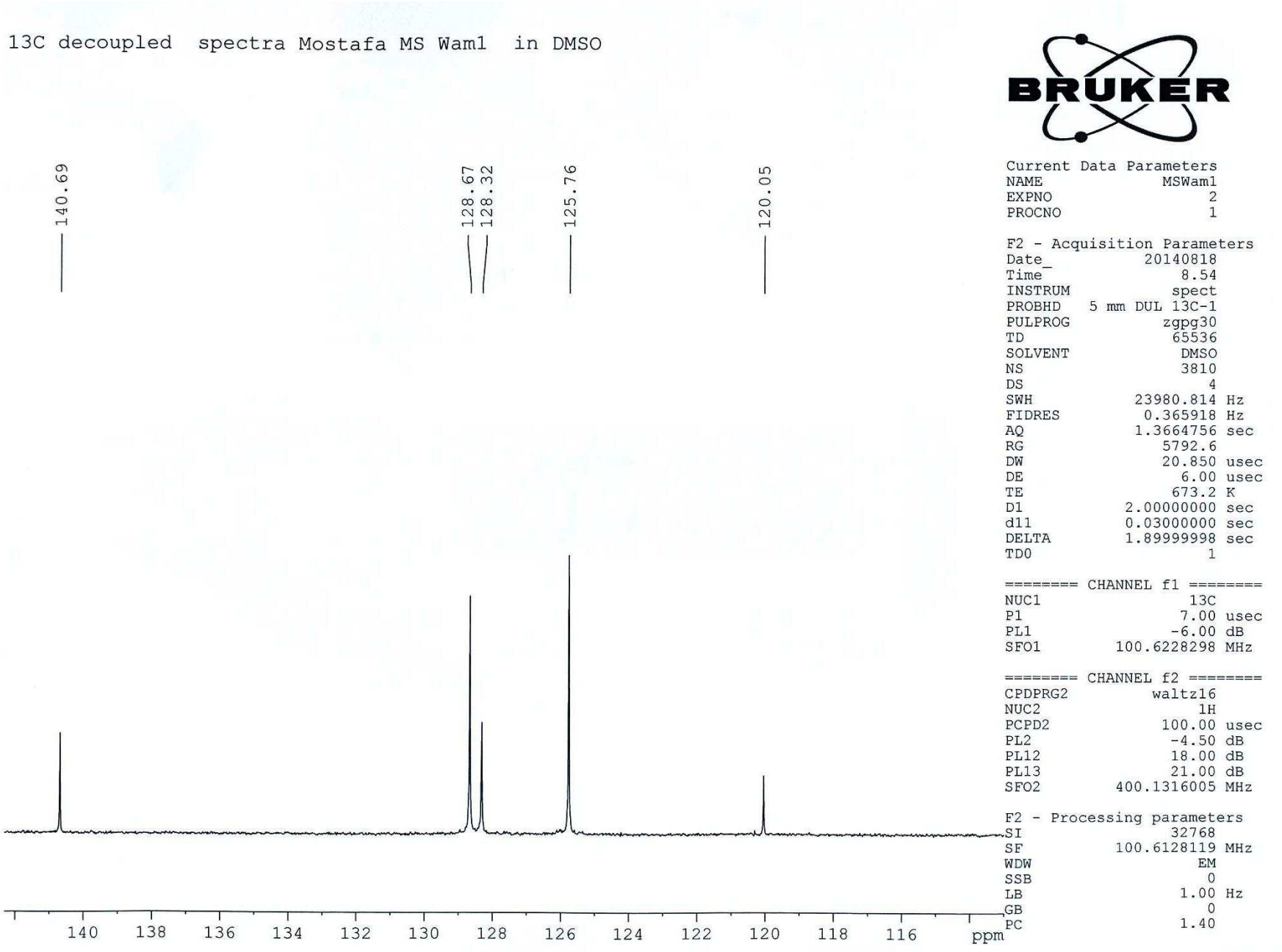

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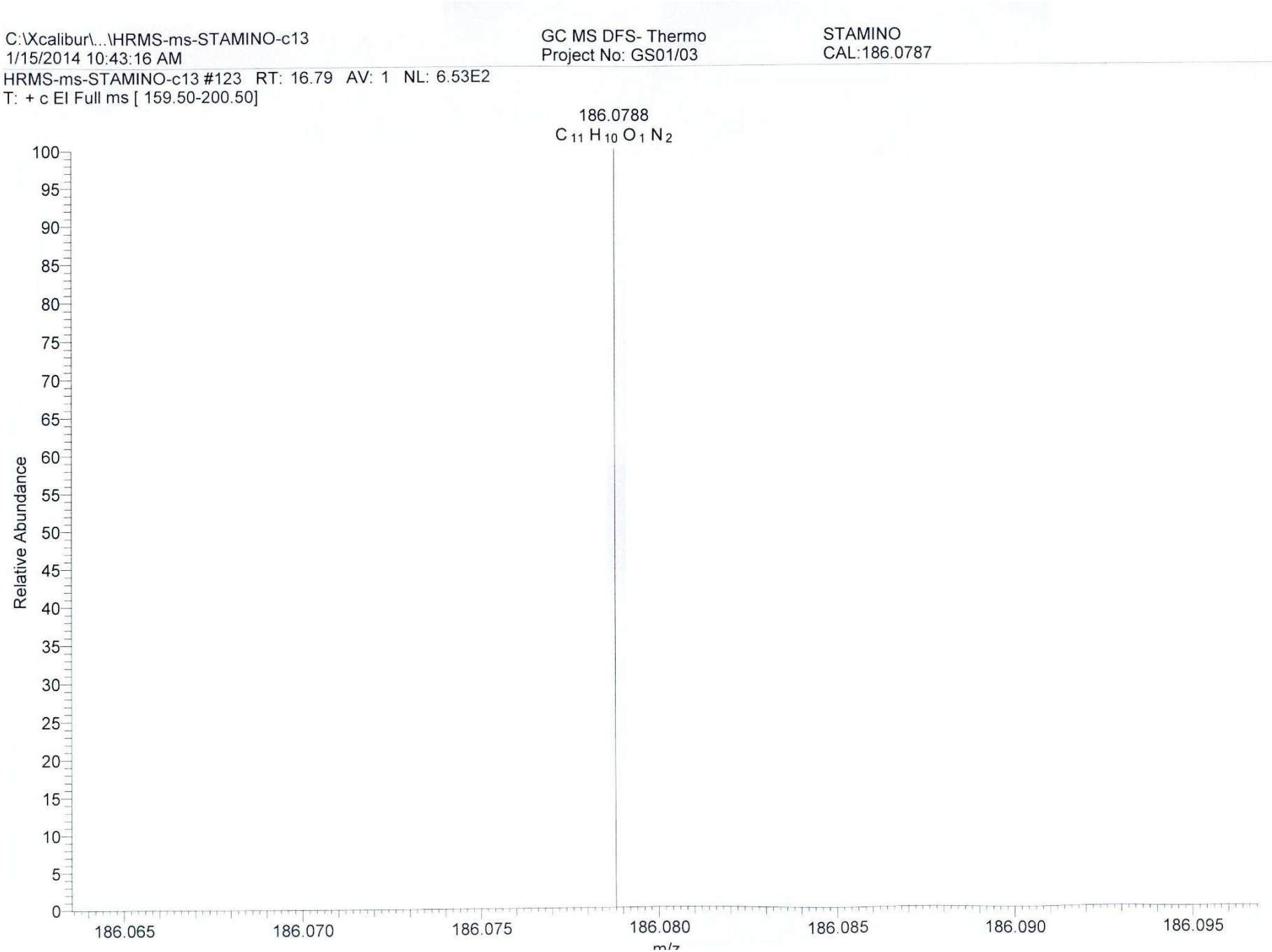
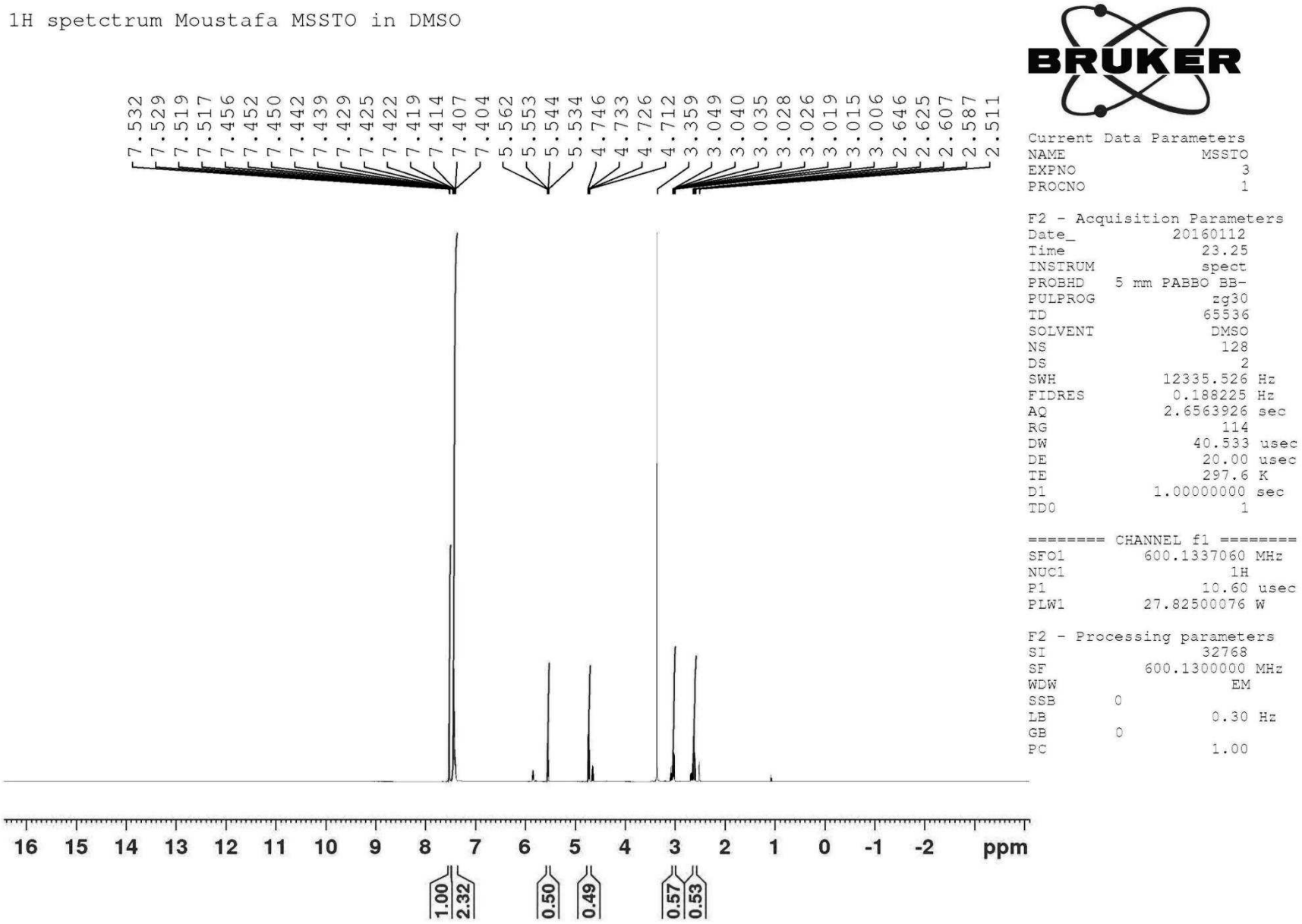


High resolution mass spectra for compound **12**

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PROCNO                    1

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RG                     114
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TE                297.6 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
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NUC1                    1H
P1                  10.60 usec
PLW1          27.82500076 W

F2 - Processing parameters
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PC                   1.00
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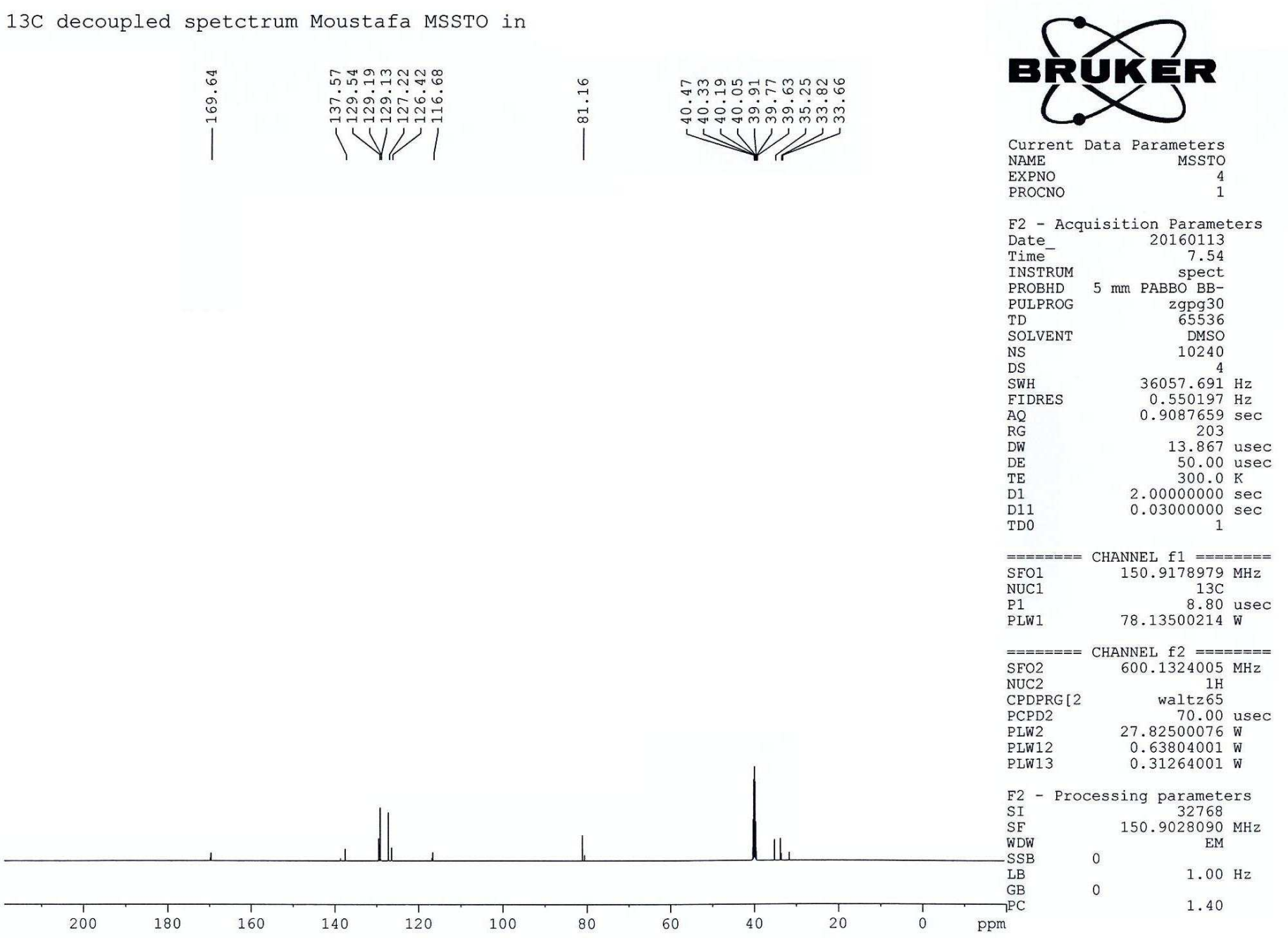
^{1}H NMR for compound **13**



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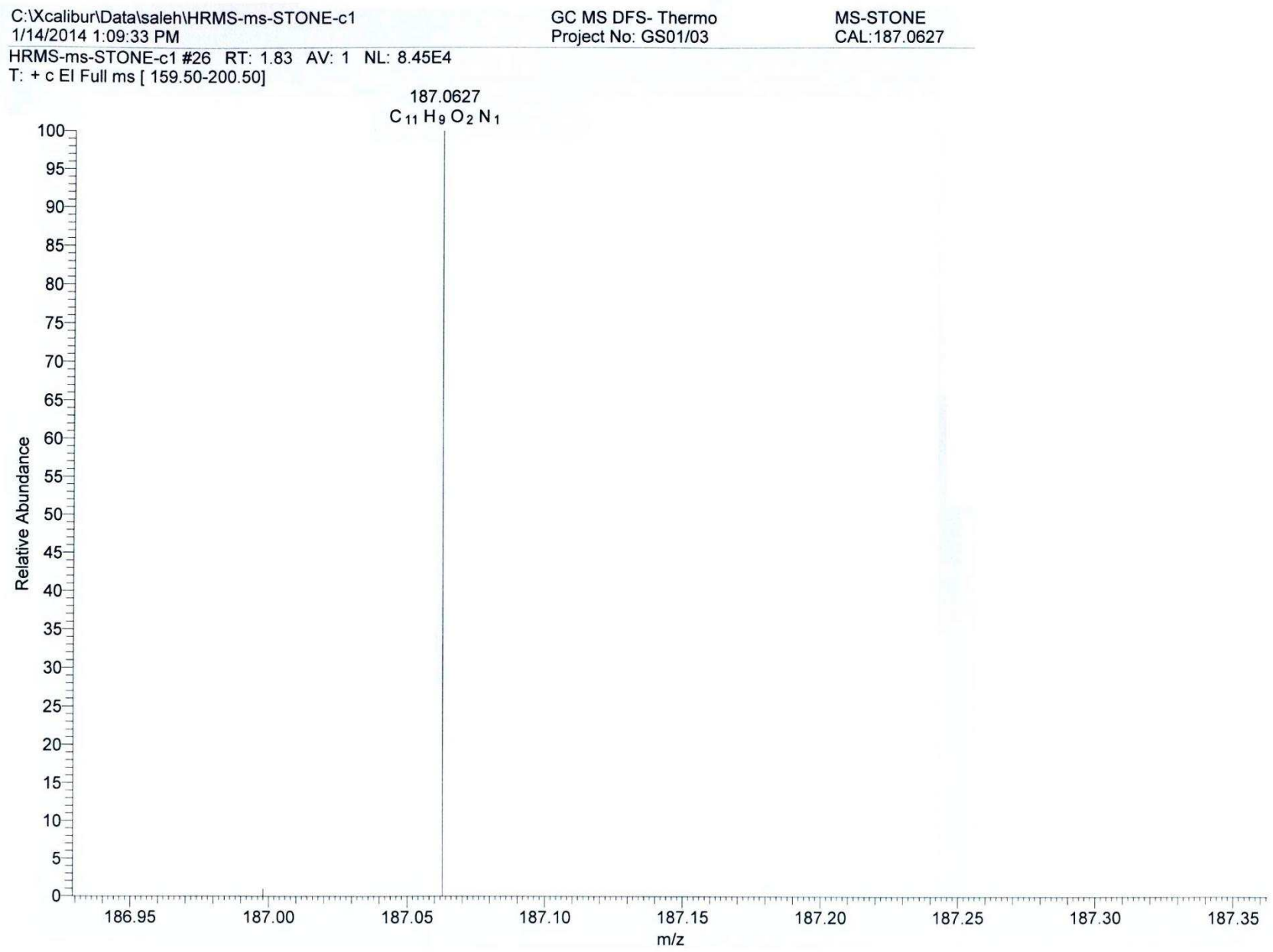
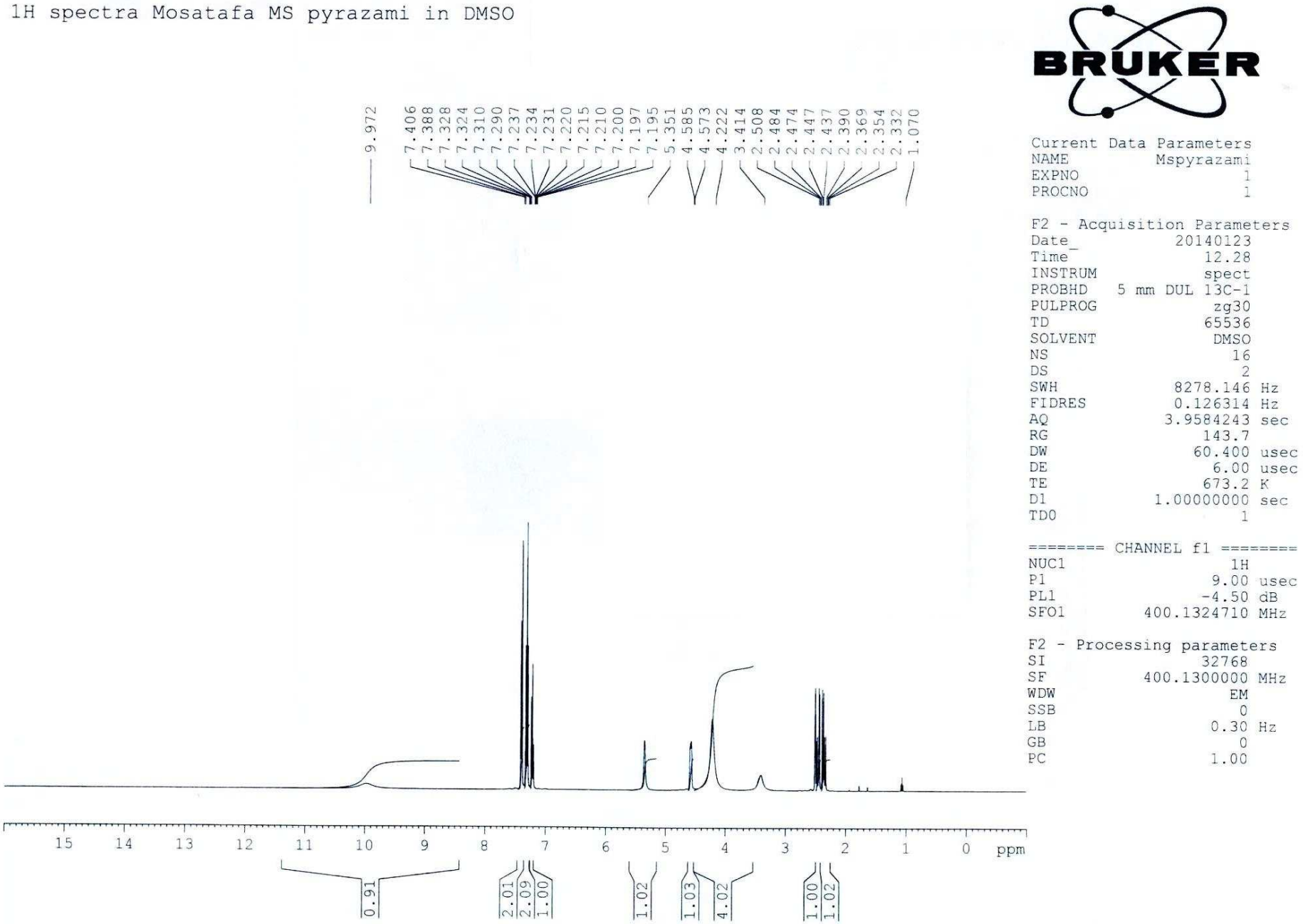
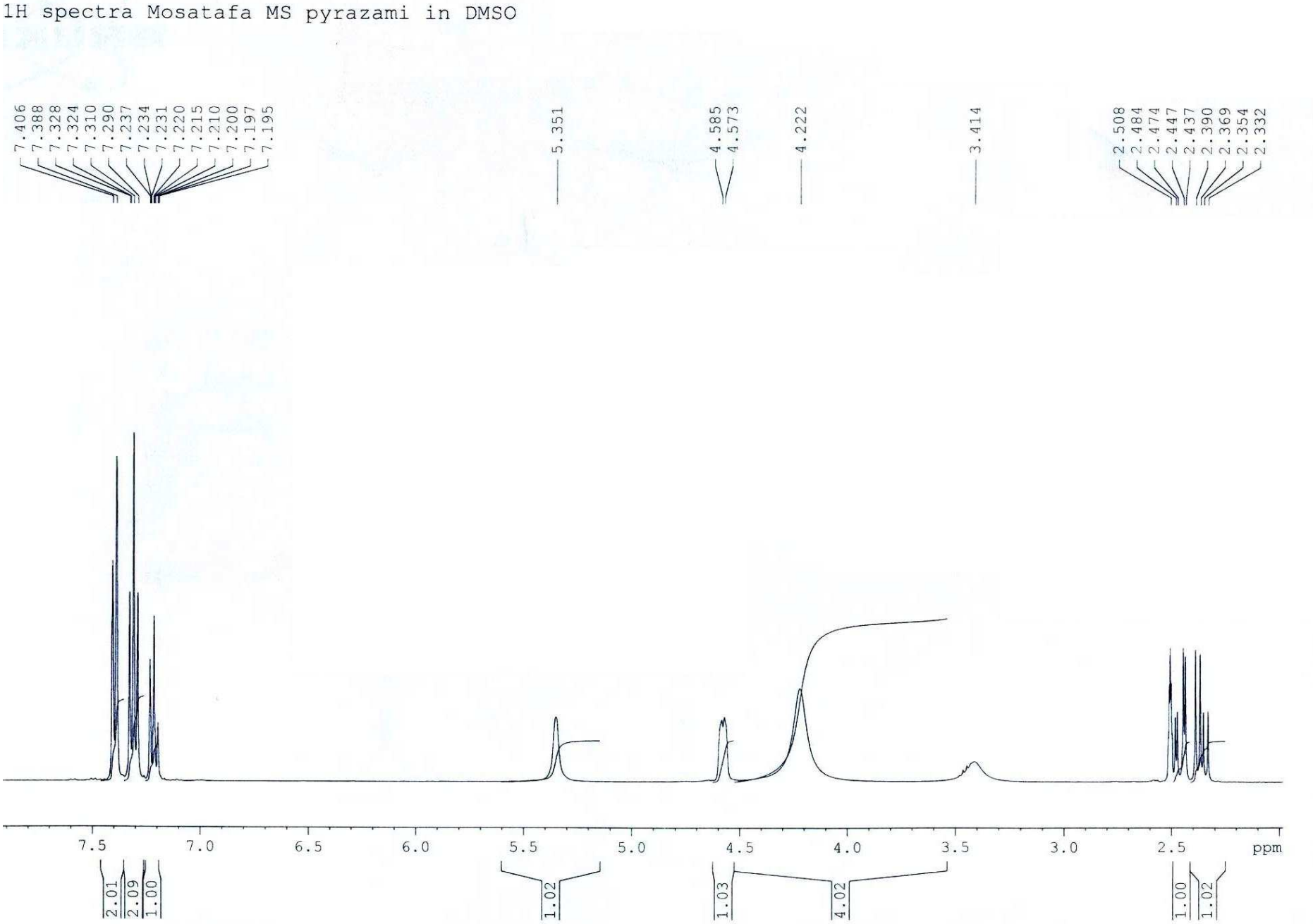


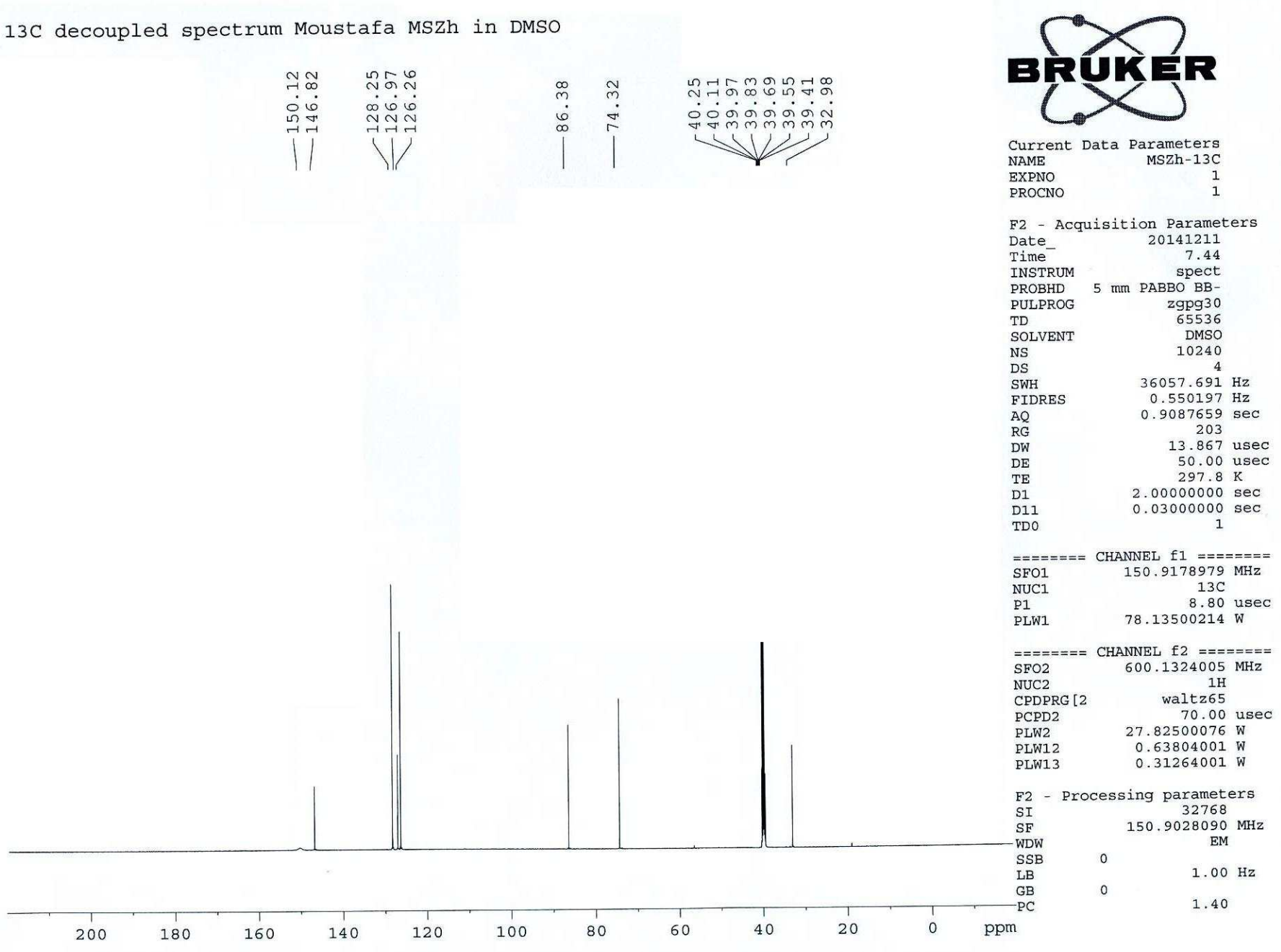
High resolution mass spectra for compound **13**



^{1}H NMR for compound **2h**



[1]H NMR for compound **2h**



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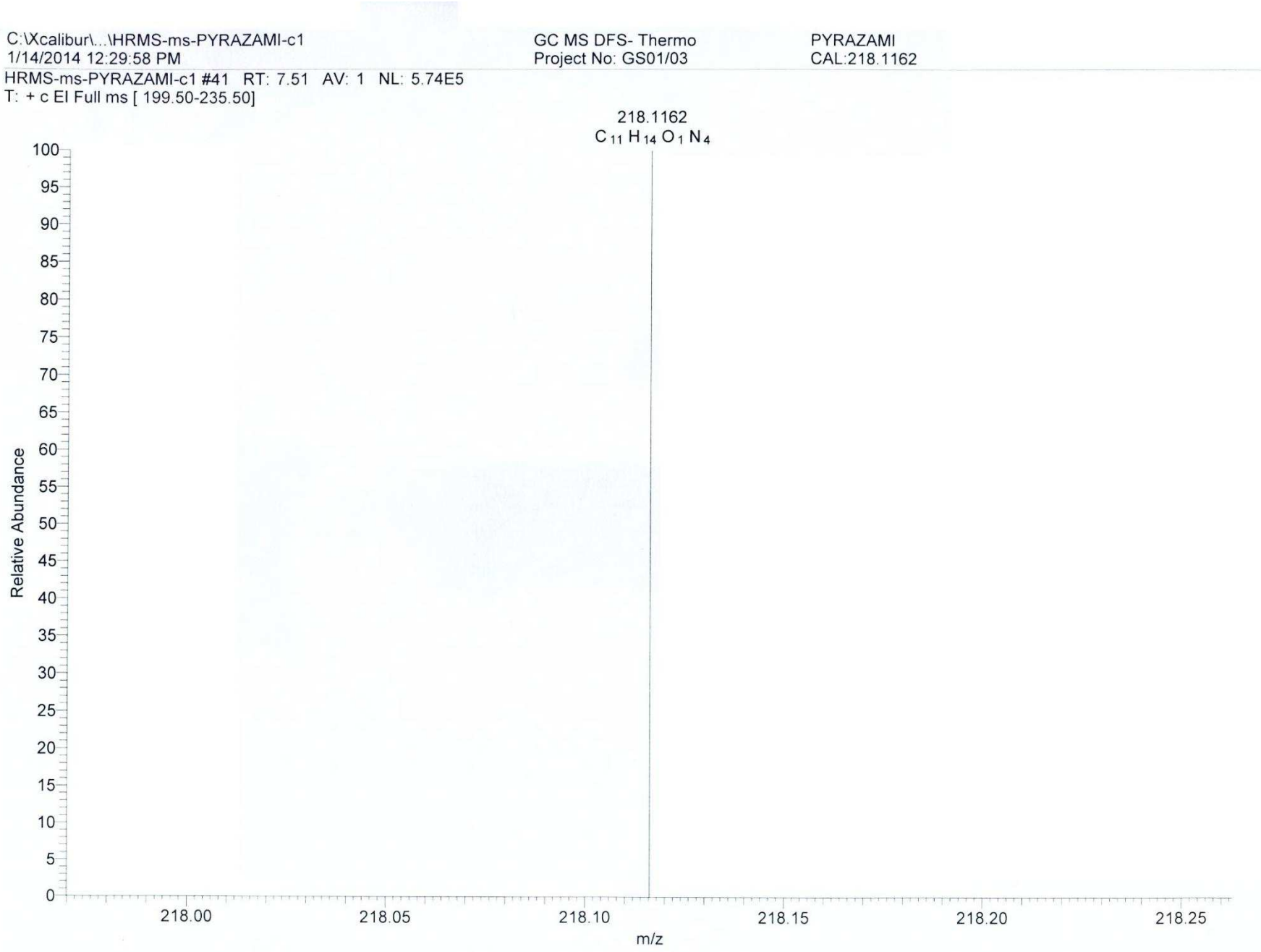
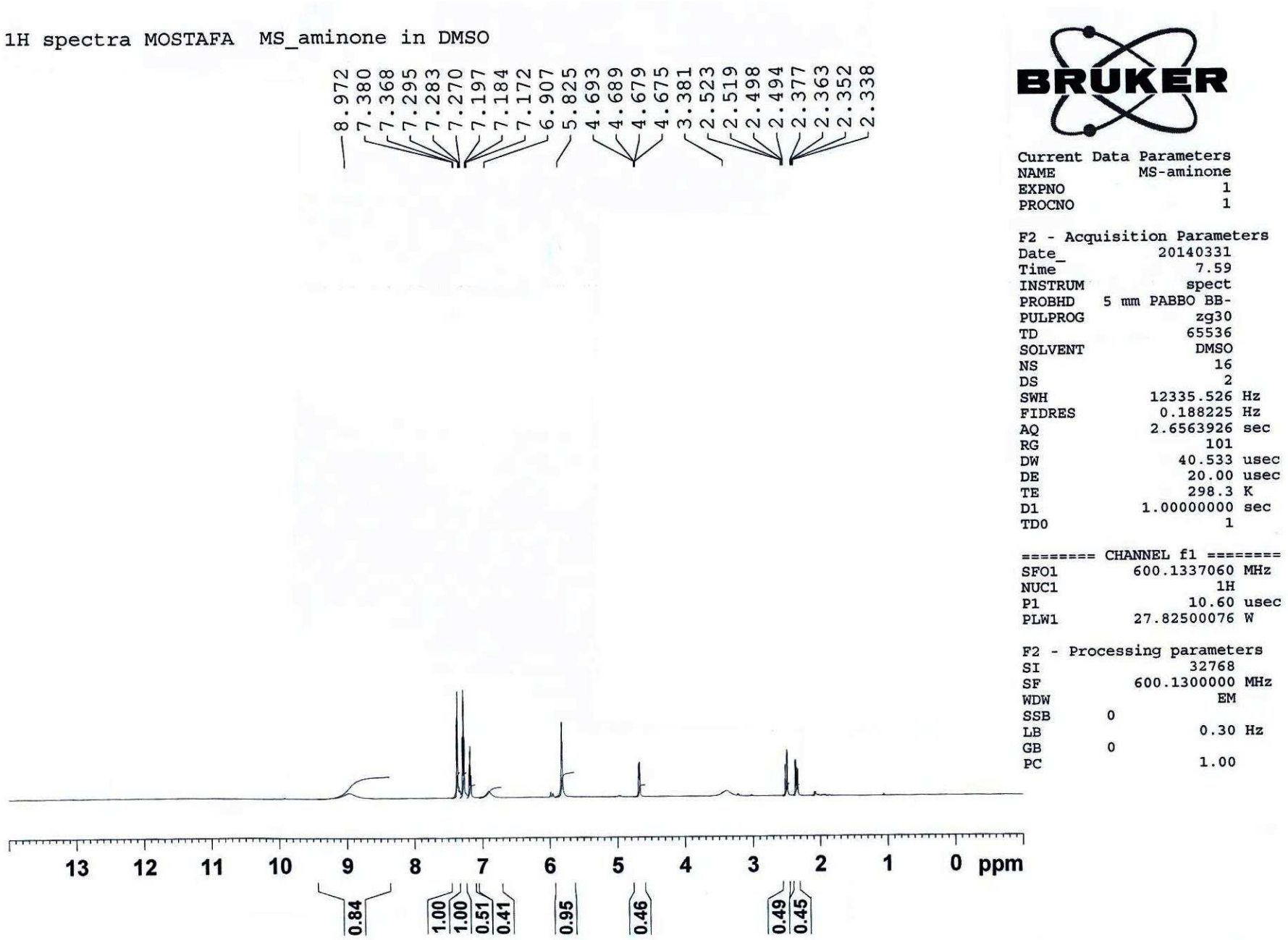
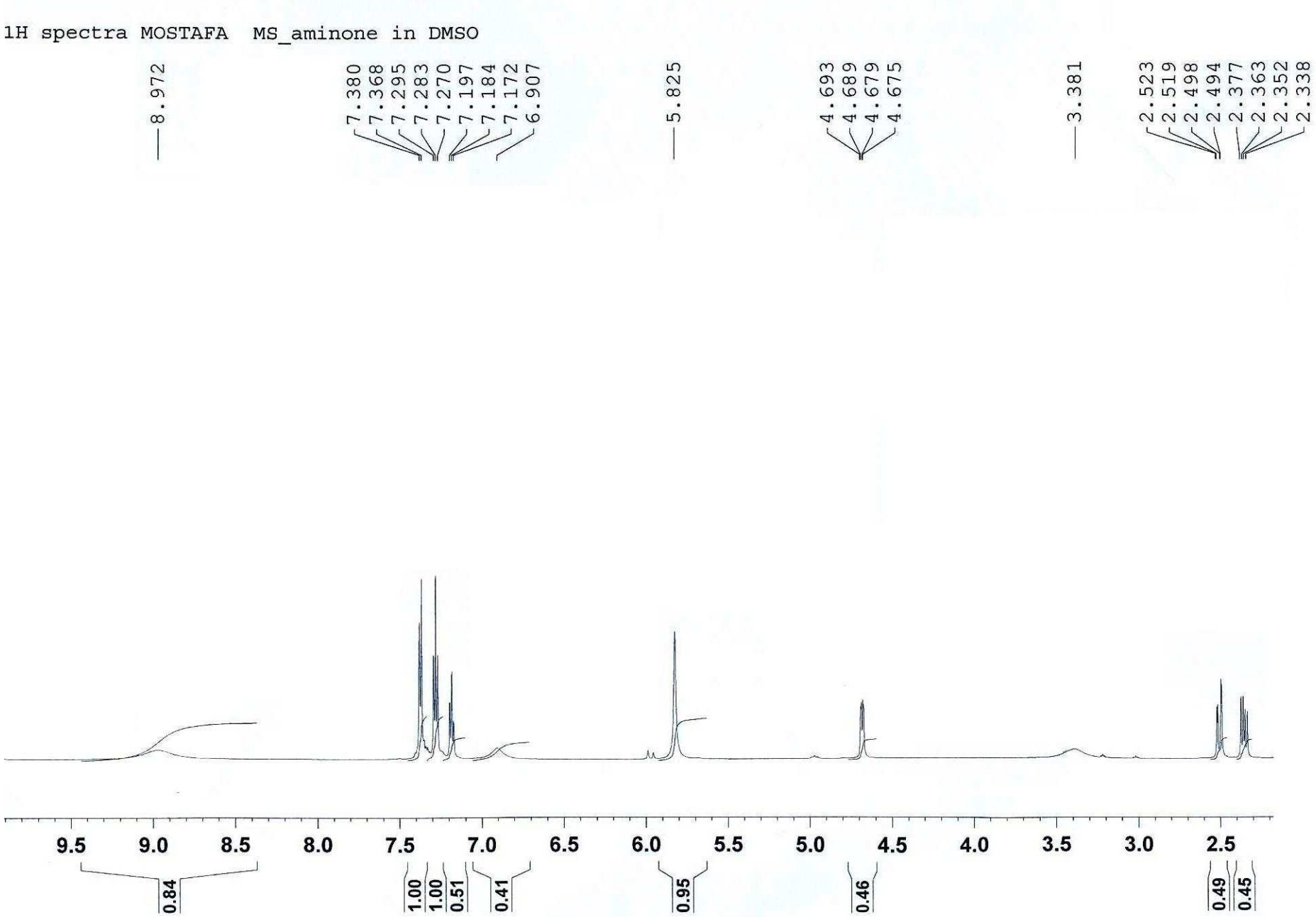


High resolution mass spectra for compound **2h**



^{1}H NMR for compound **14**



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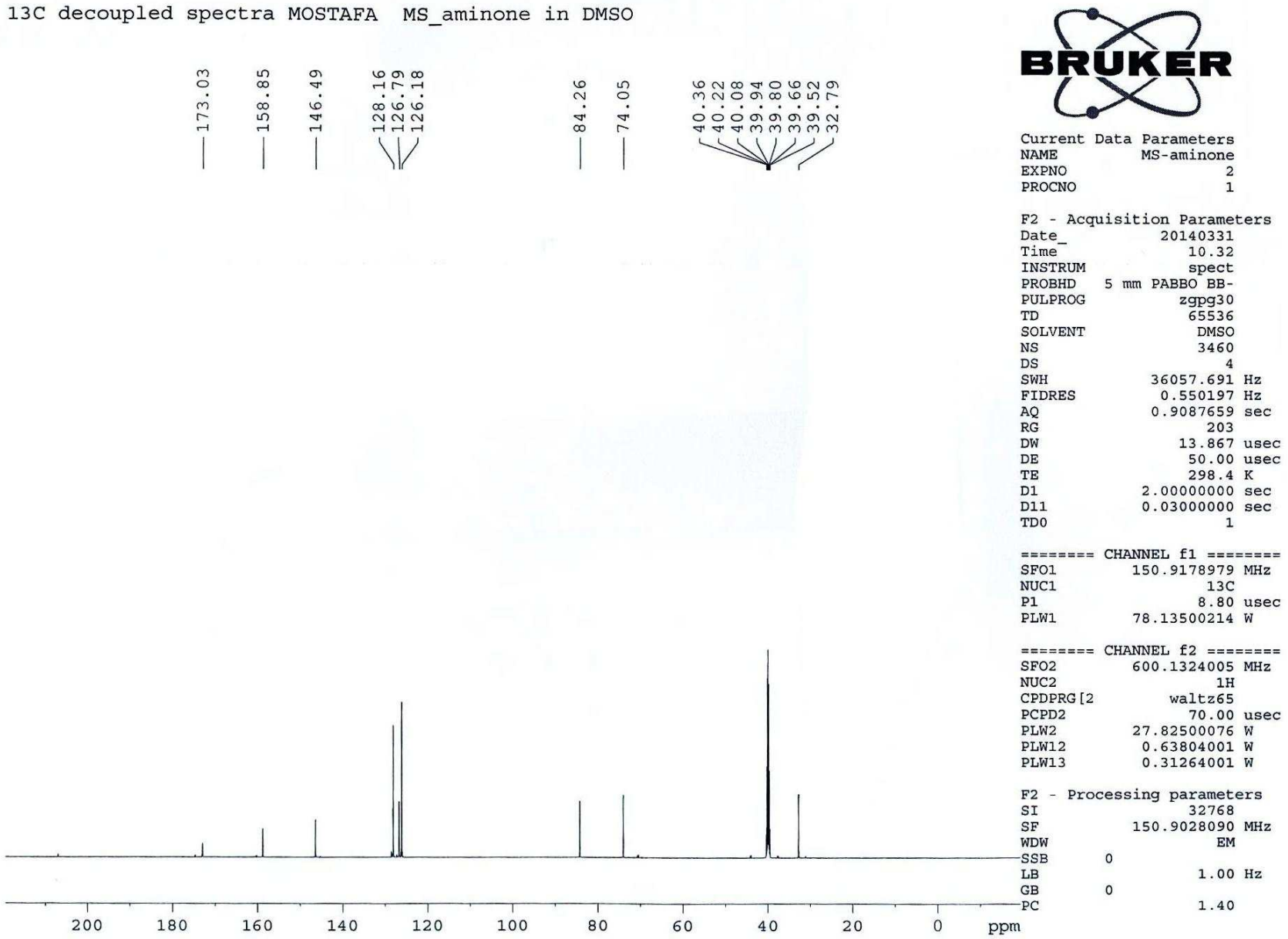

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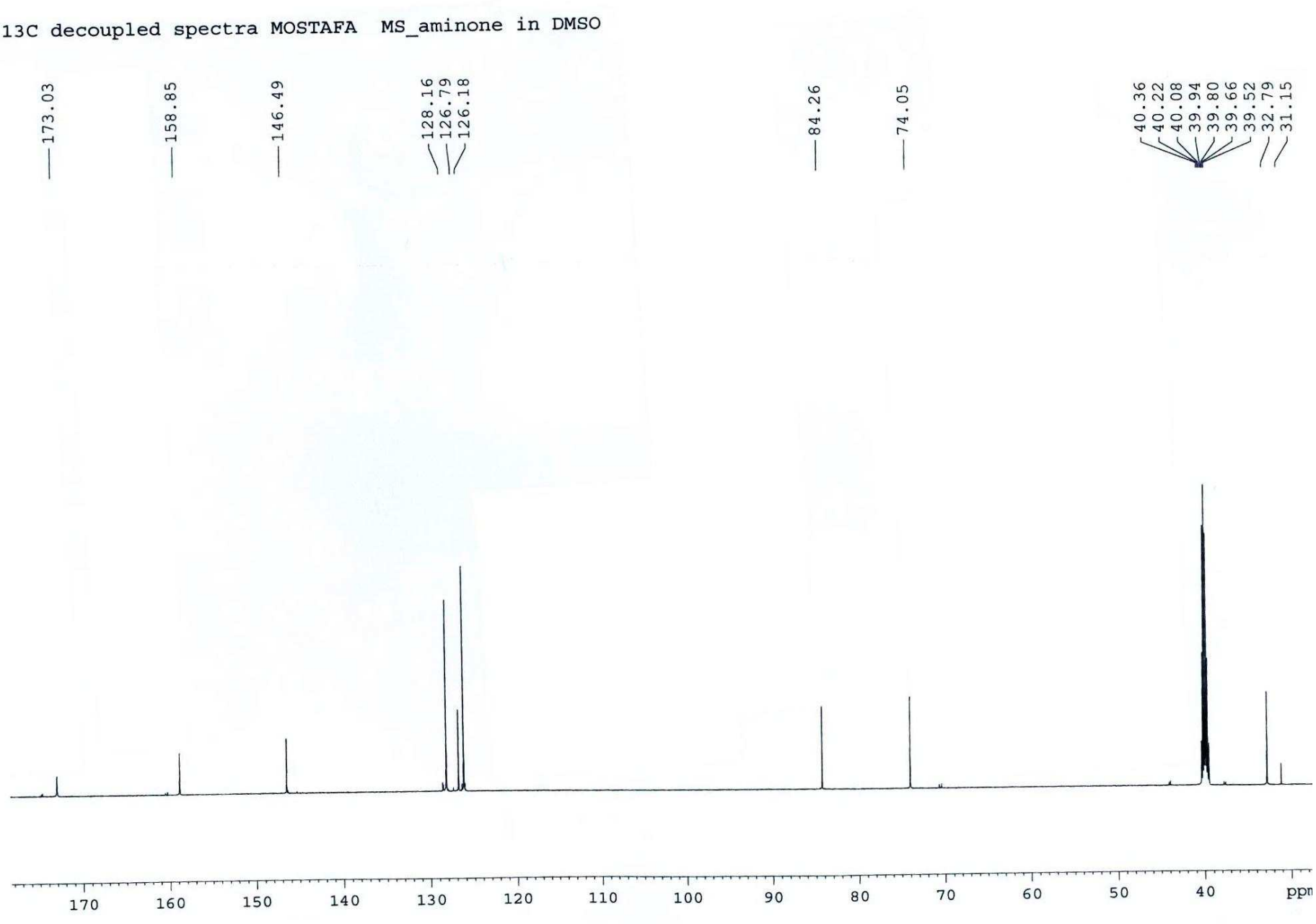
^{13}C NMR for compound **14**



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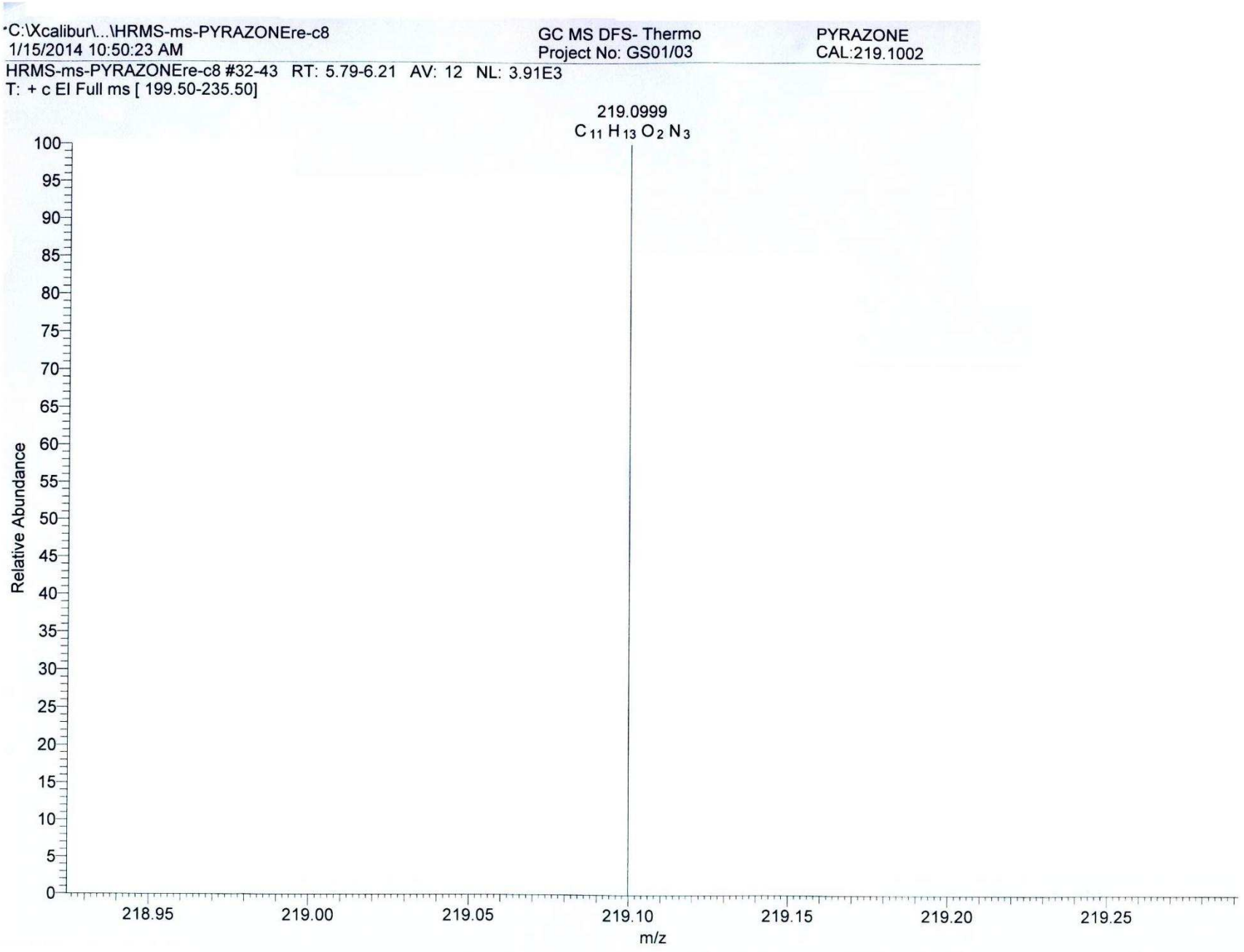
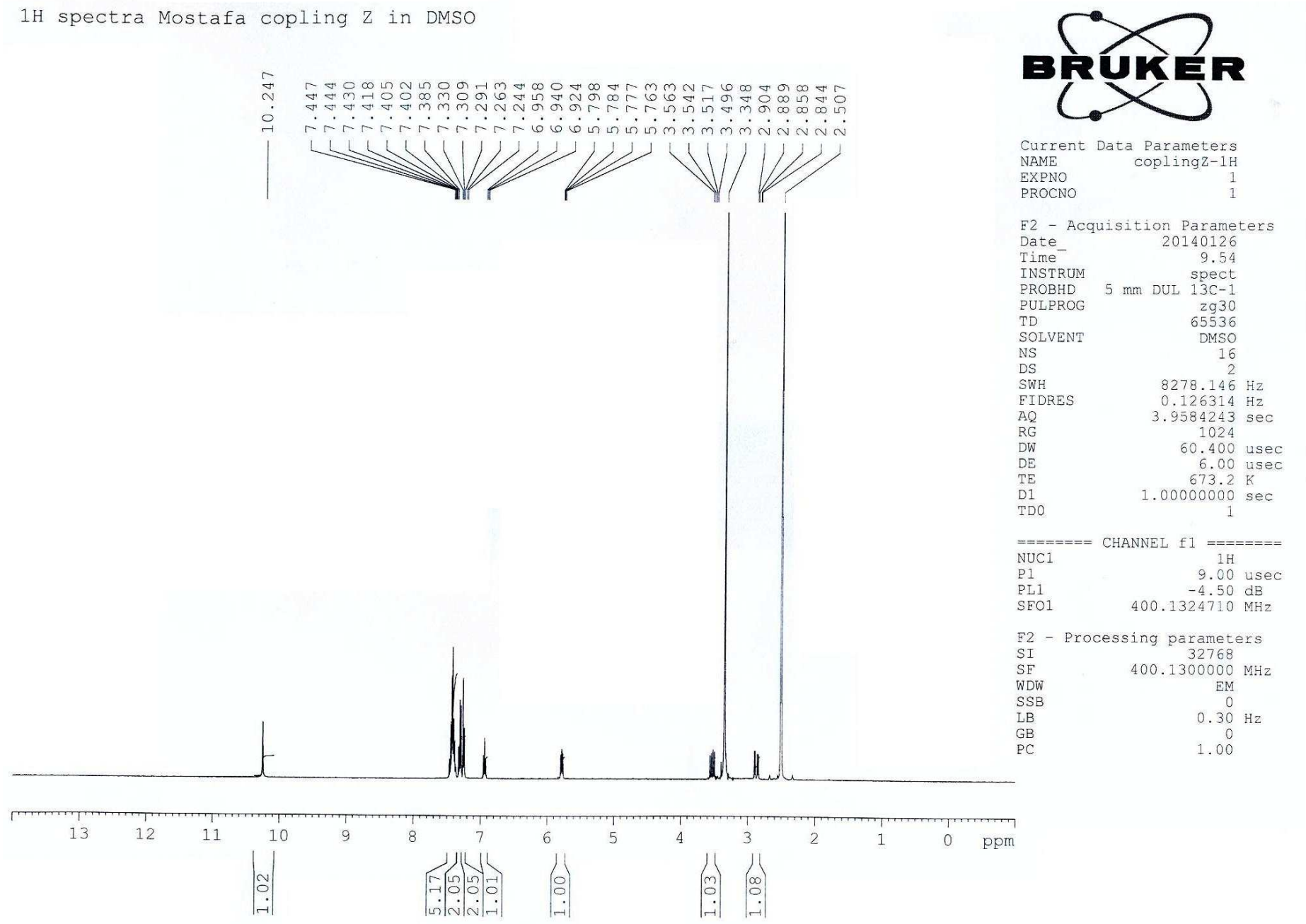
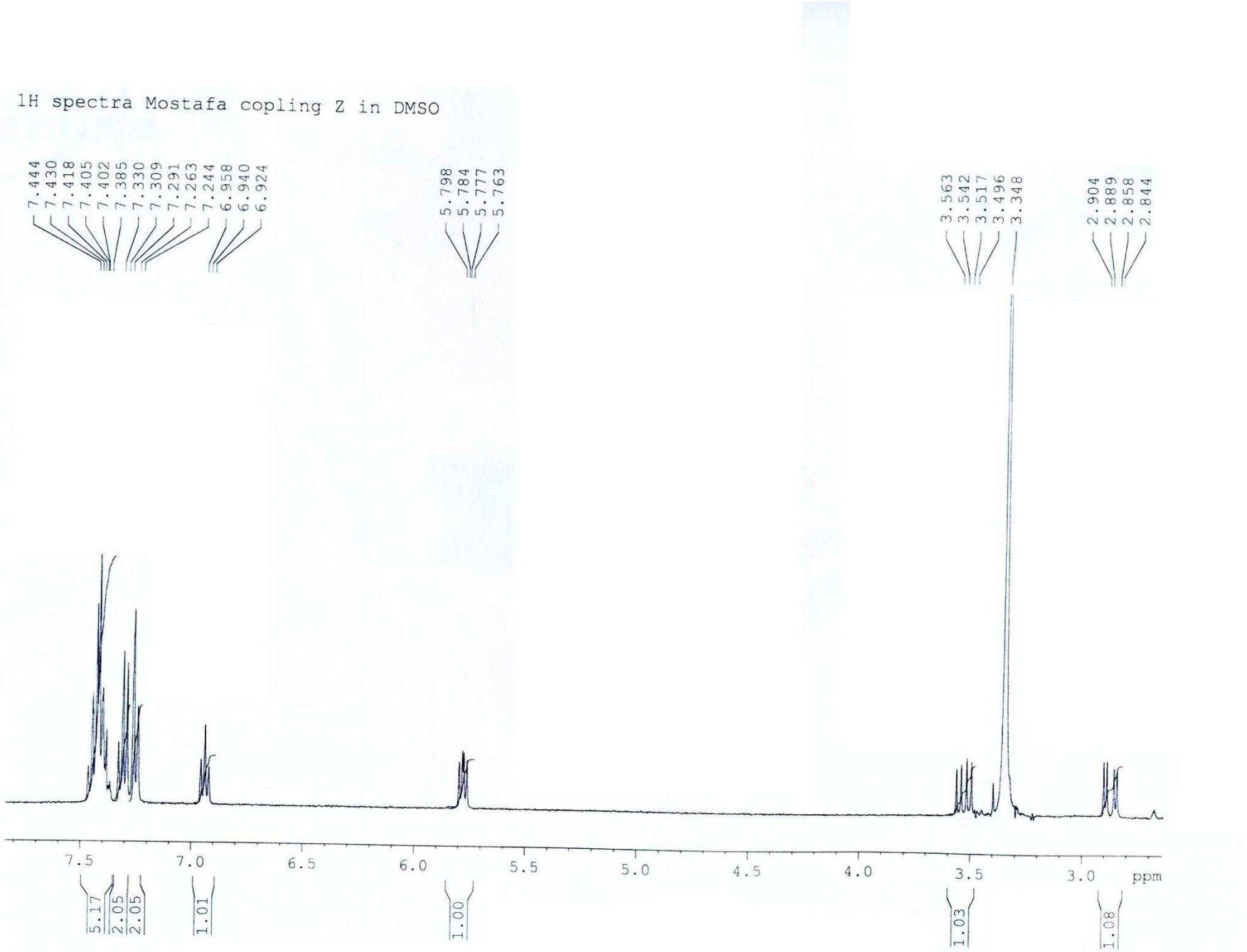


High resolution mass spectra for compound **14**



^{1}H NMR for compound **15**



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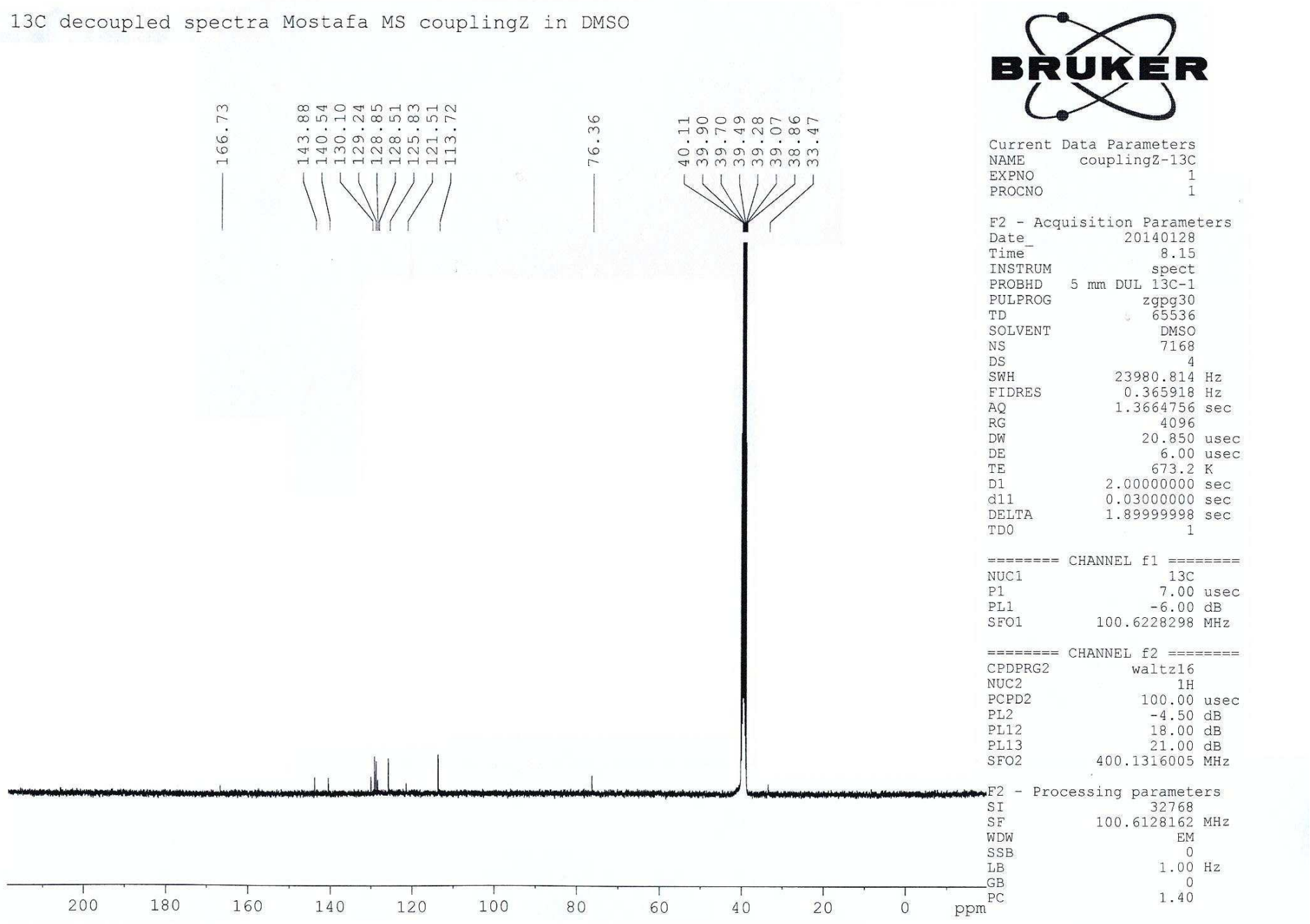

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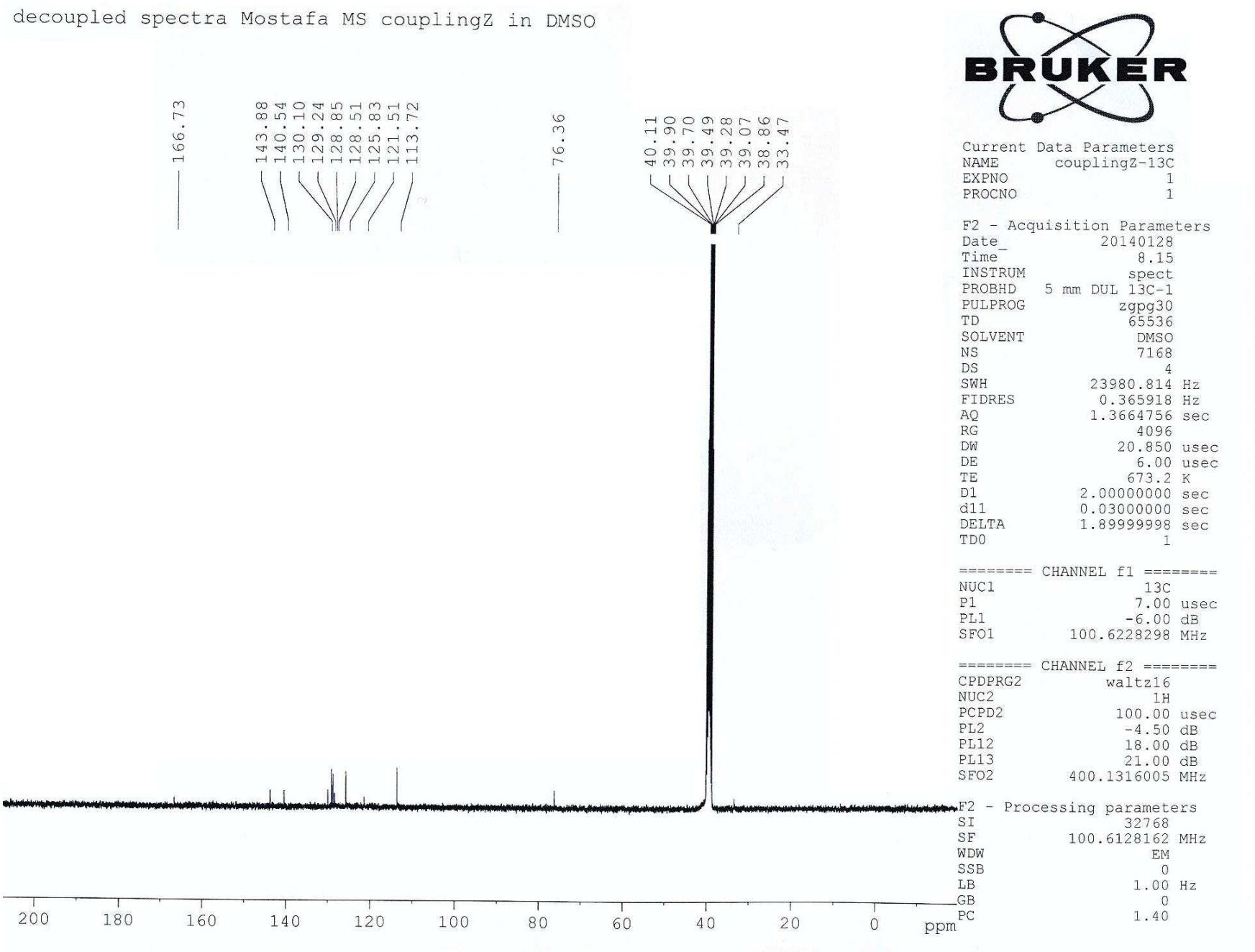

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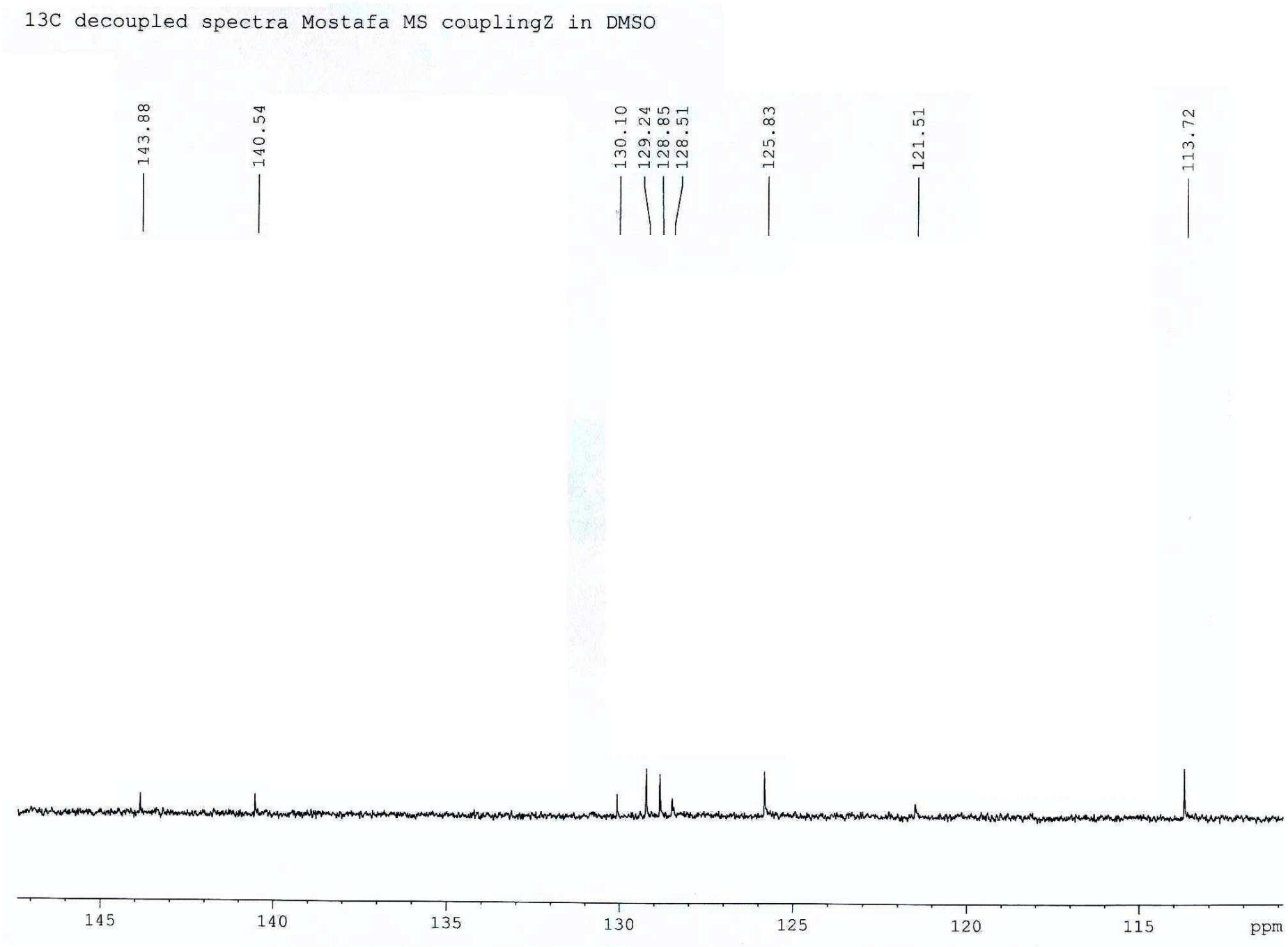

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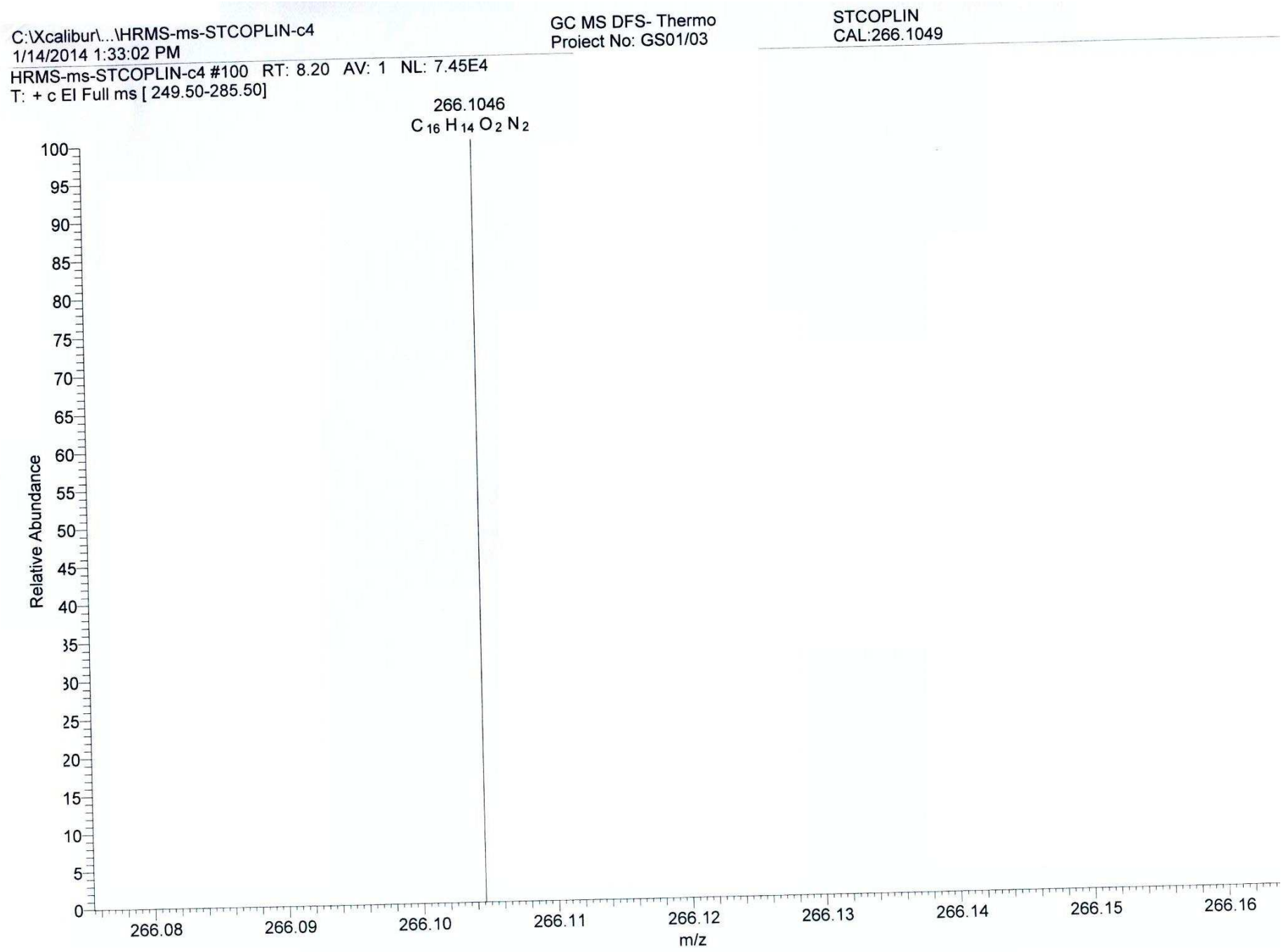
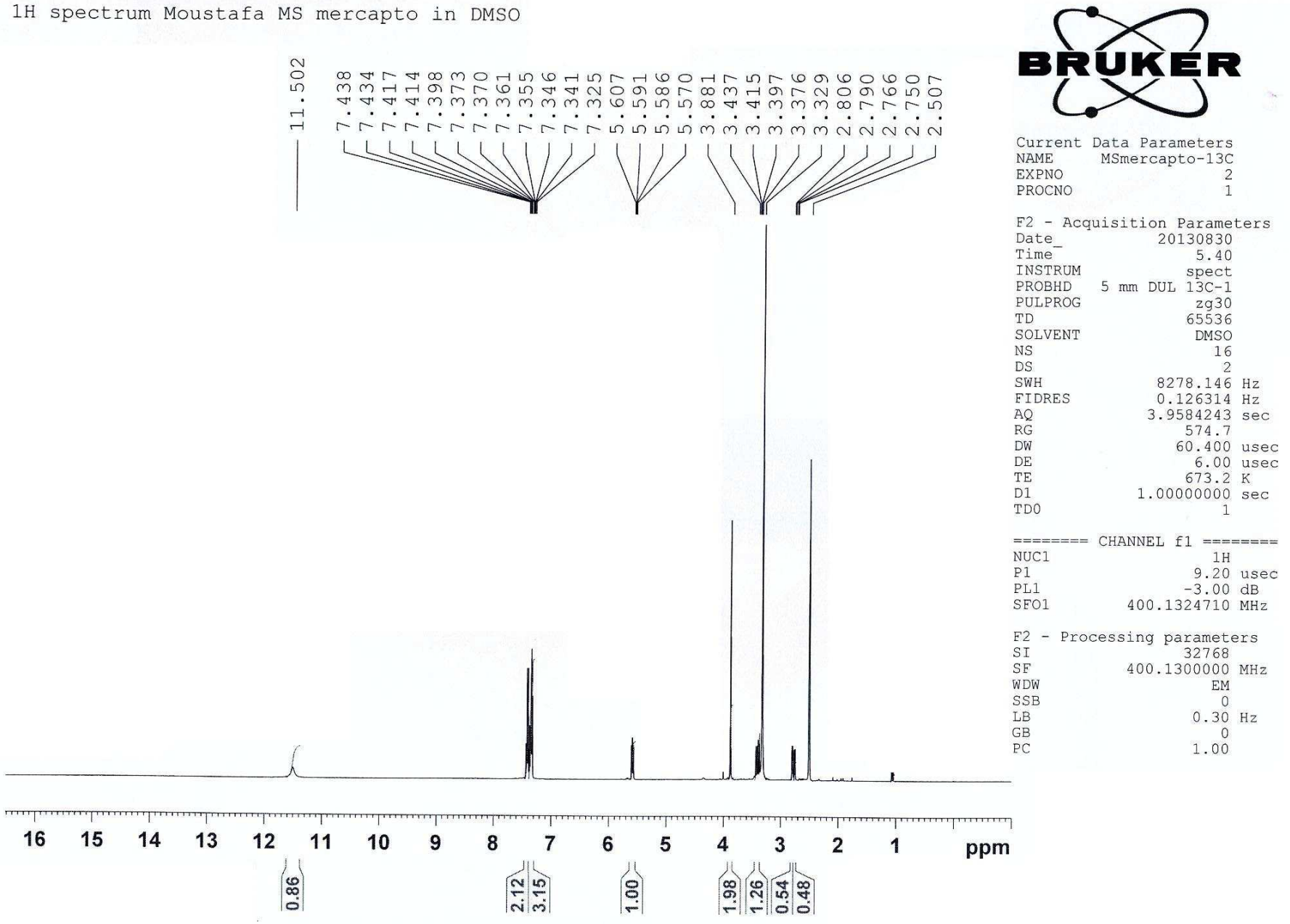


High resolution mass spectra for compound **15**



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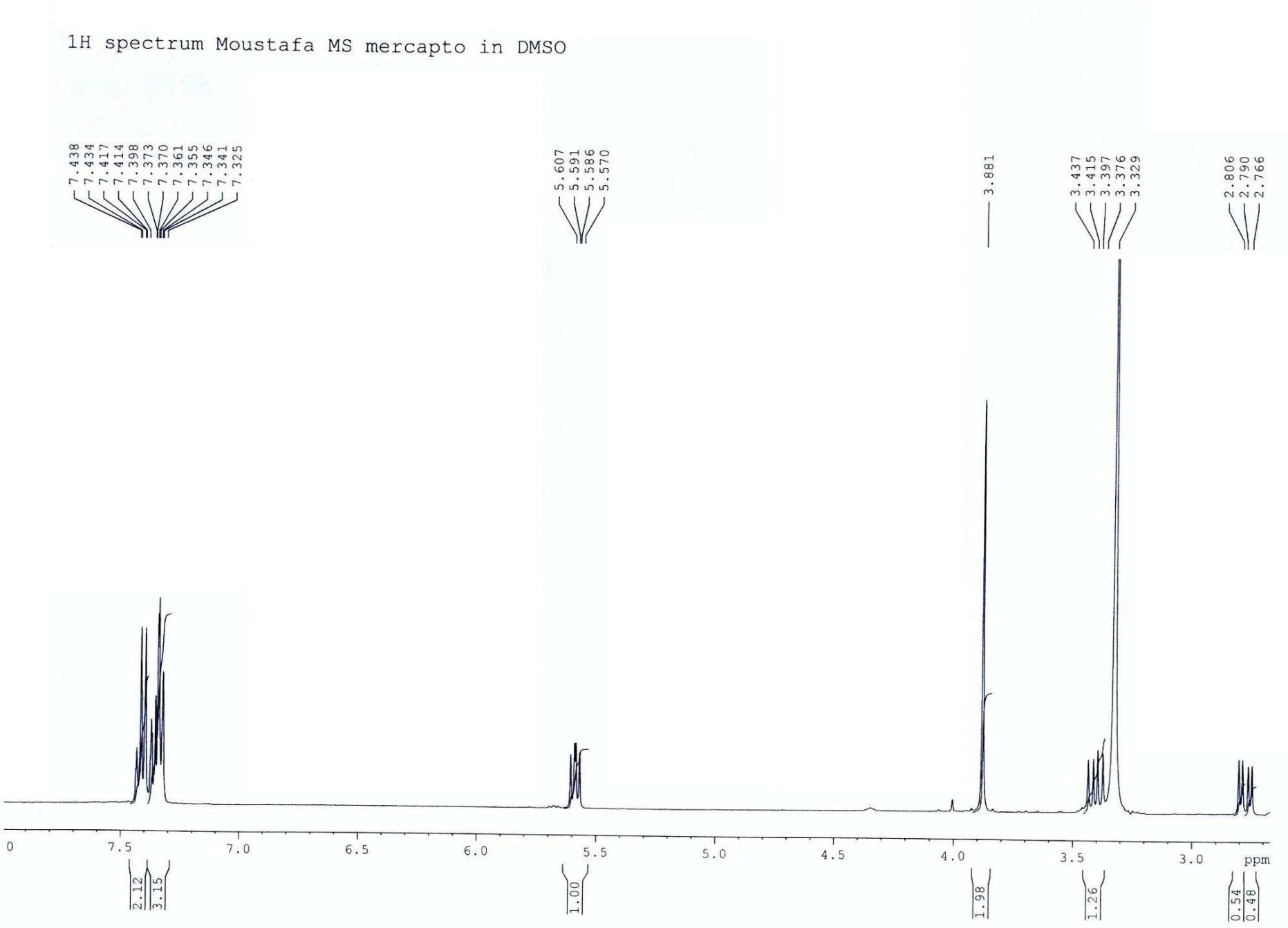

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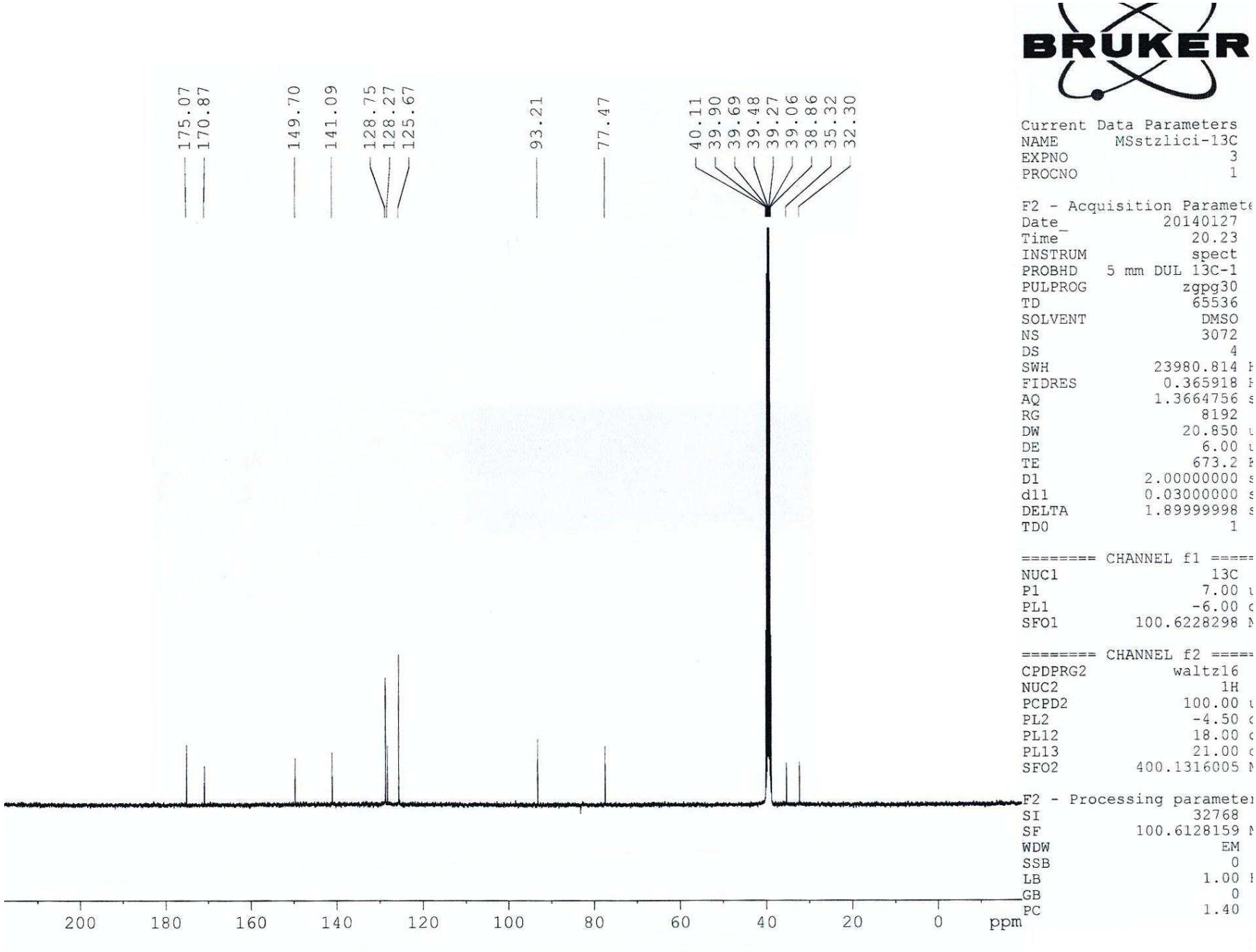

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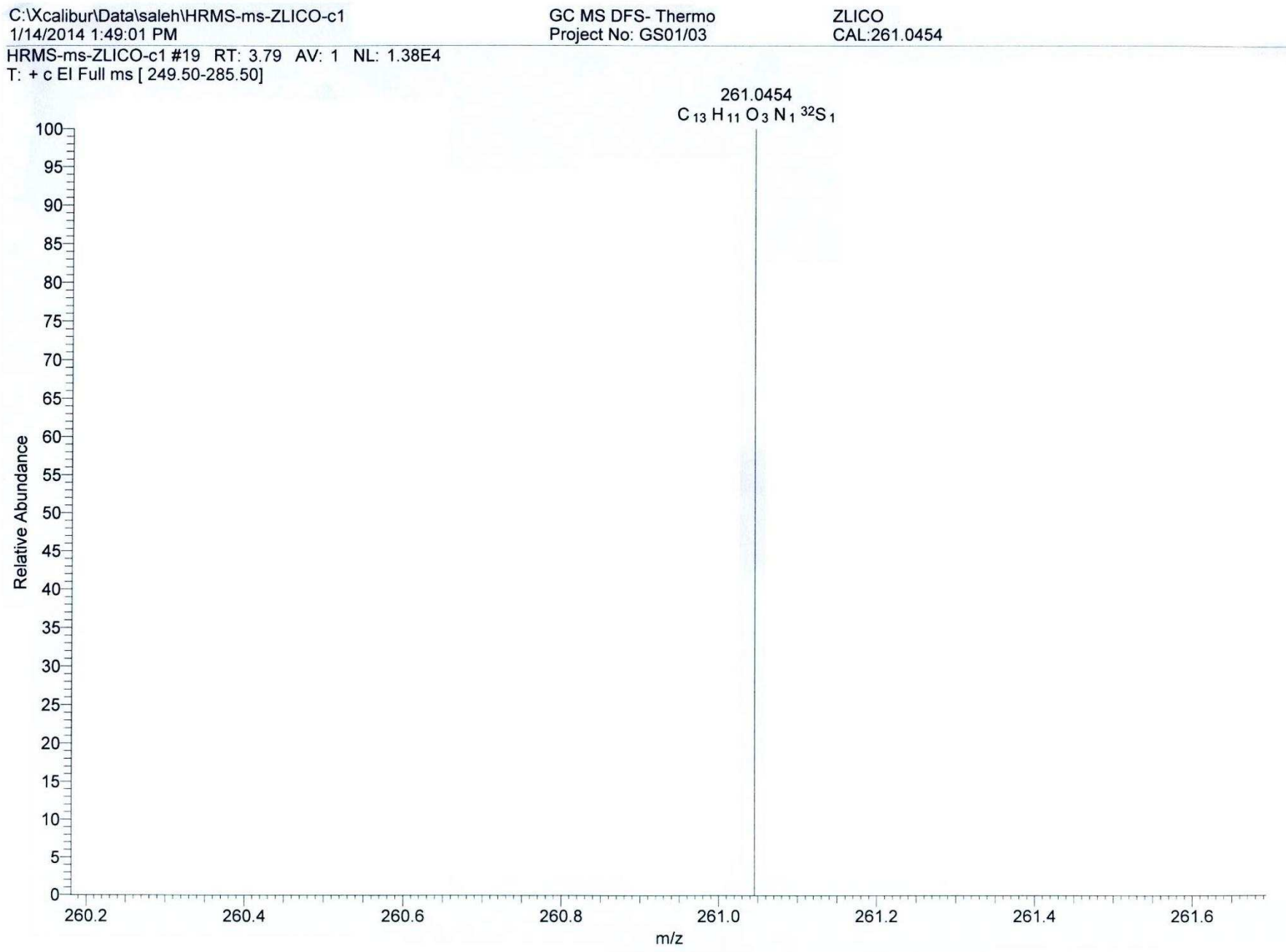
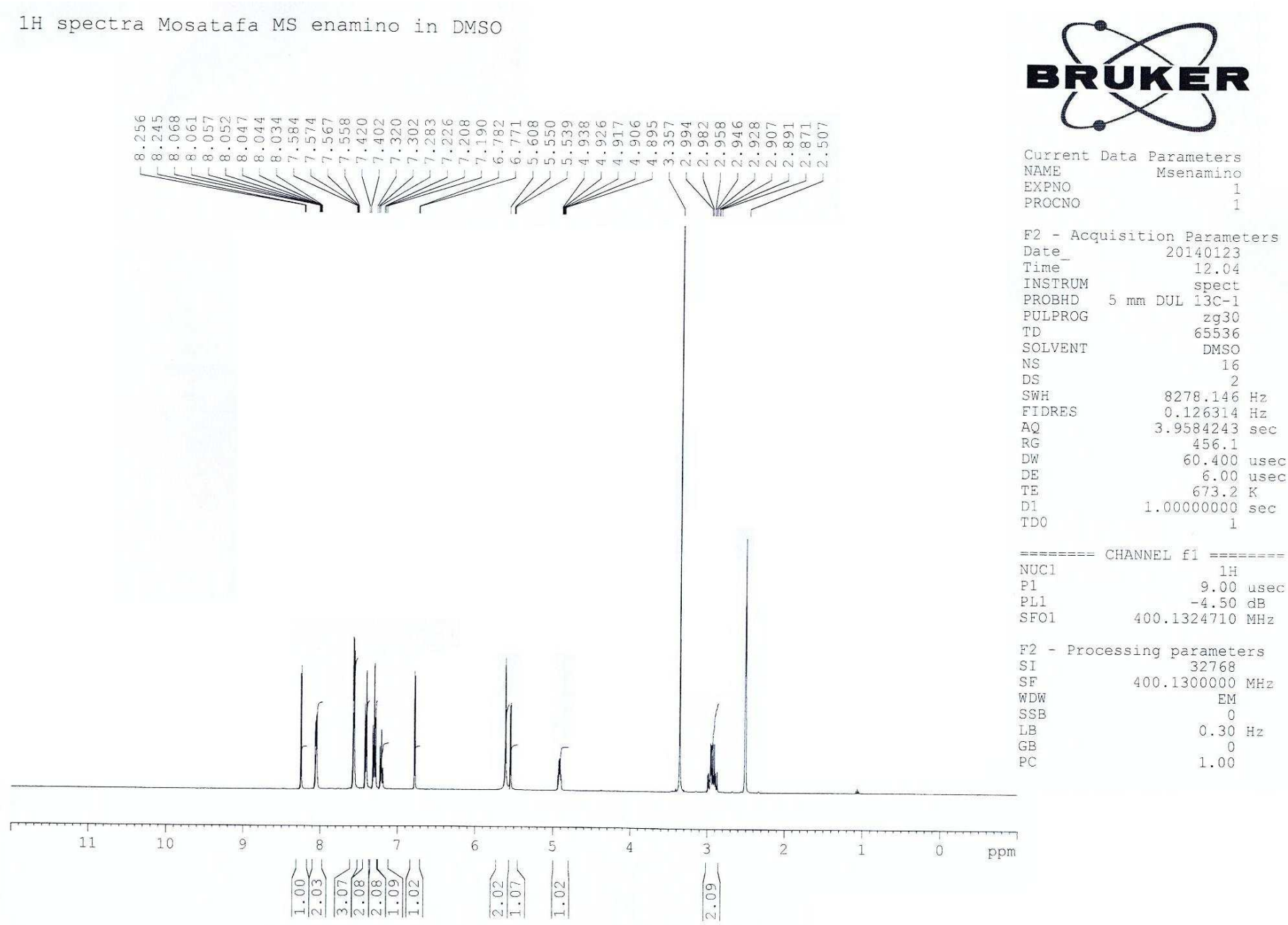
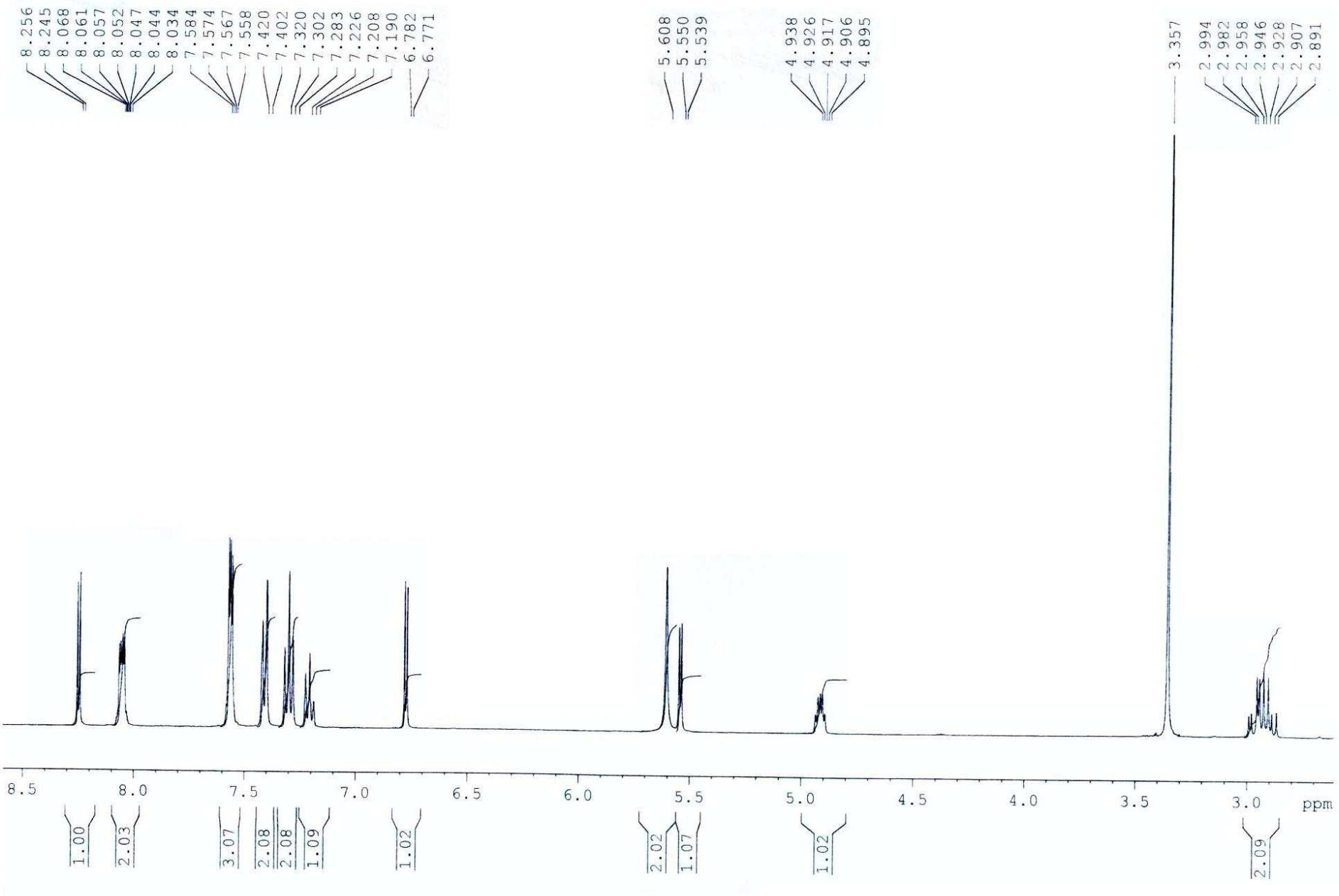


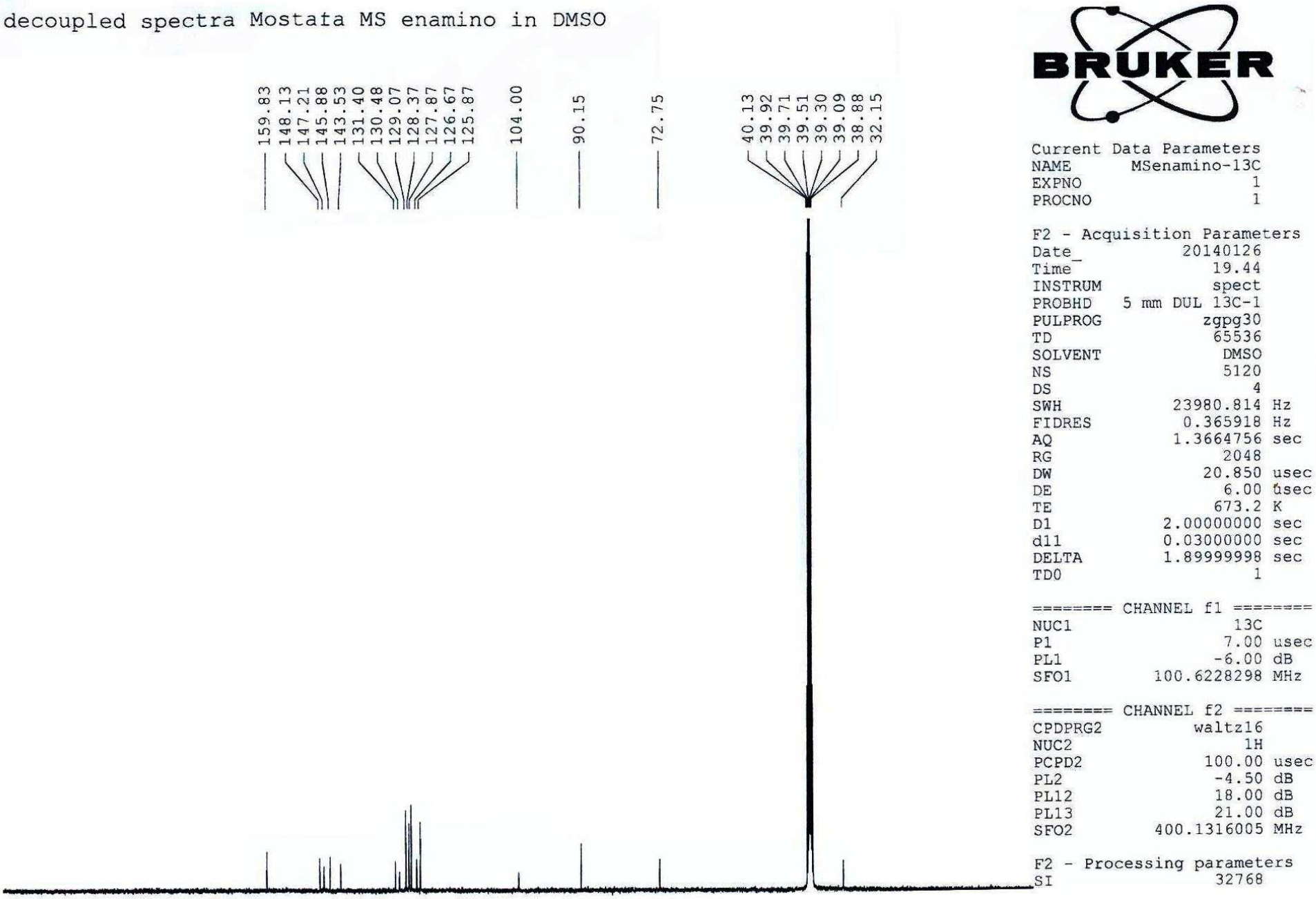
High resolution mass spectra for compound **18**



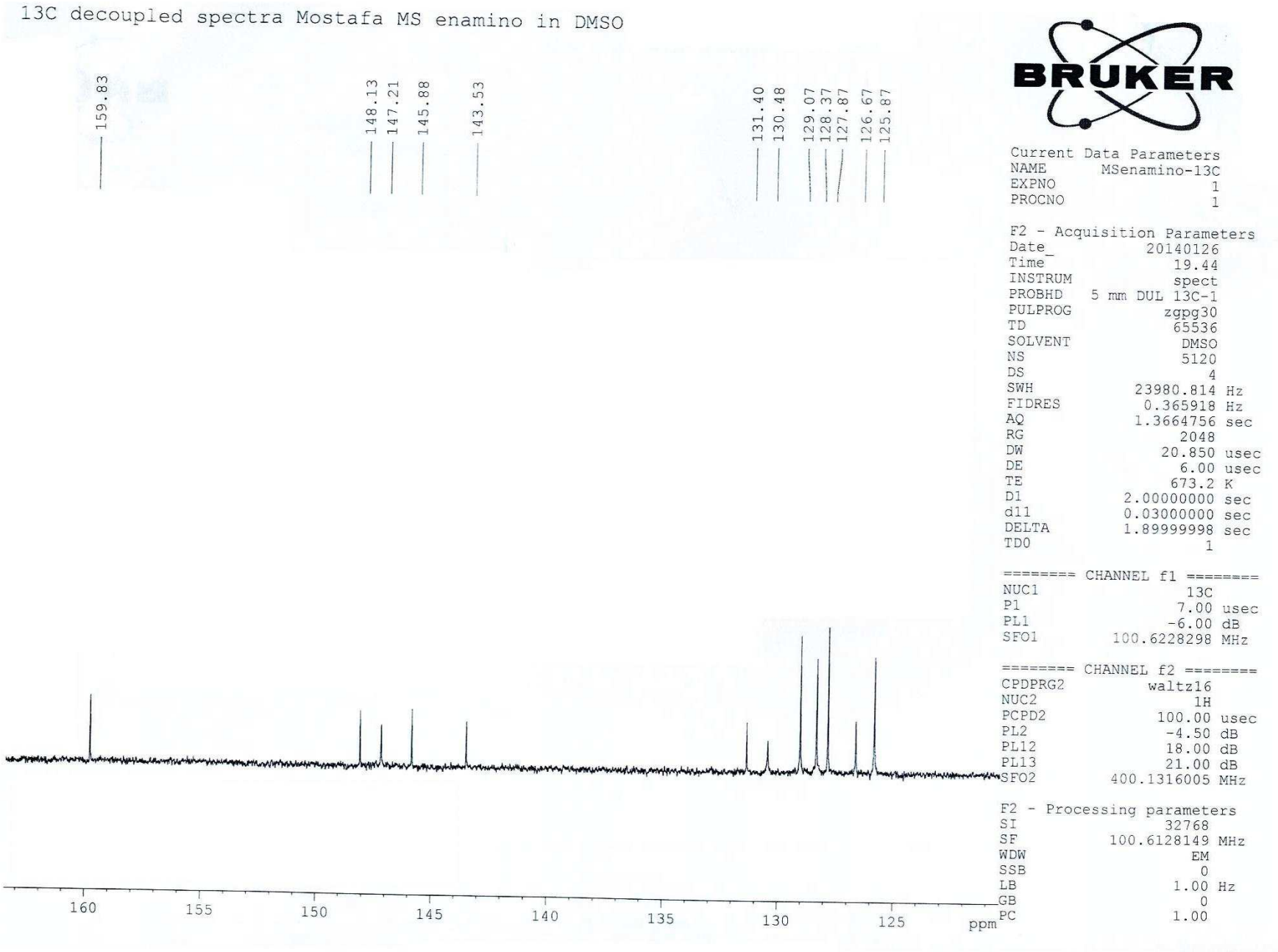
^{1}H NMR for compound **21**



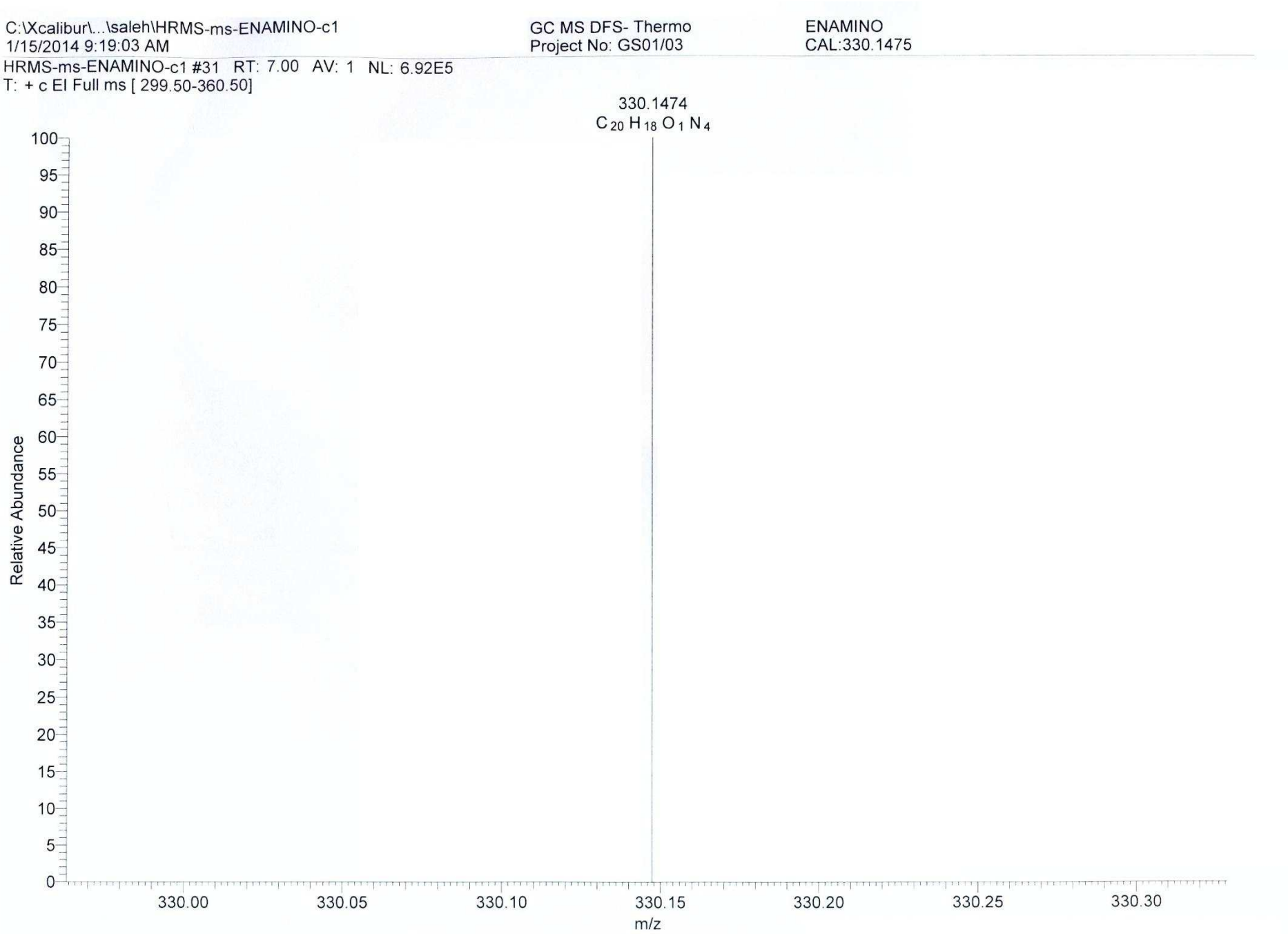
^{1}H NMR for compound **21**



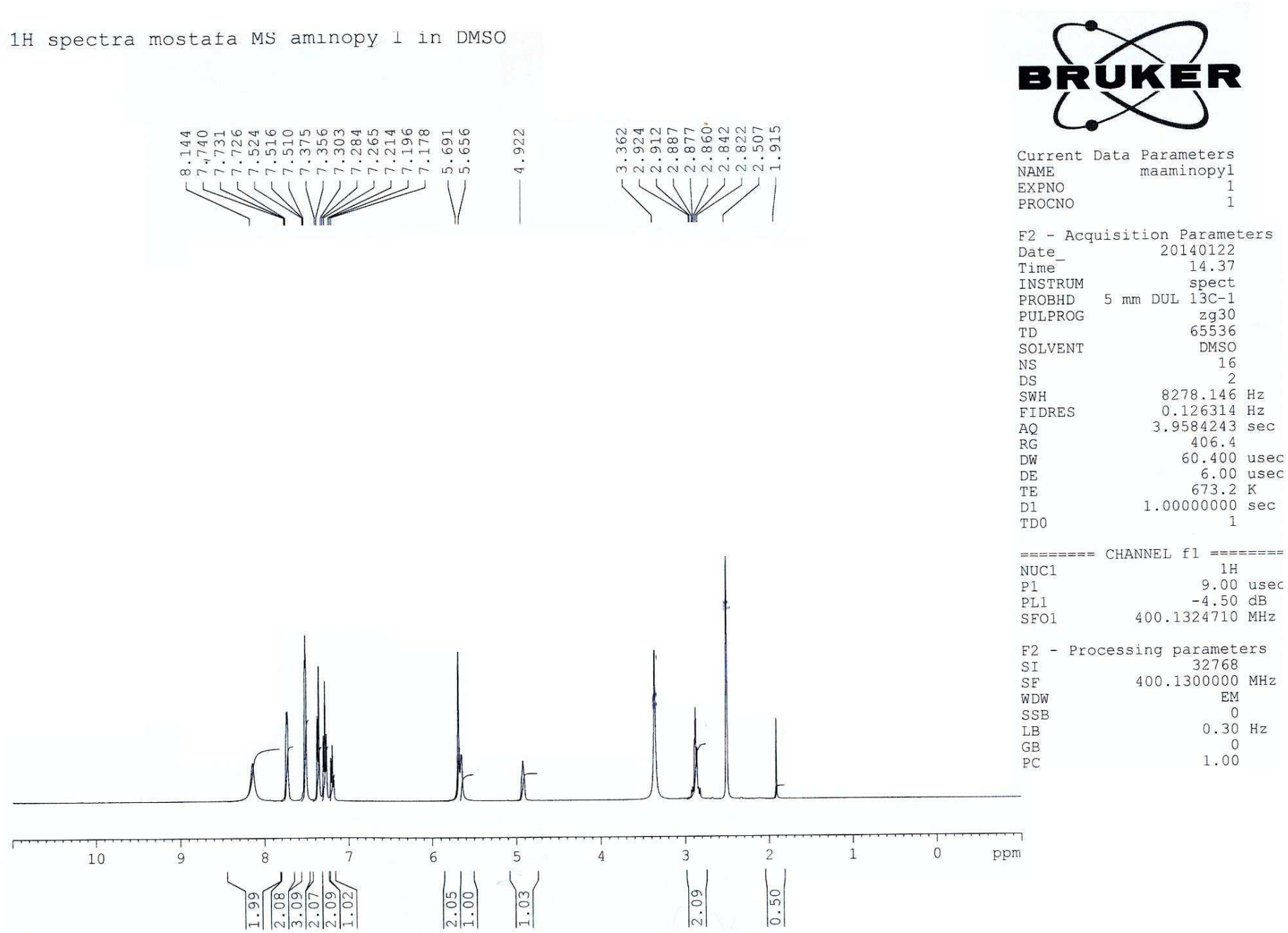
^{13}C NMR for compound **21**



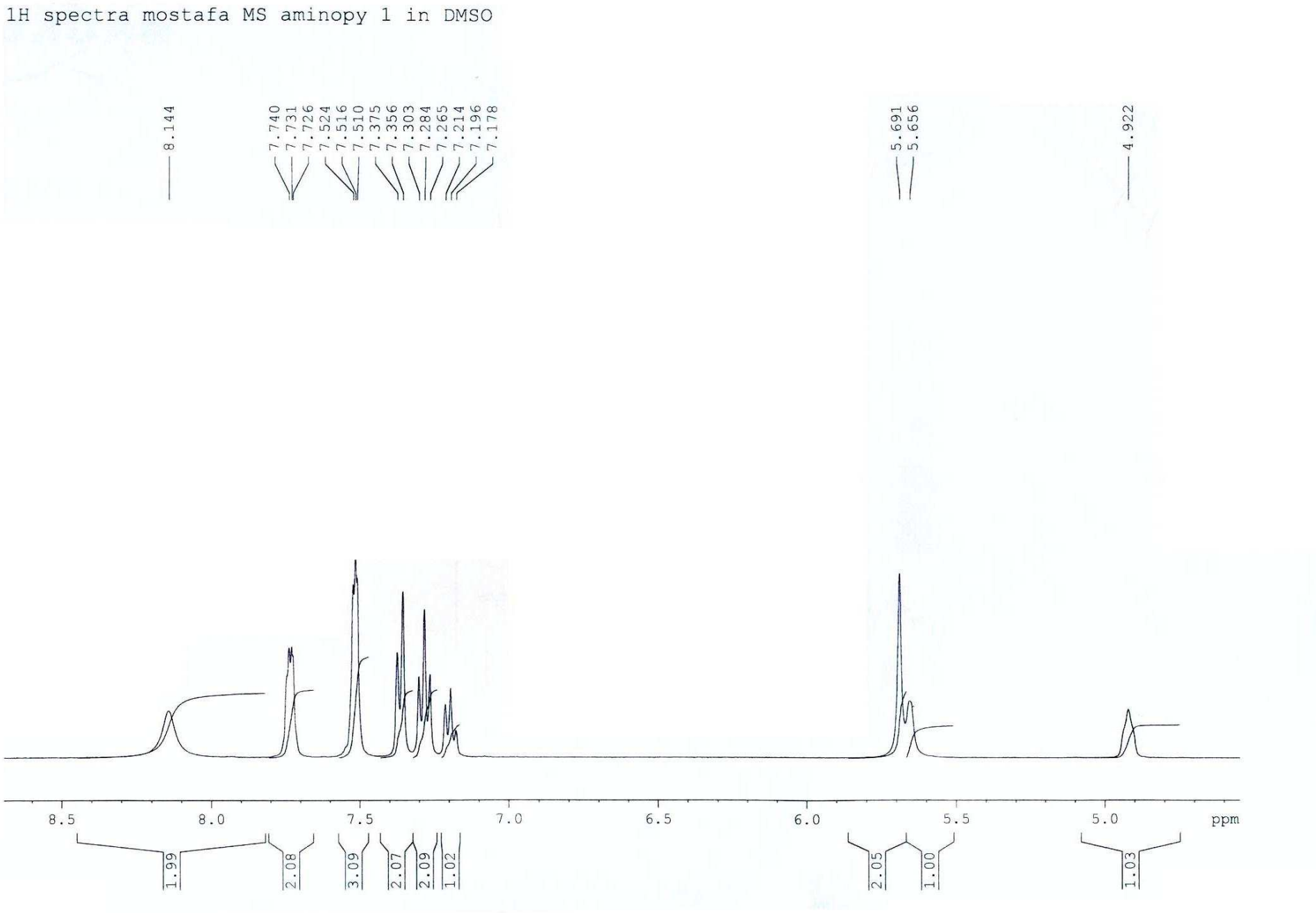
^{13}C NMR for compound **21**



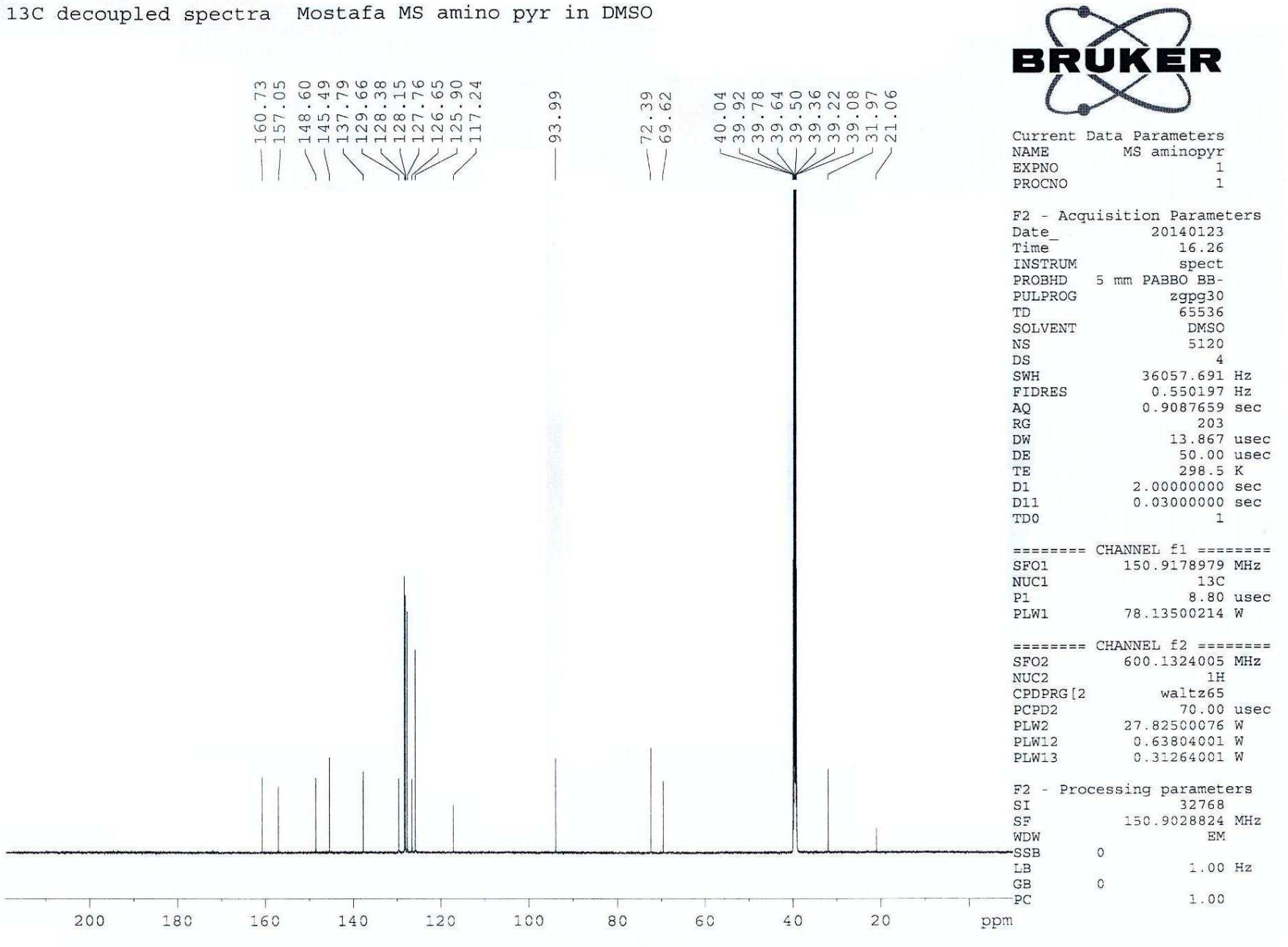
High resolution mass spectra for compound **21**



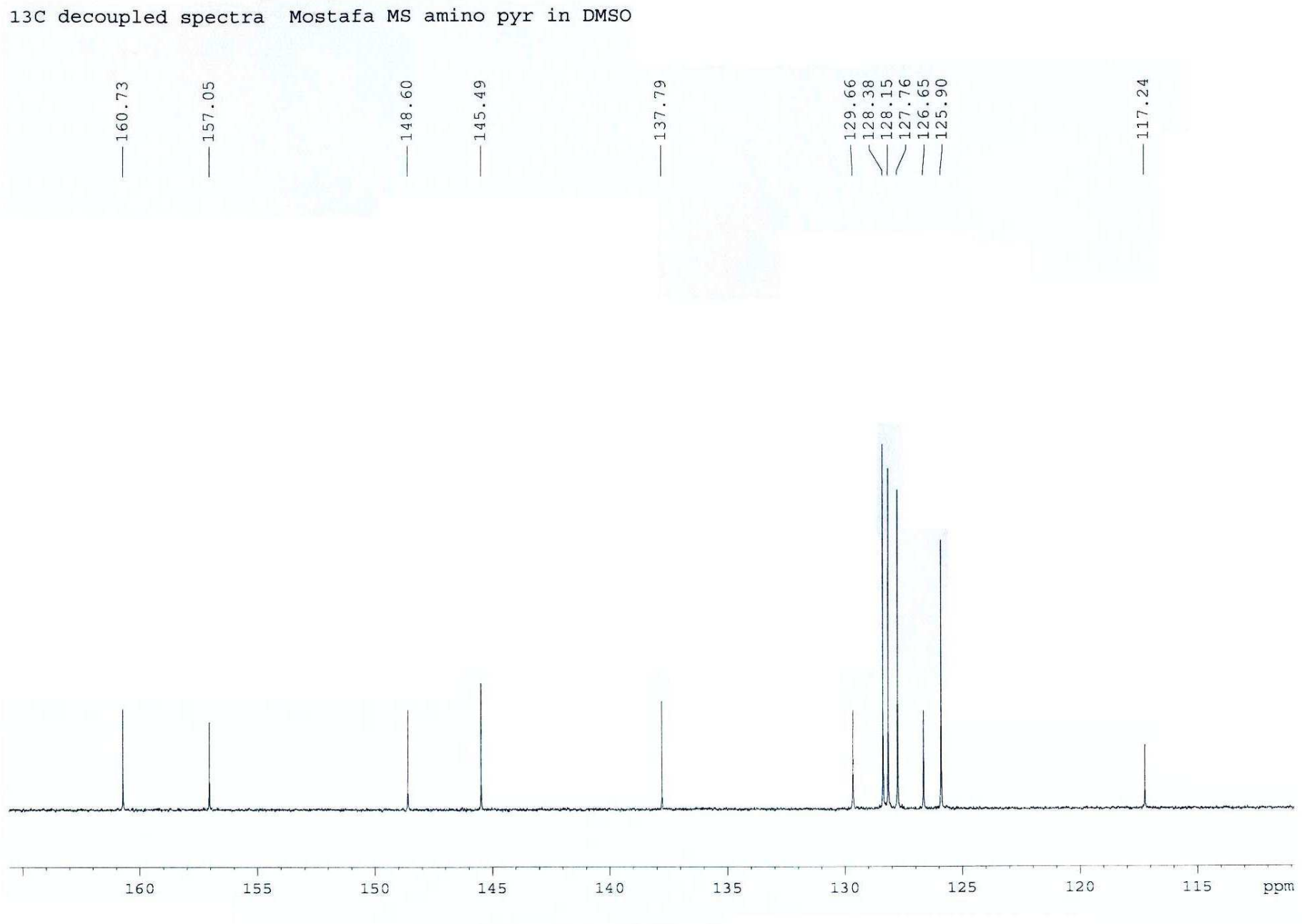
^{1}H NMR for compound **23**



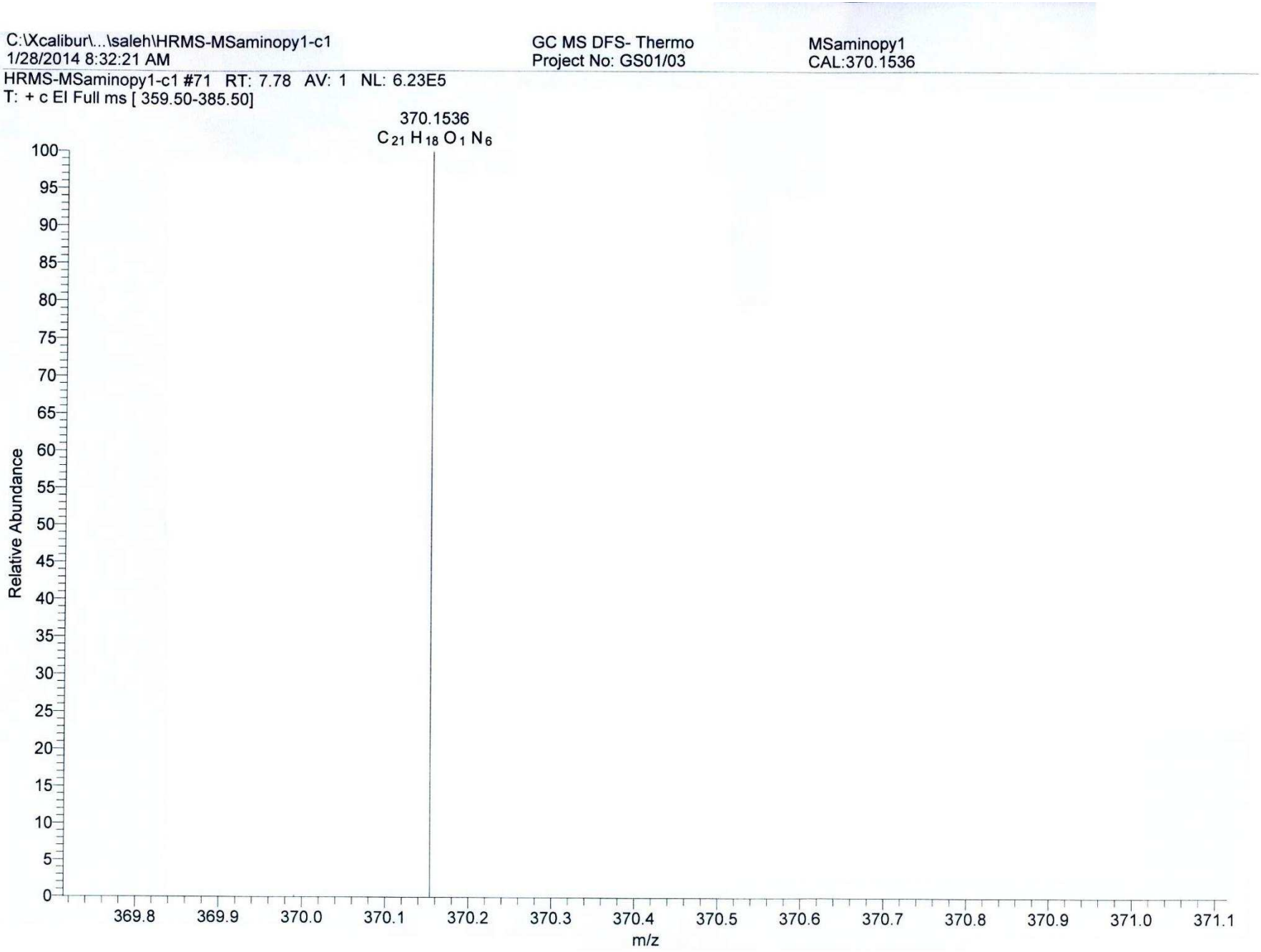
^{1}H NMR for compound **23**



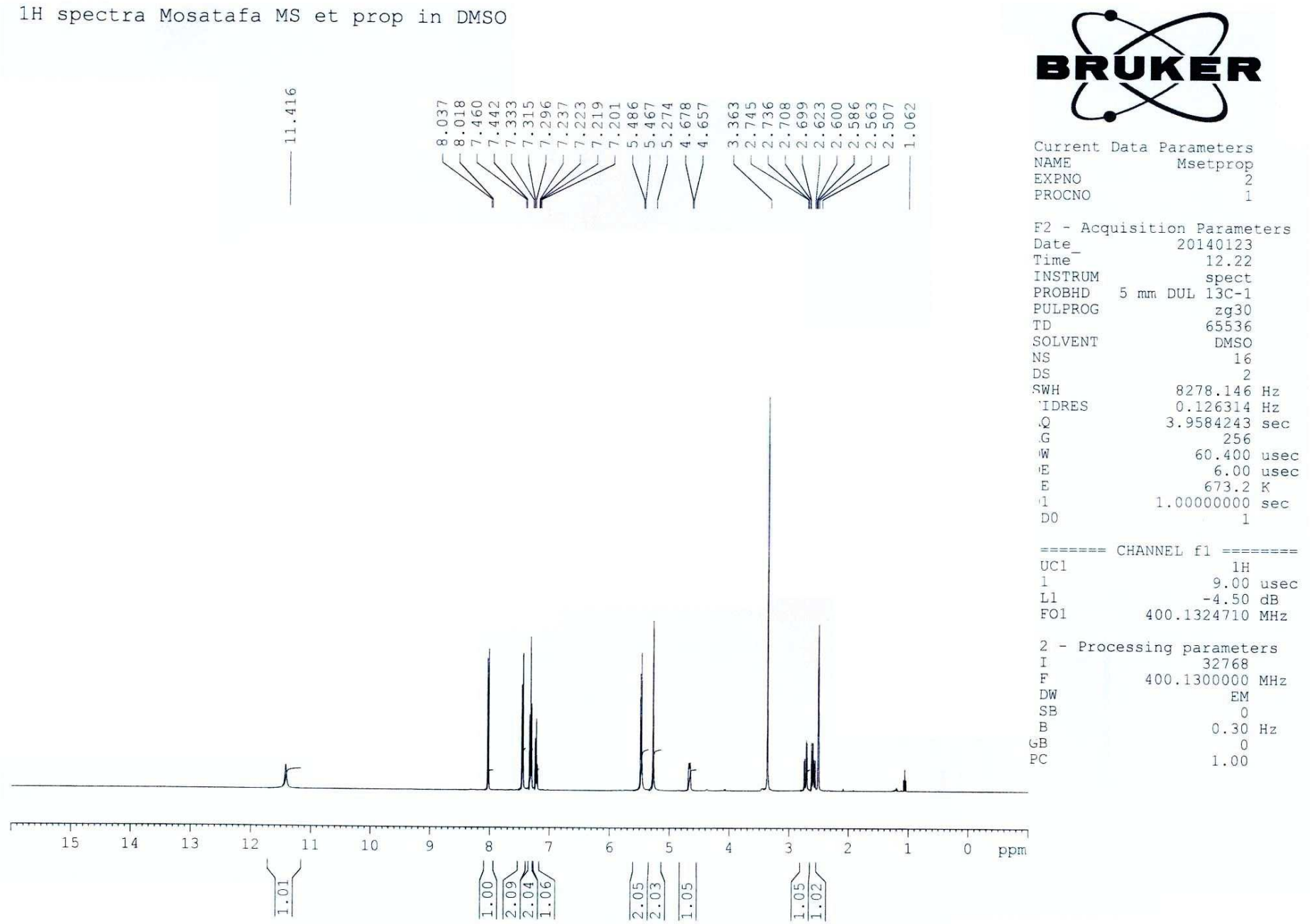
^{13}C NMR for compound **23**



^{13}C NMR for compound **23**



High resolution mass spectra for compound **23**



BRUKER

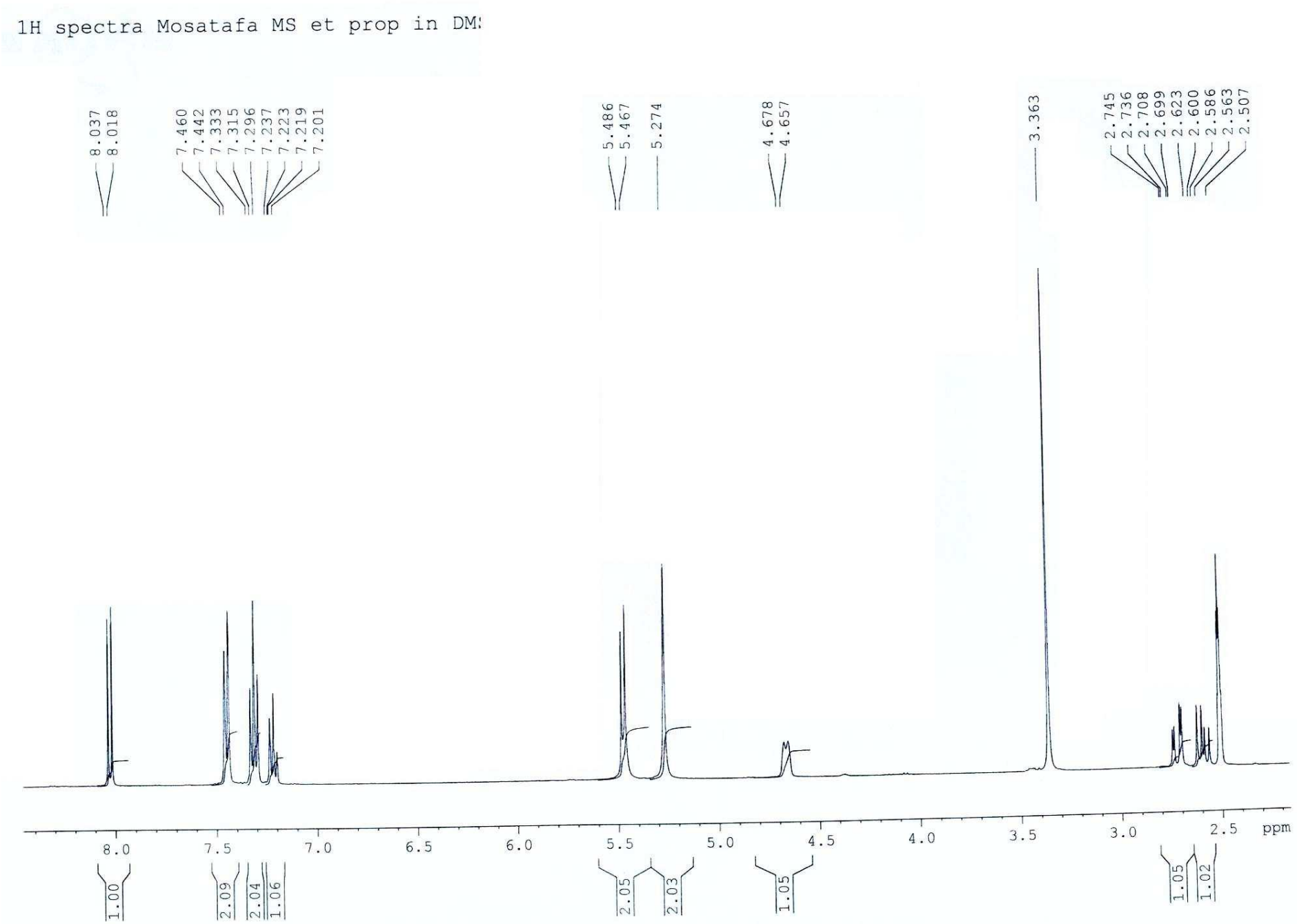
Current Data Parameters
NAME Msetprop
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140123
Time 12.22
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8278.146 Hz
IDRES 0.126314 Hz
AQ 3.9584243 sec
RG 256
DW 60.400 usec
DE 6.00 usec
TE 673.2 K
D1 1.00000000 sec
D0 1

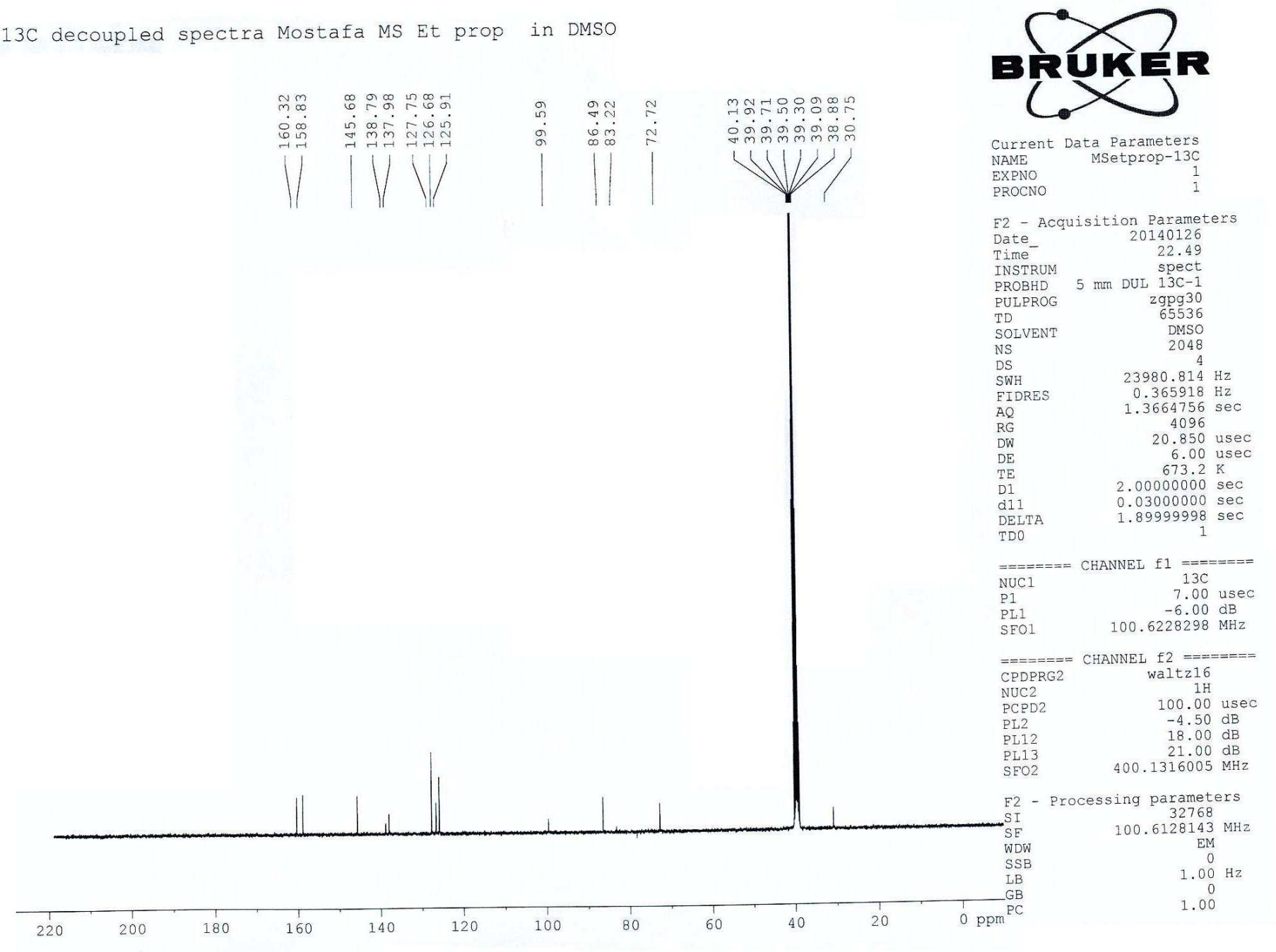
======= CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 -4.50 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

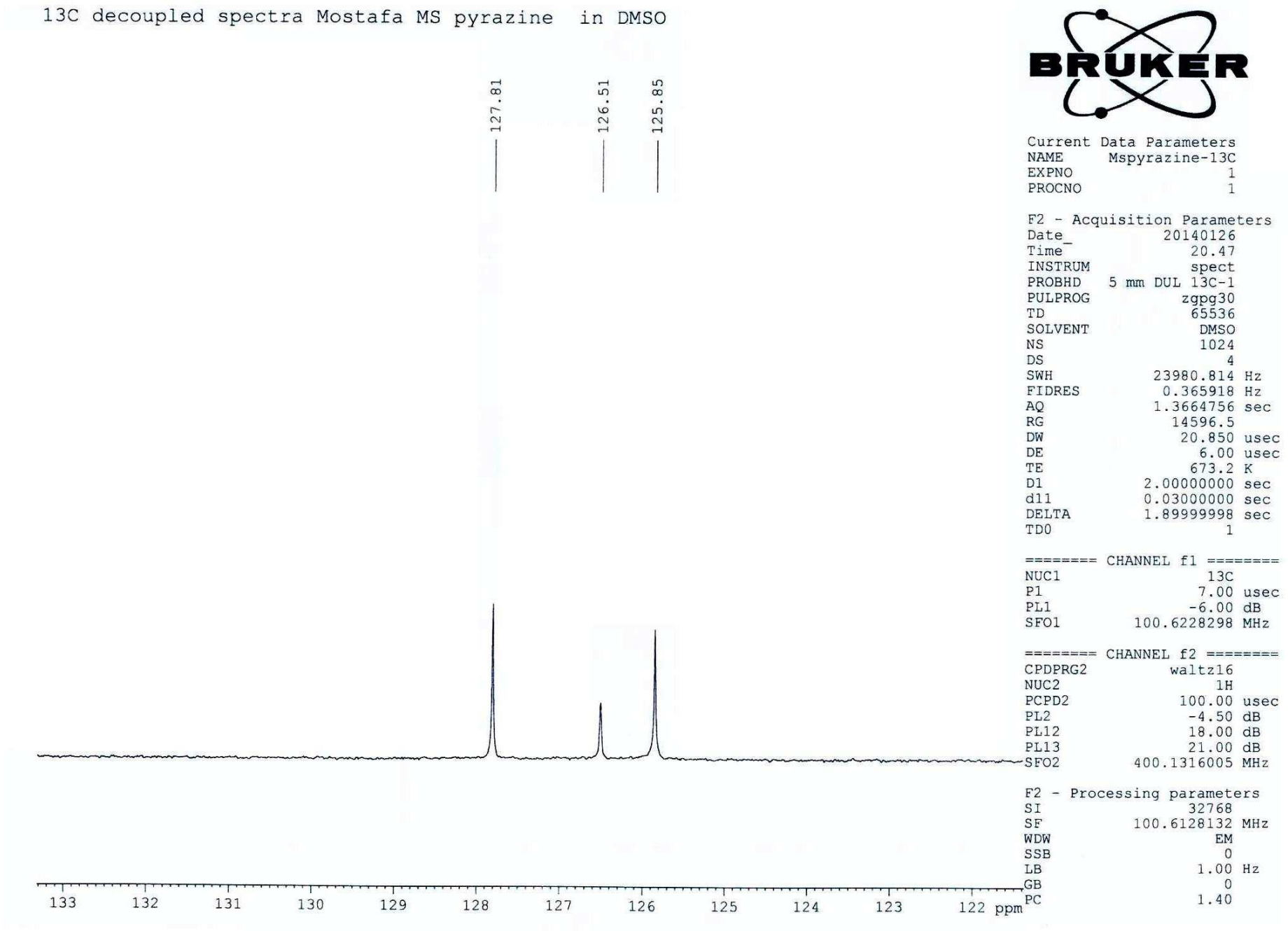
[1]H NMR for compound **26a**



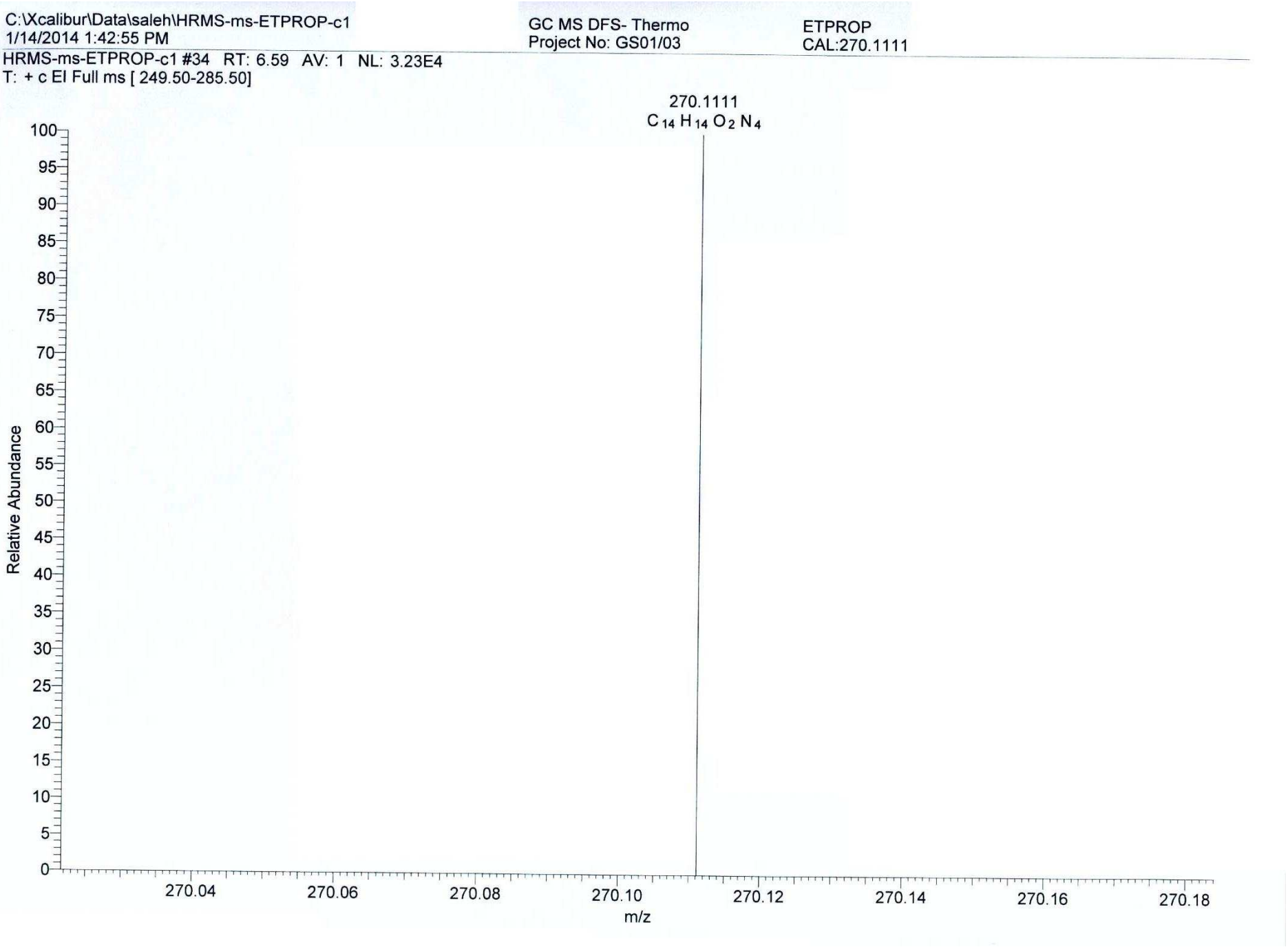
[1]H NMR for compound **26a**



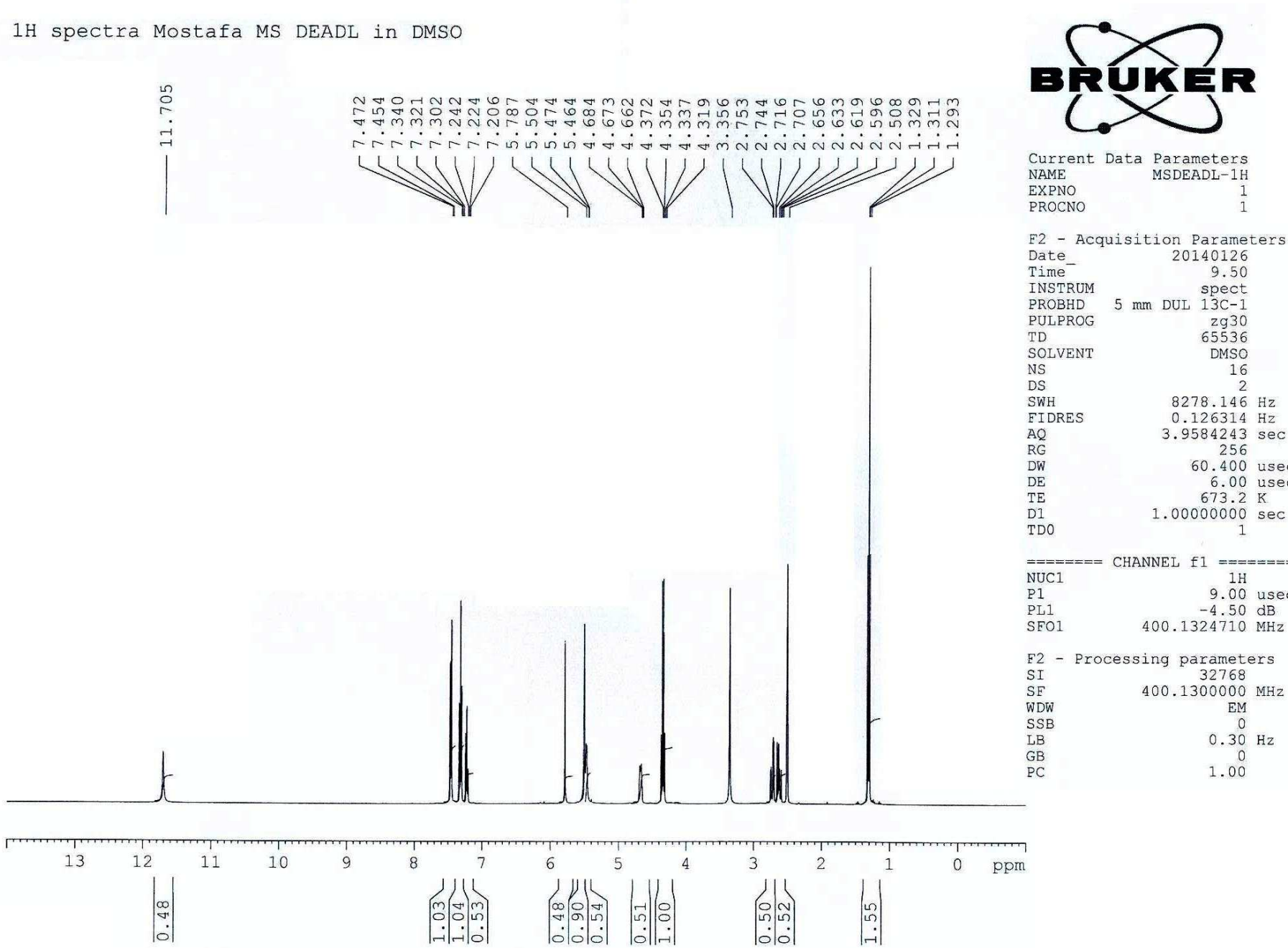
^{13}C NMR for compound **26a**



^{13}C NMR for compound **26a**



High resolution mass spectra for compound **26a**



Current Data Parameters

NAME	MSDEADL-1H
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20140126
Time	9.50
INSTRUM	spect
PROBHD	5 mm DUL 13C-1
PULPROG	zg30
TD	65536
SOLVENT	DMSO
NS	16
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	256
DW	60.400 usec
DE	6.00 usec
TE	673.2 K
D1	1.00000000 sec
TD0	1

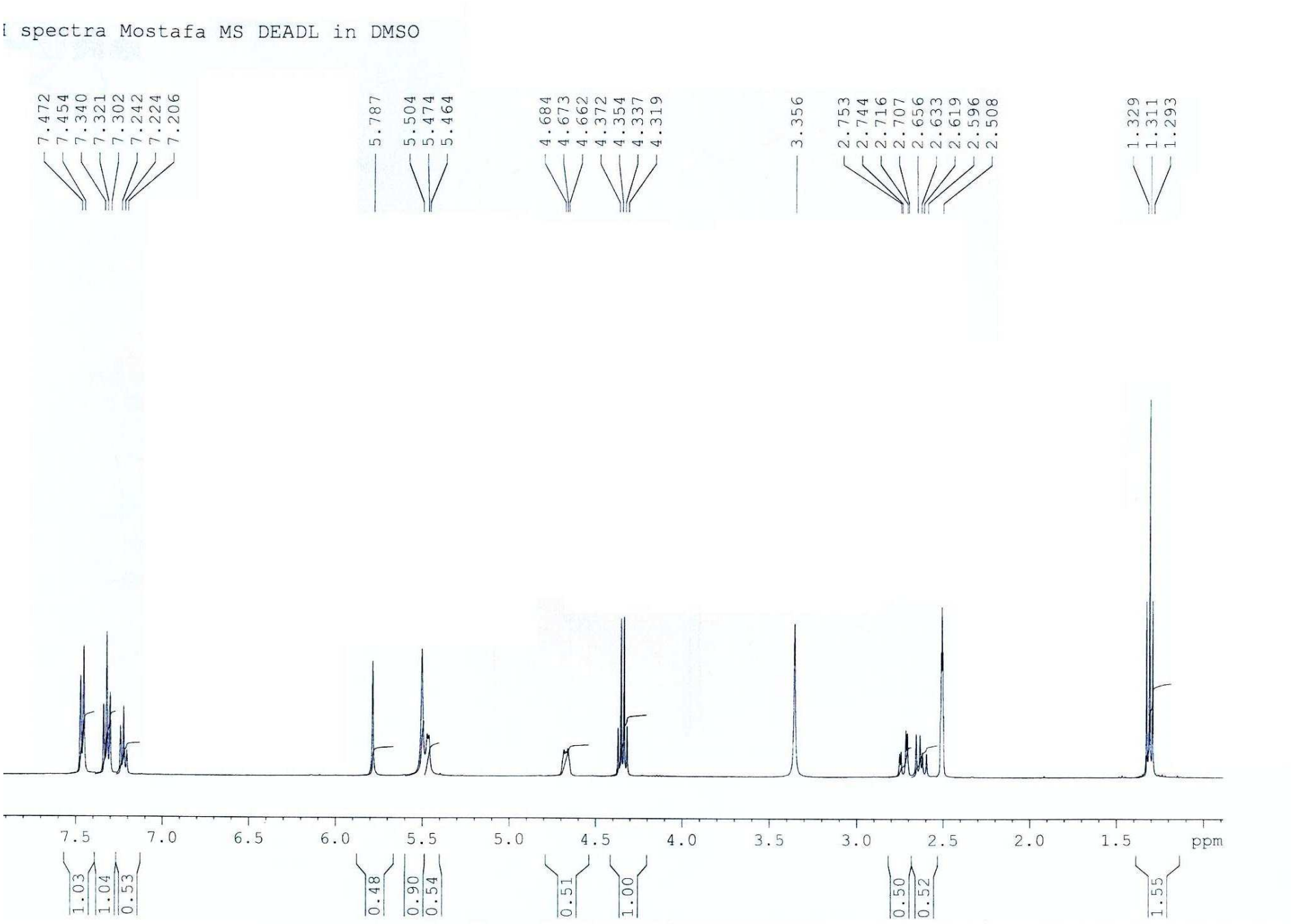
======== CHANNEL f1 ========

NUC1	1H
P1	9.00 usec
PL1	-4.50 dB
SFO1	400.1324710 MHz

F2 - Processing parameters

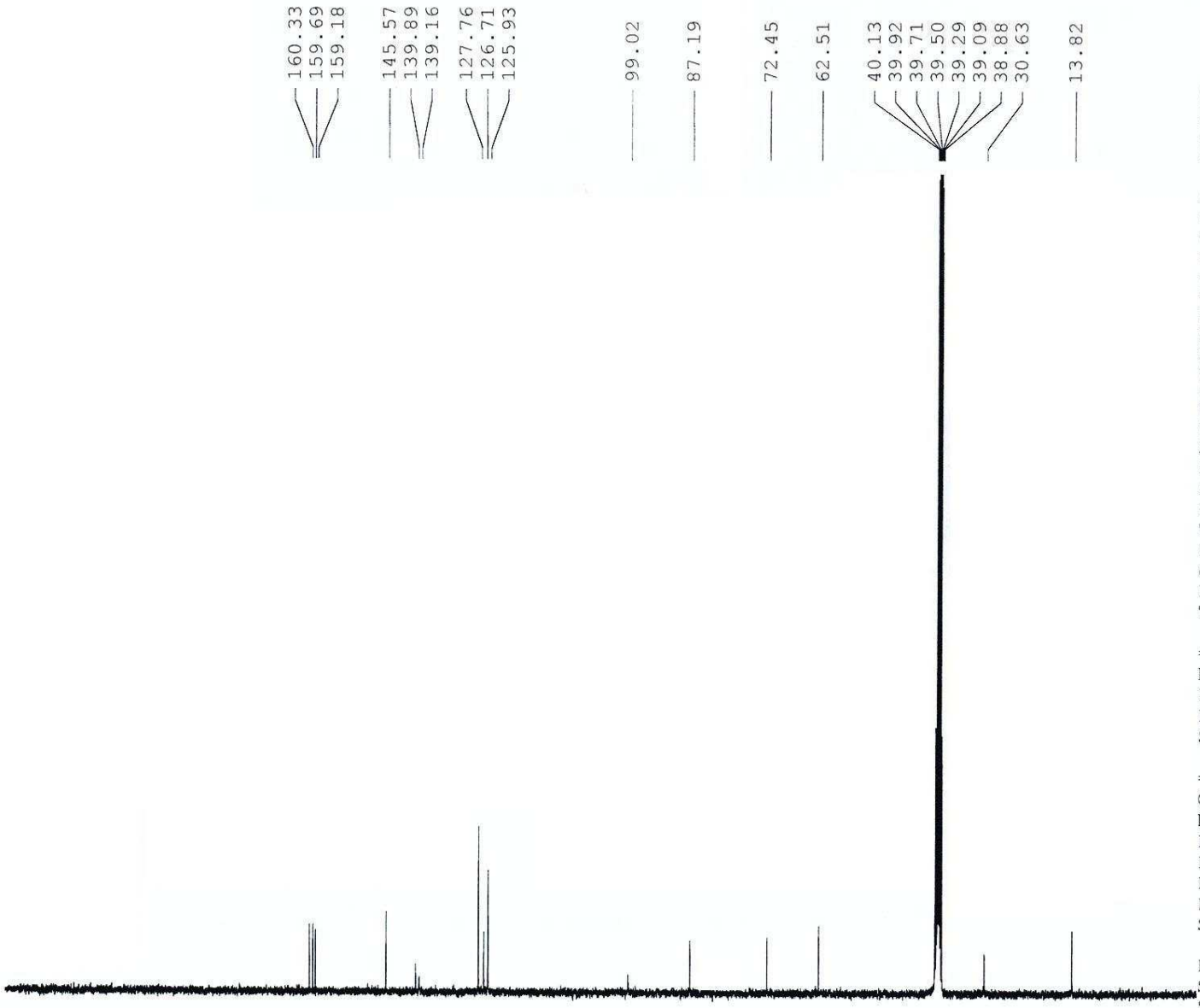
SI	32768
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

^{1}H NMR for compound **26b**



^{1}H NMR for compound **26b**

13C decoupled spectra Mostafa MS deadL in DMSO



Current Data Parameters
NAME MSdeadL-13C
EXPNO 1
PROCNO 1

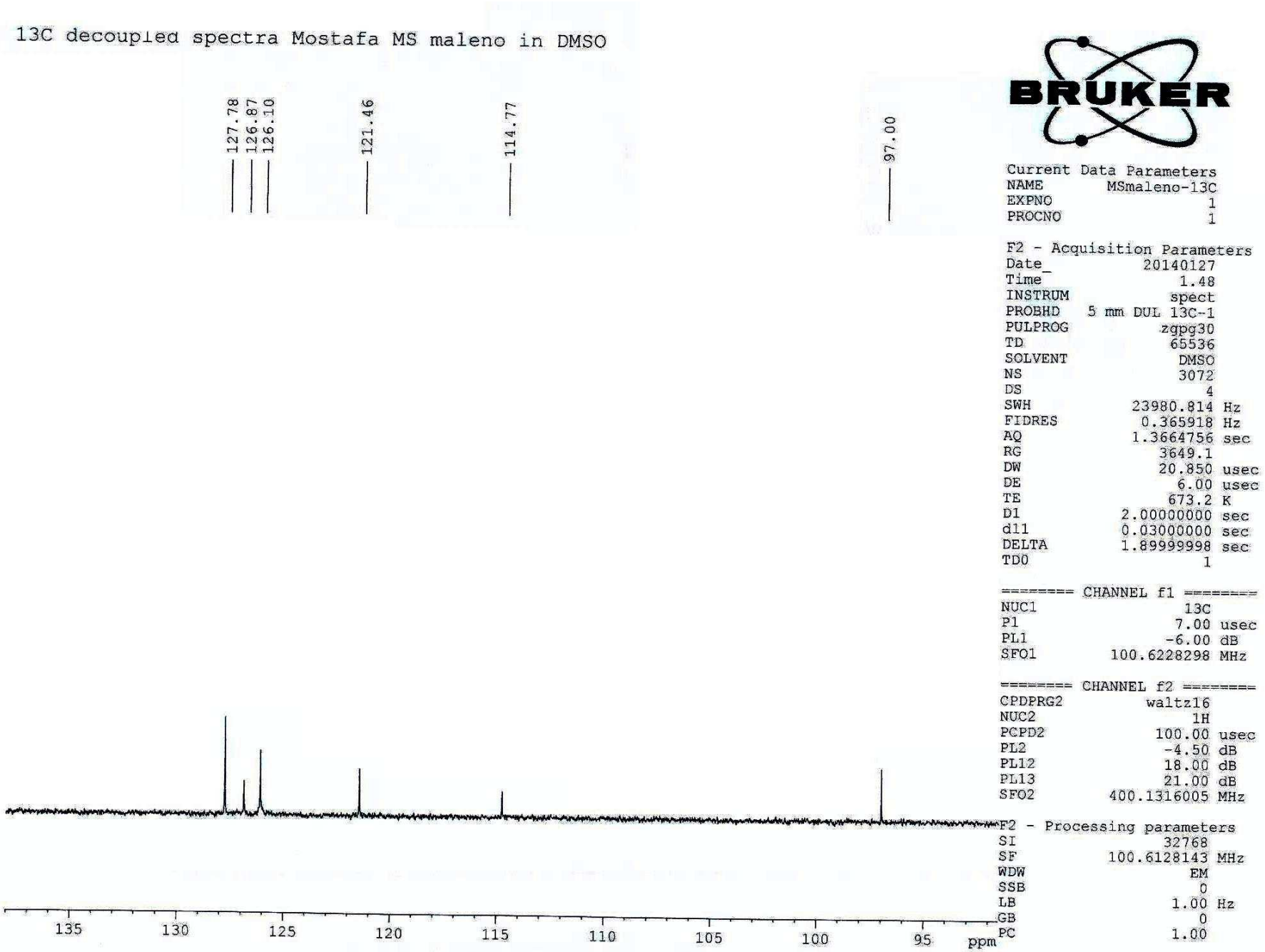
F2 - Acquisition Parameters
Date_ 20140127
Time 3.50
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 2048
DS 4
SWH 23980.814 Hz
FIDRES 0.365918 Hz
AQ 1.3664756 sec
RG 4096
DW 20.850 usec
DE 6.00 usec
TE 673.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 7.00 usec
PL1 -6.00 dB
SFO1 100.6228298 MHz

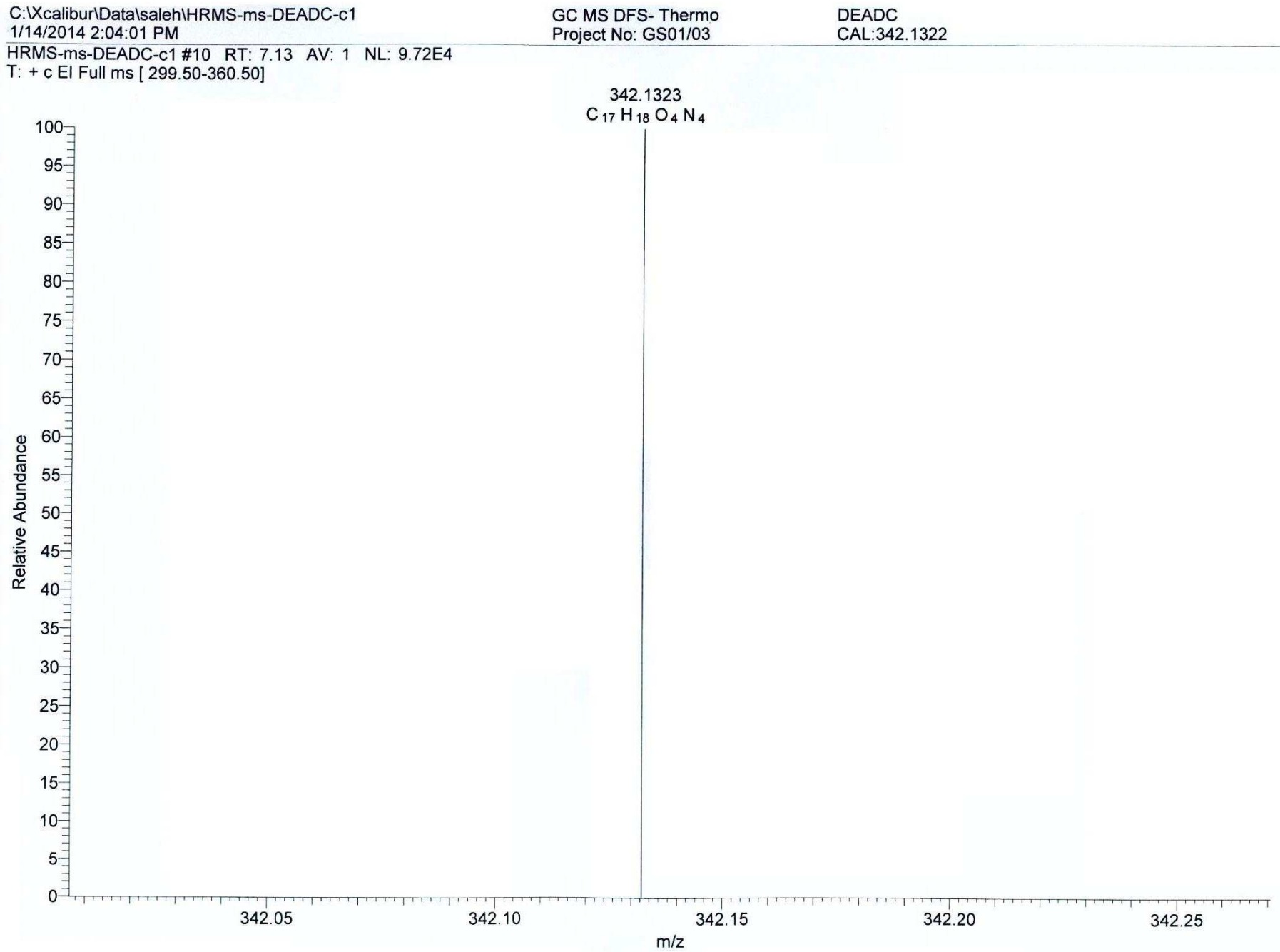
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -4.50 dB
PL12 18.00 dB
PL13 21.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6128151 MHz
WDW EM

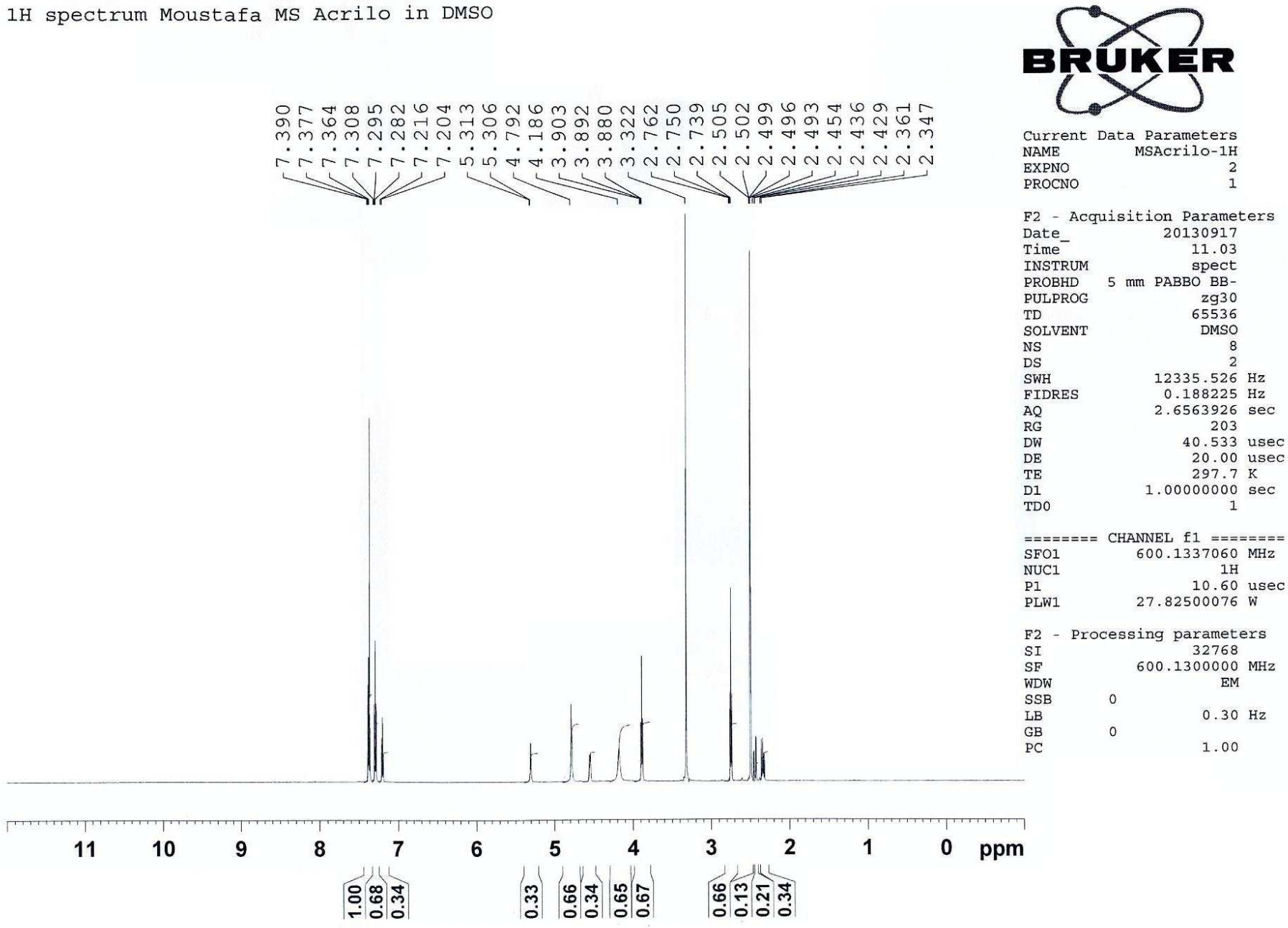
^{13}C NMR for compound **26b**



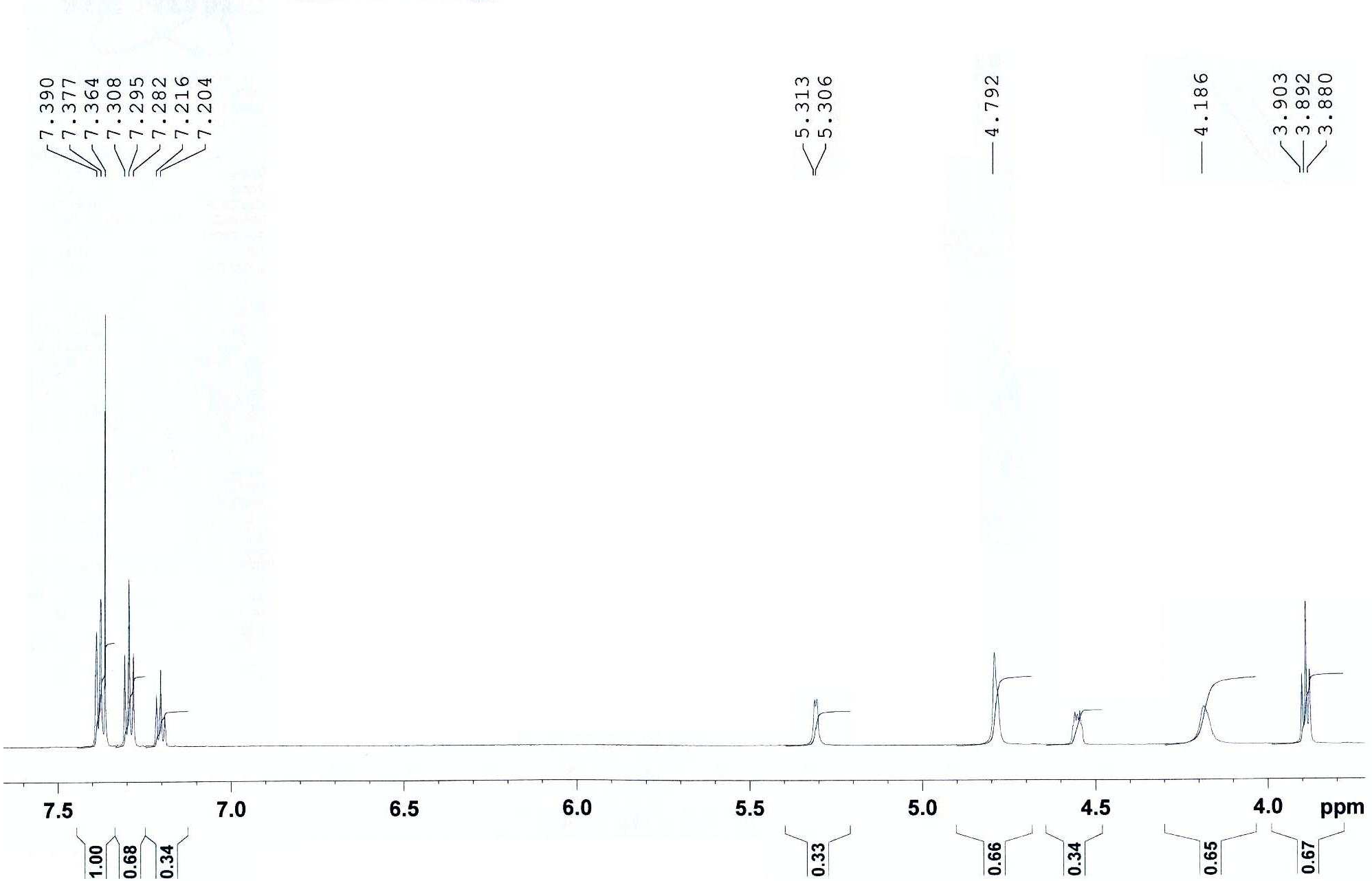
^{13}C NMR for compound **26b**



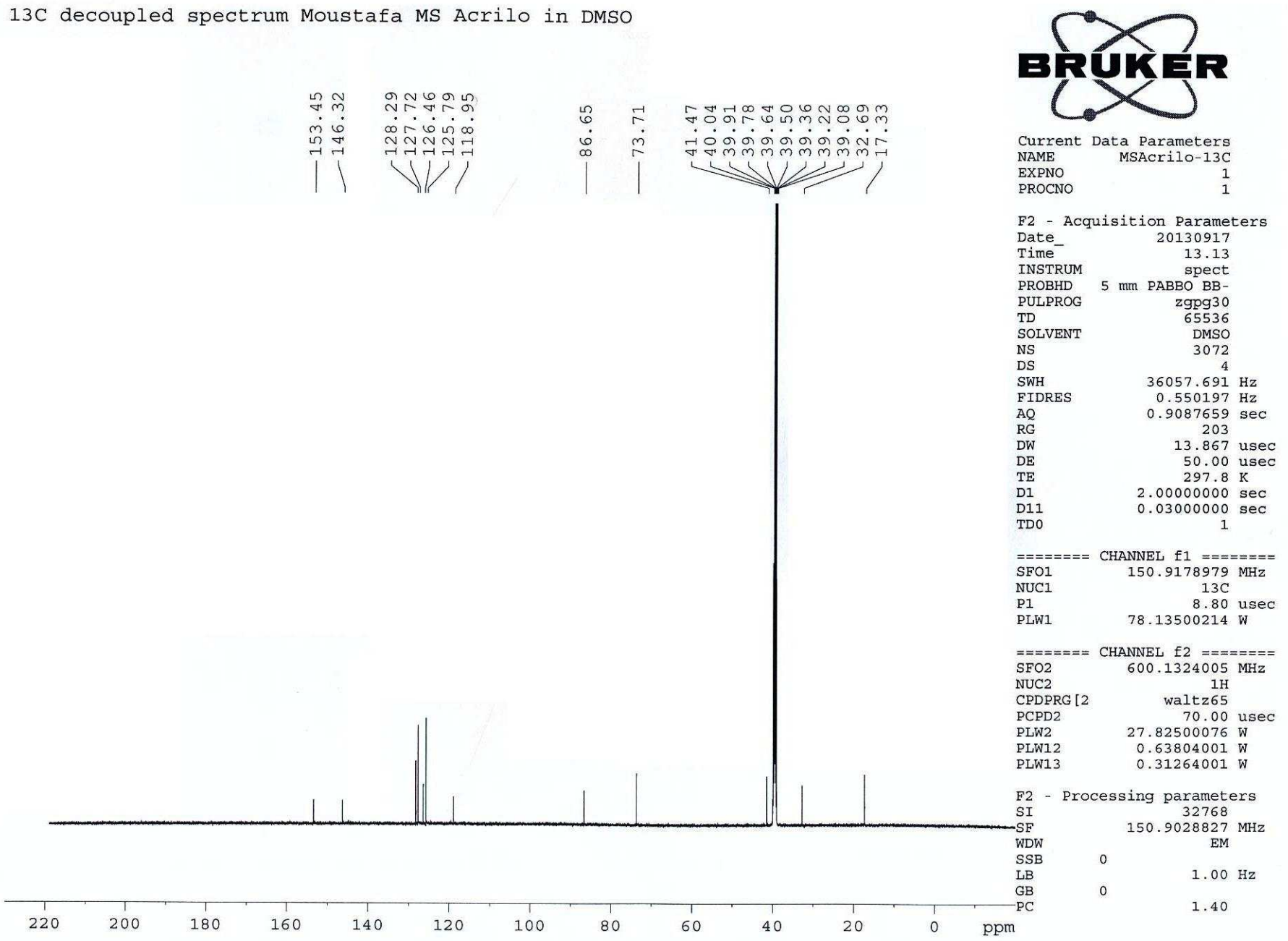
High resolution mass spectra for compound **26b**



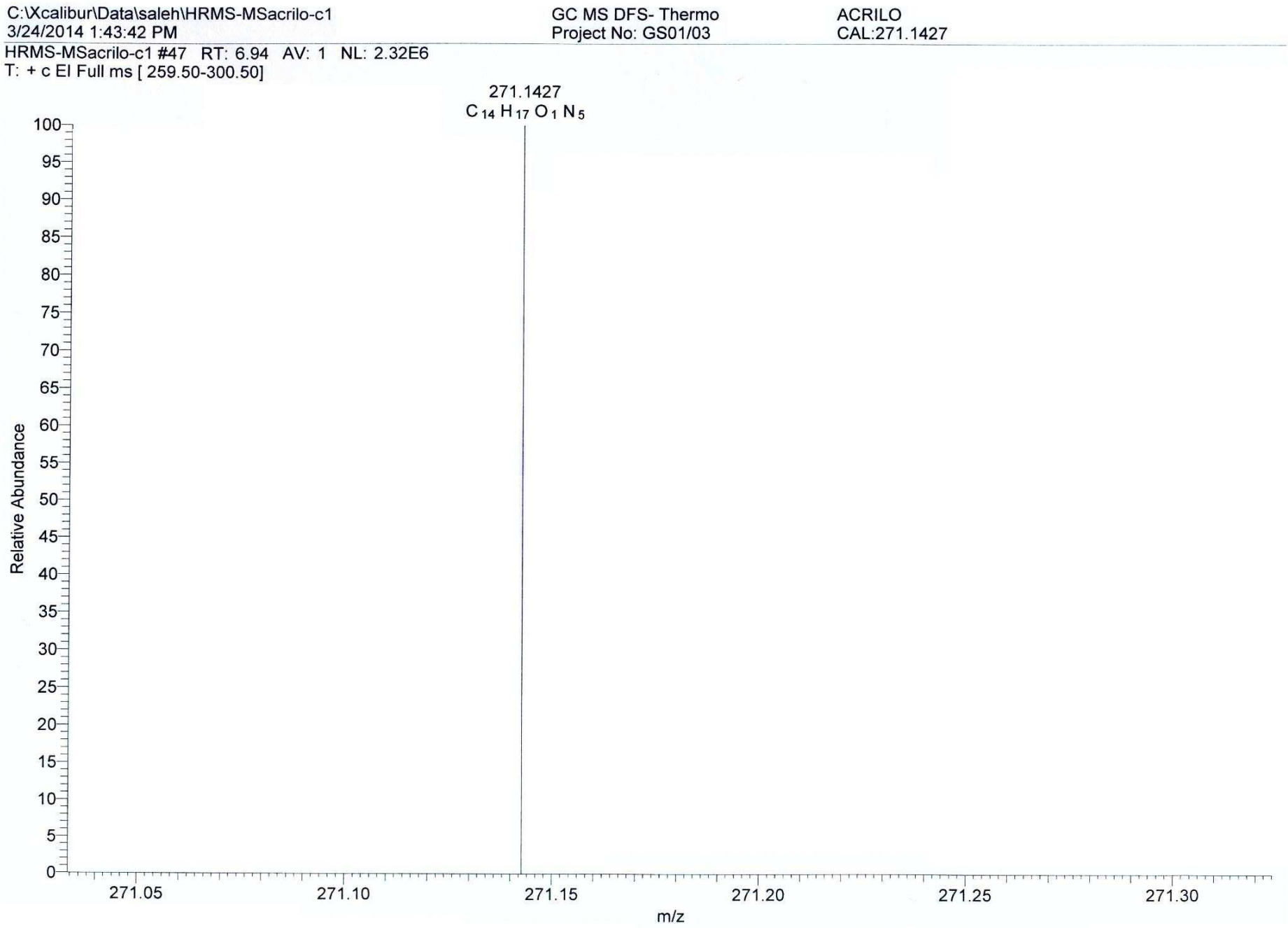
^{1}H NMR for compound **29**



[1]H NMR for compound **29**

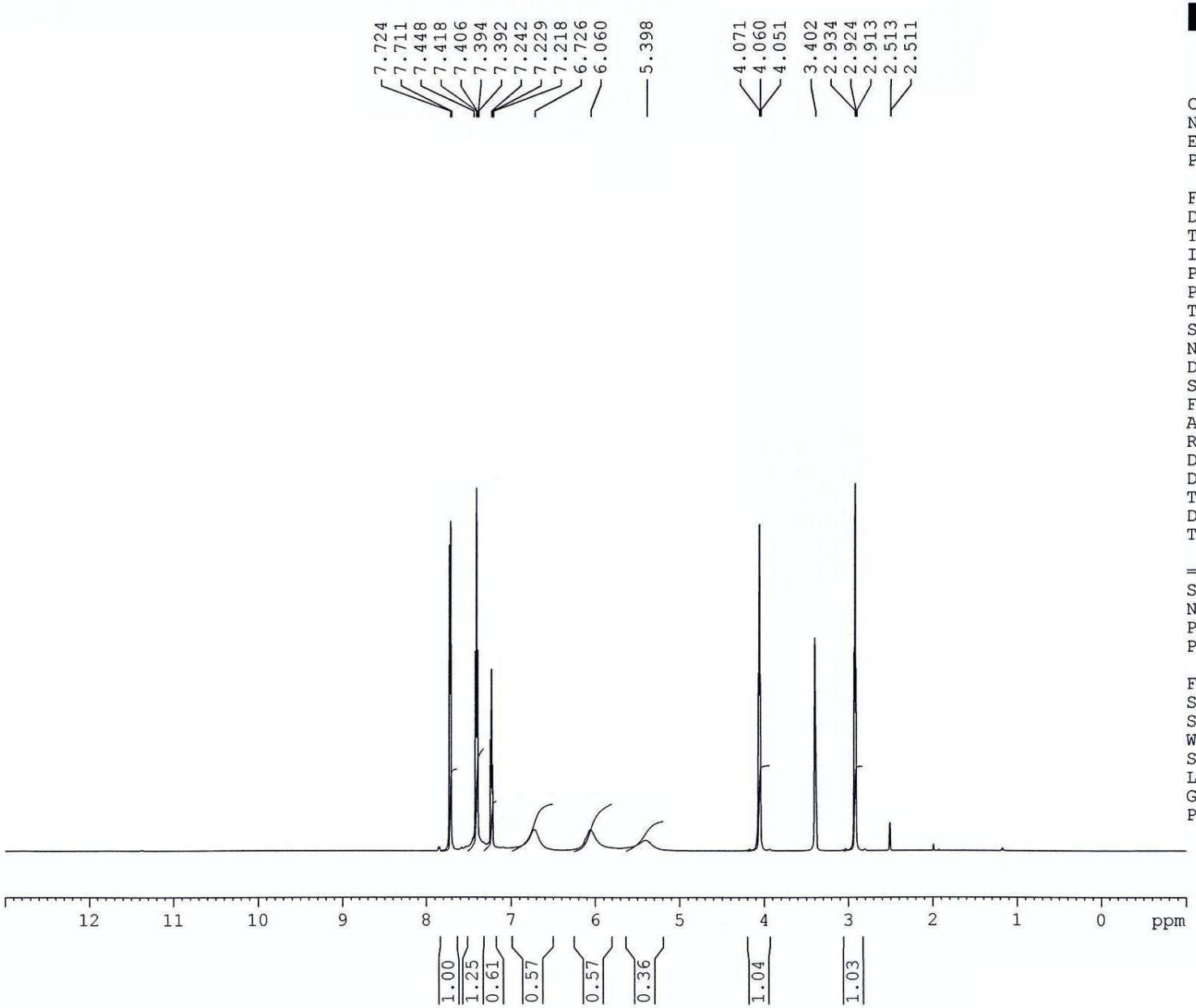


^{13}C NMR for compound **29**



High resolution mass spectra for compound **29**

13C decoupled spetctrum Moustafa MS NG1 in DMSO



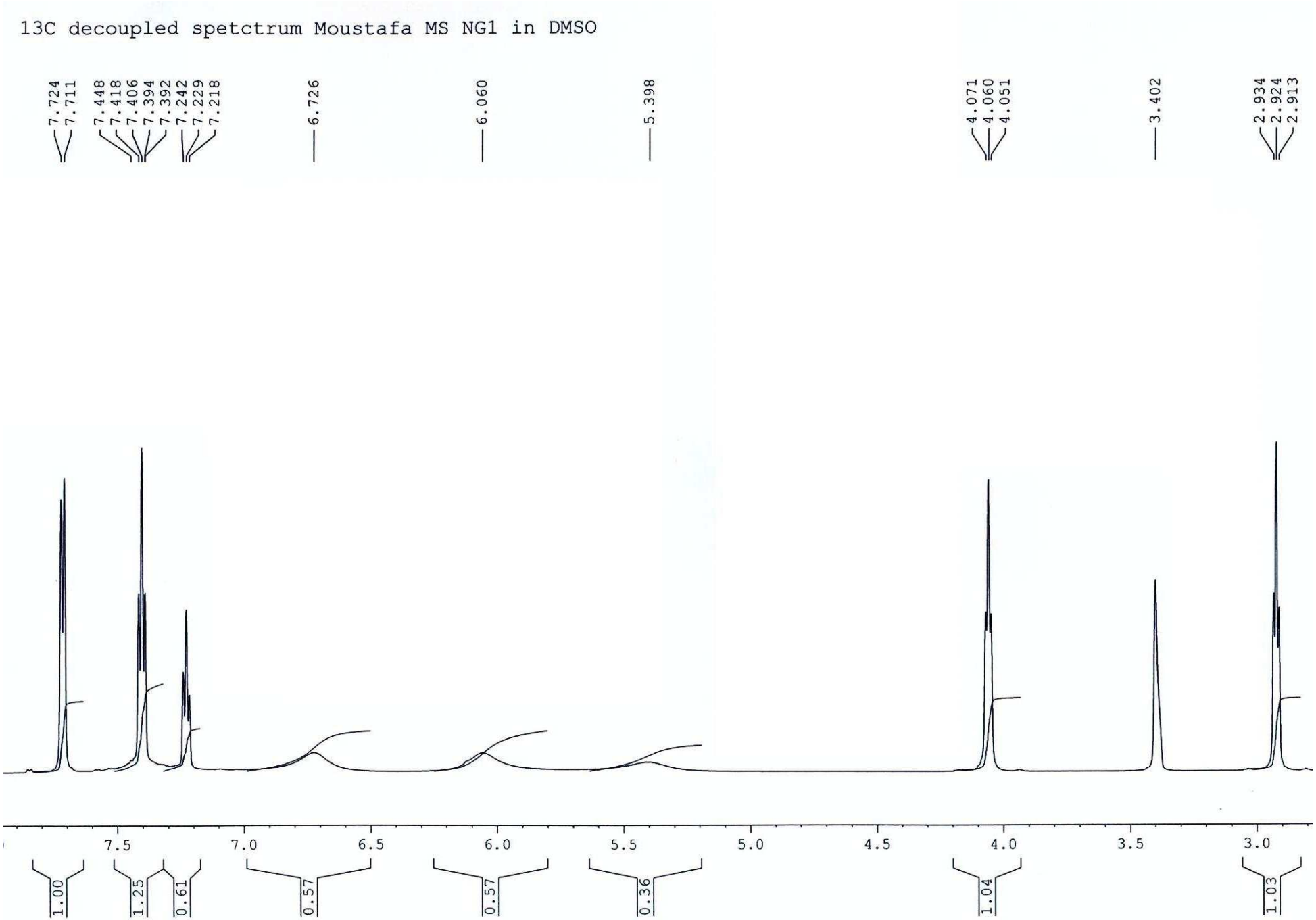
Current Data Parameters
NAME MSNG1
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160112
Time 23.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 128
DS 2
SWH 12335.526 Hz
FIDRES 0.188225 Hz
AQ 2.6563926 sec
RG 64
DW 40.533 usec
DE 20.00 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

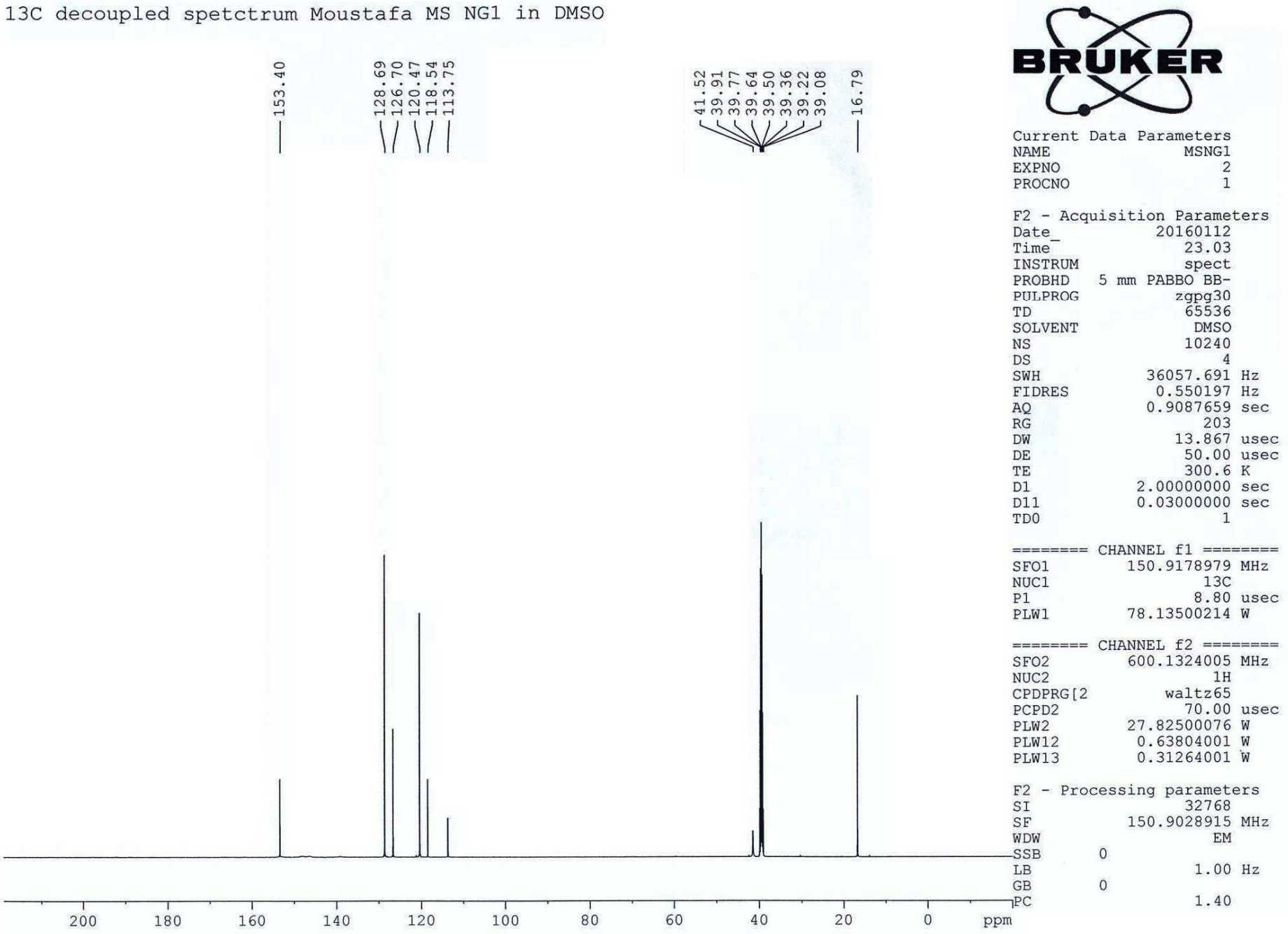
======== CHANNEL f1 ========
SFO1 600.1337060 MHz
NUC1 1H
P1 10.60 usec
PLW1 27.82500076 W

F2 - Processing parameters
SI 32768
SF 600.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

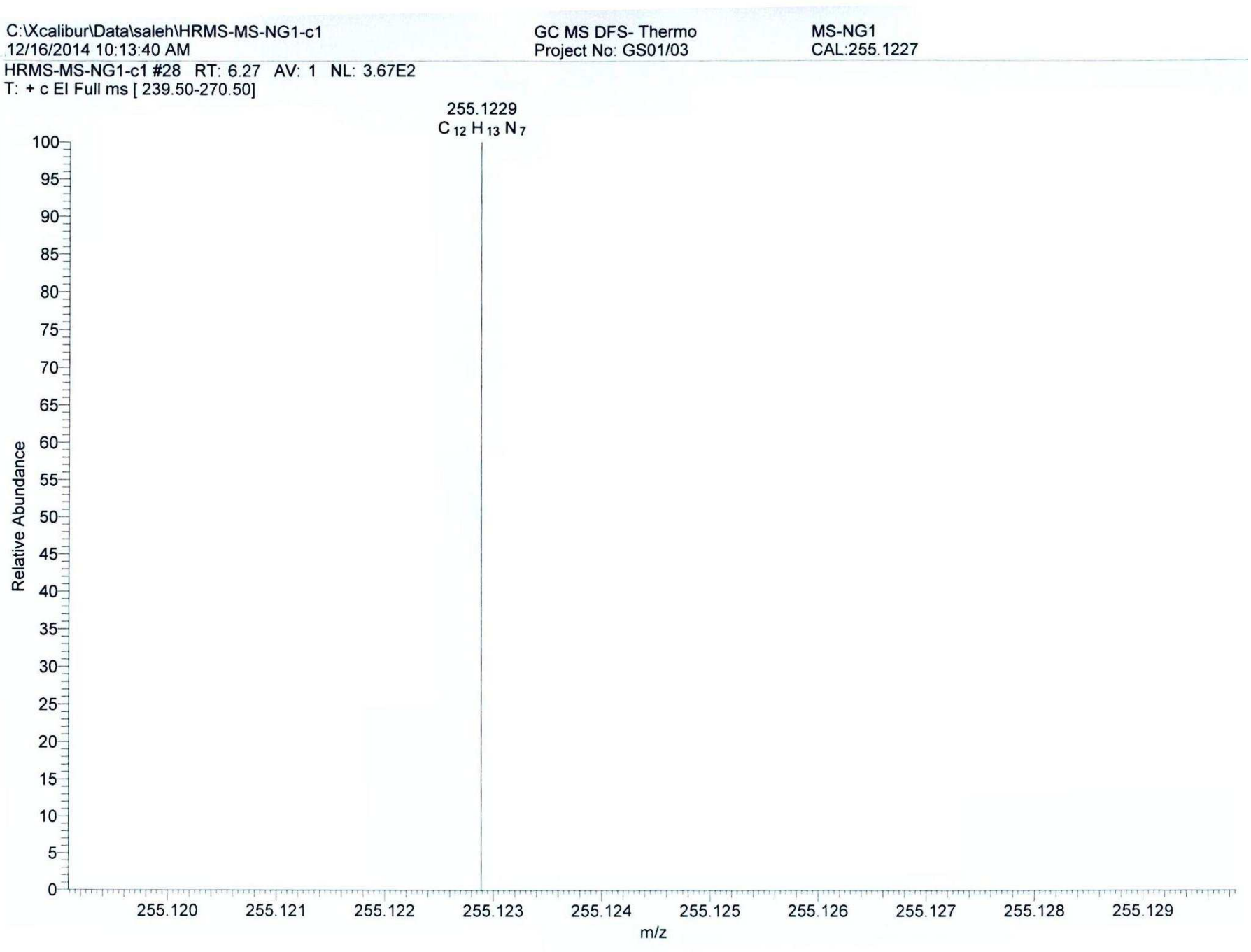
^{1}H NMR for compound **31**



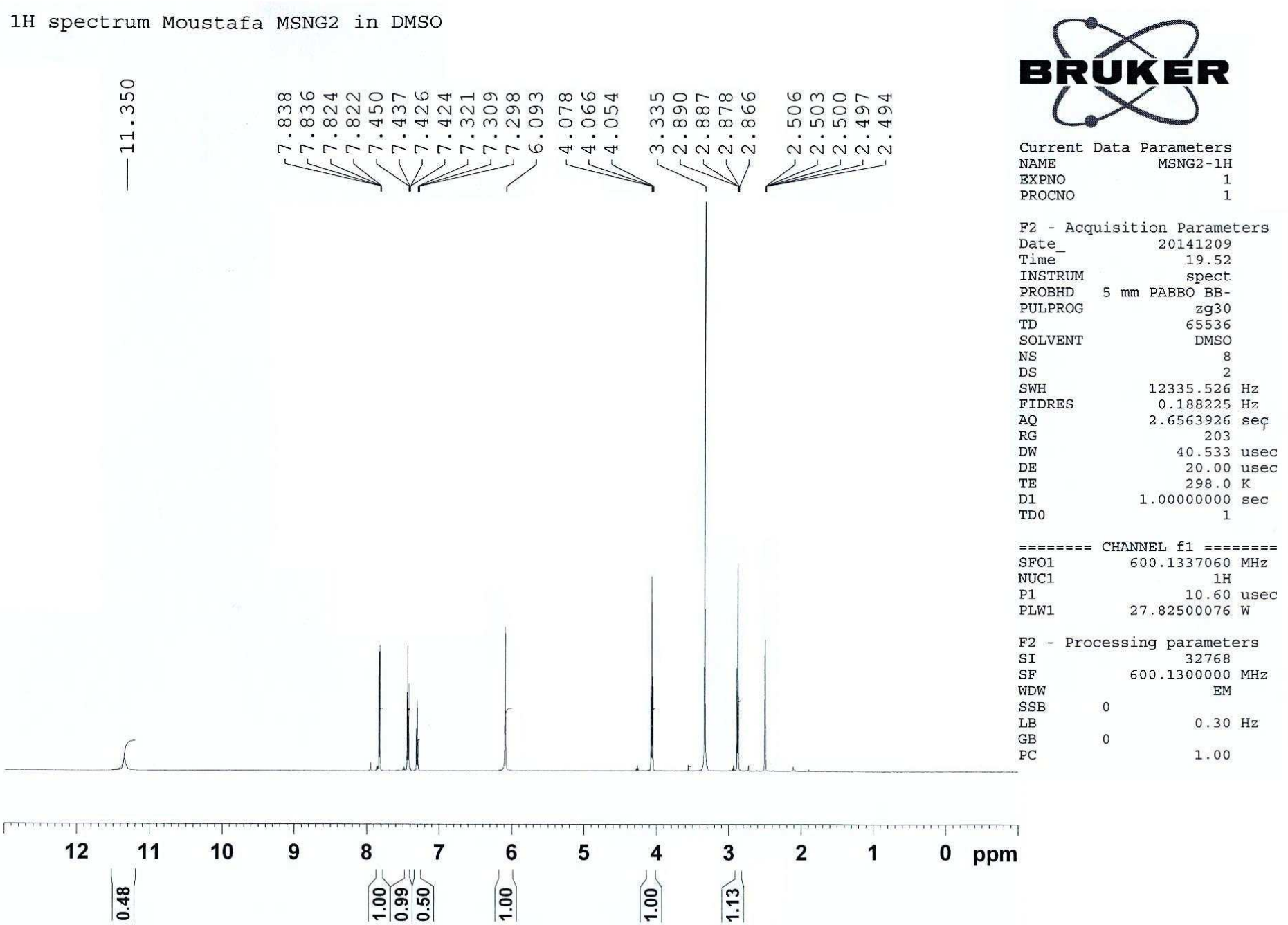
^{1}H NMR for compound **31**



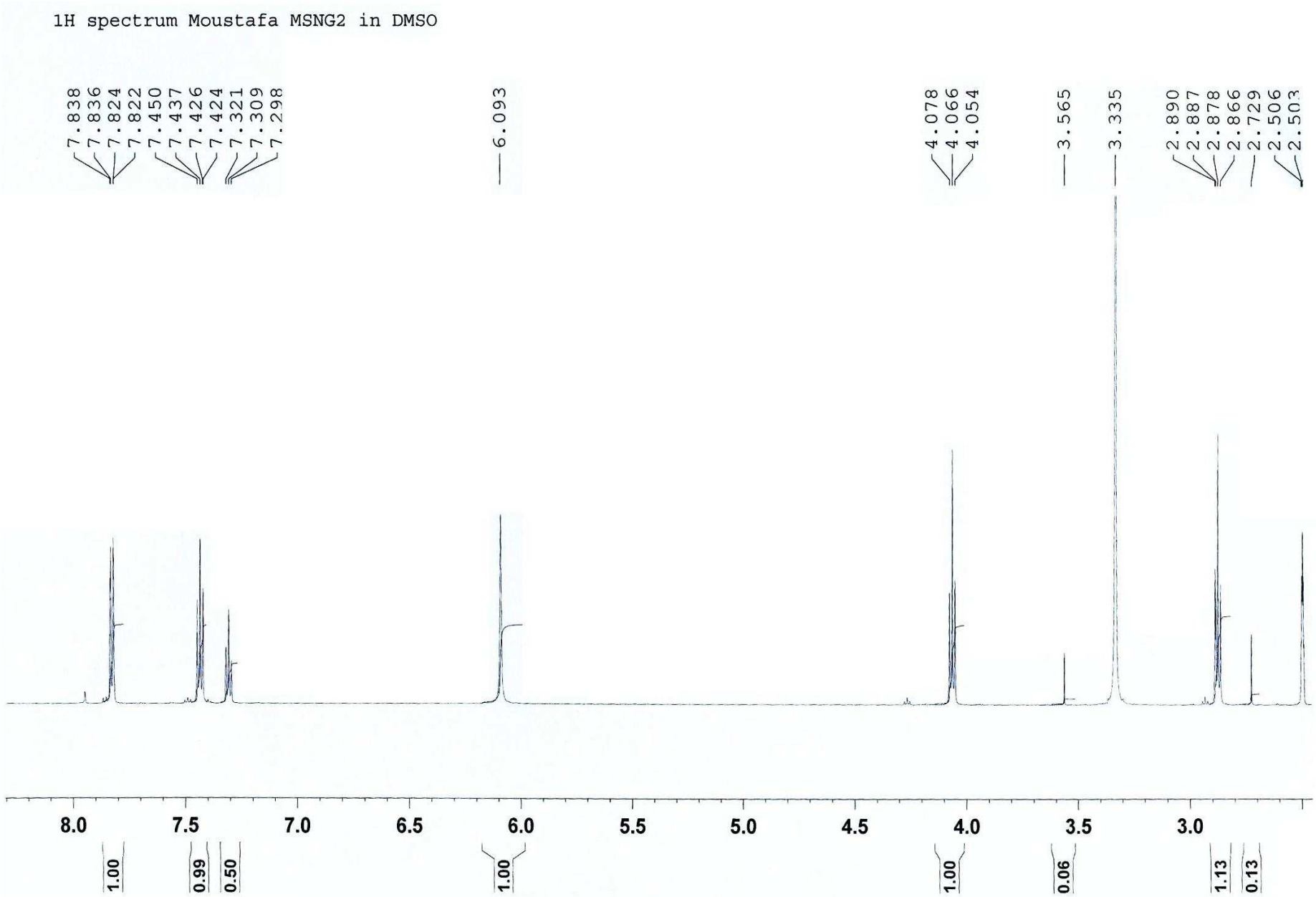
^{13}C NMR for compound **31**



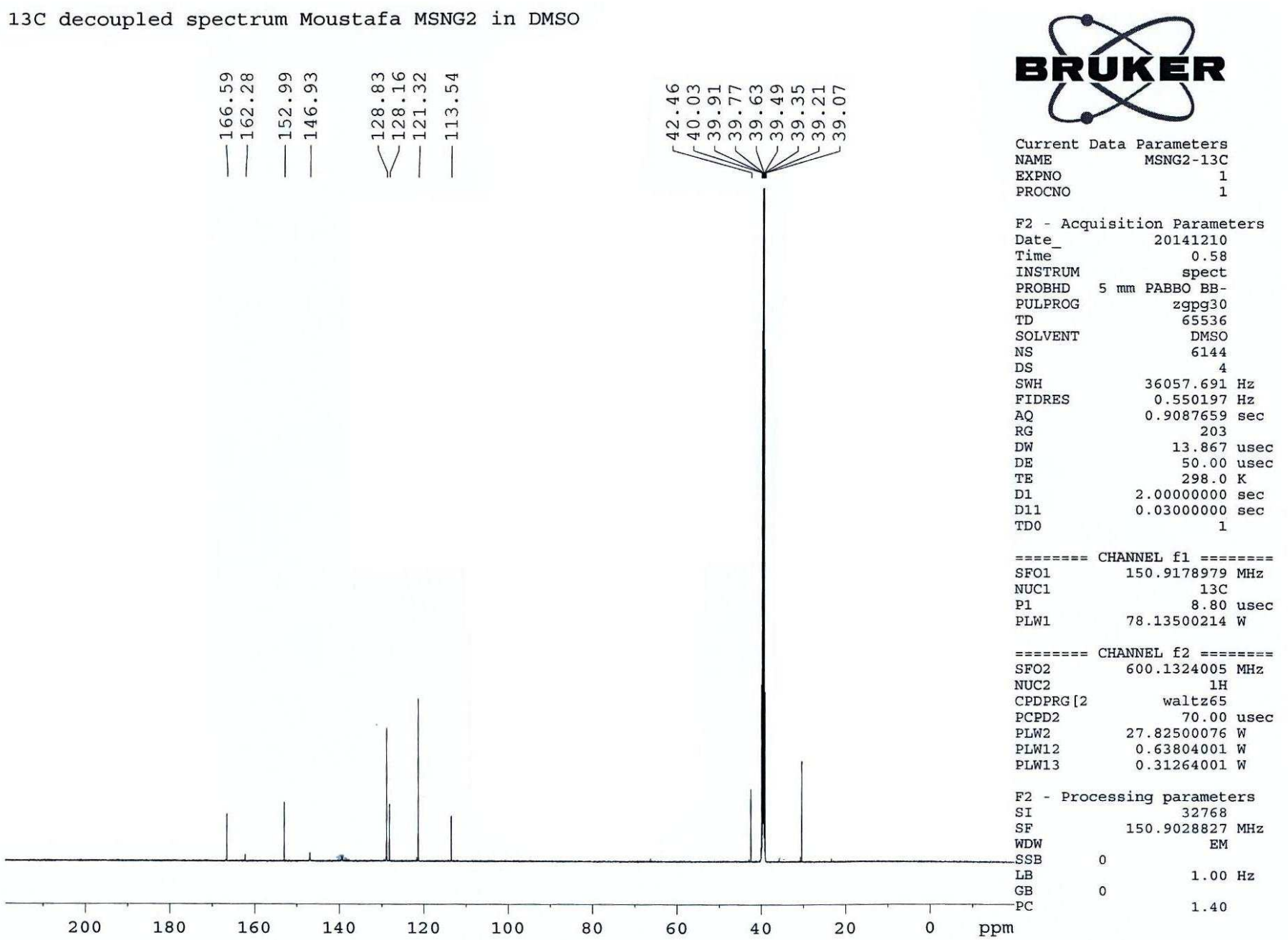
High resolution mass spectra for compound **31**



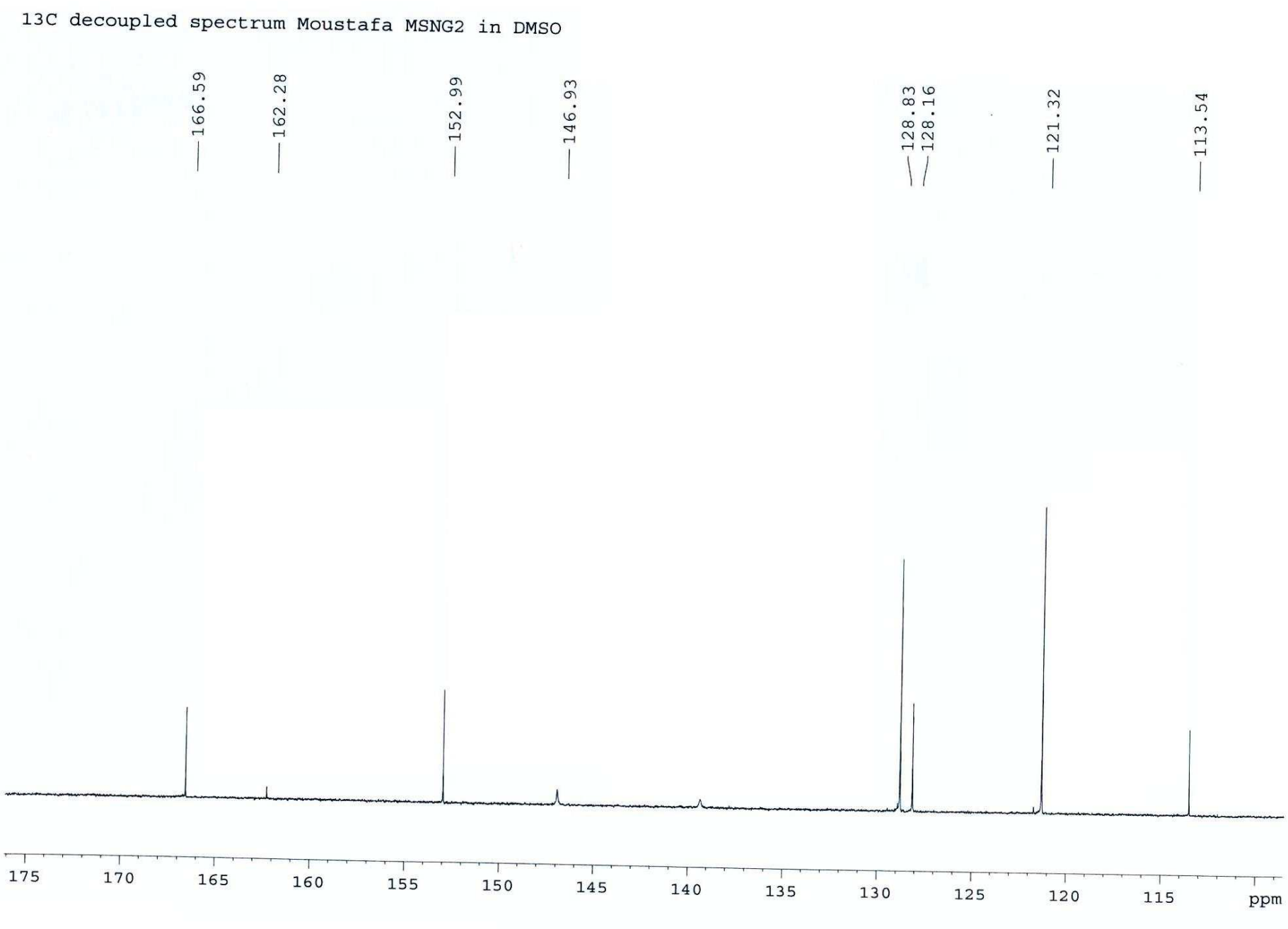
^{1}H NMR for compound **33**



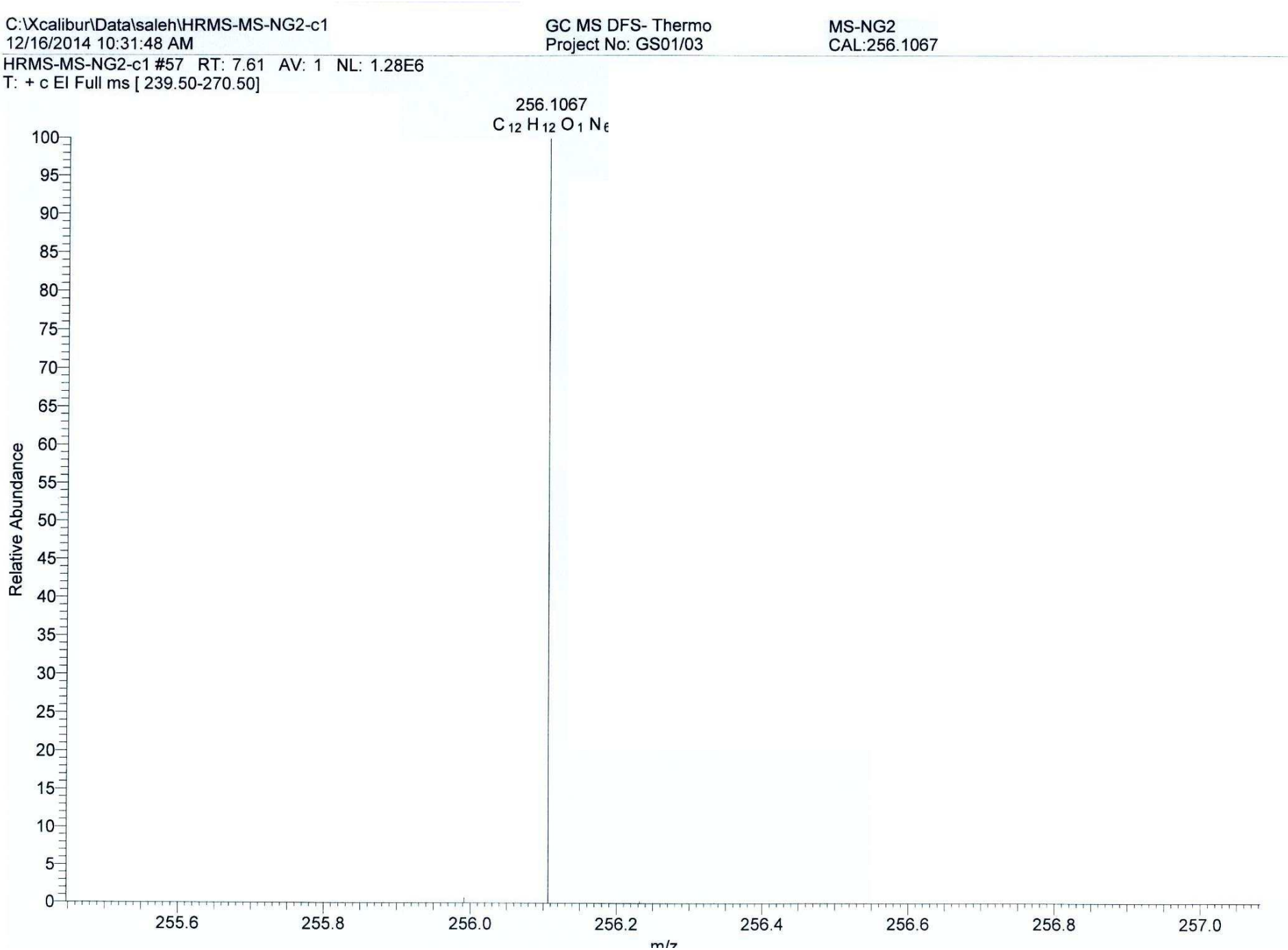
^{1}H NMR for compound **33**



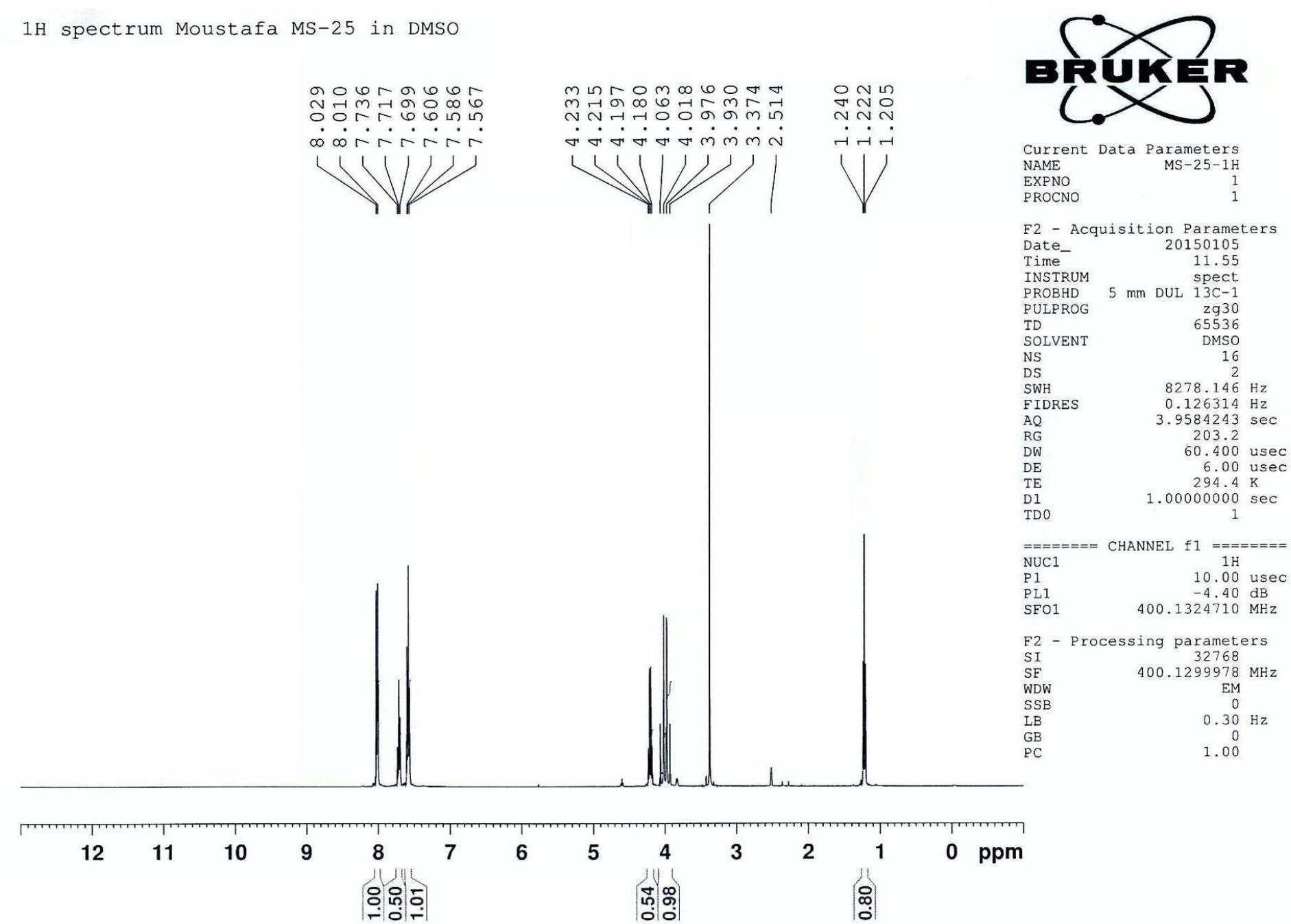
^{13}C NMR for compound **33**



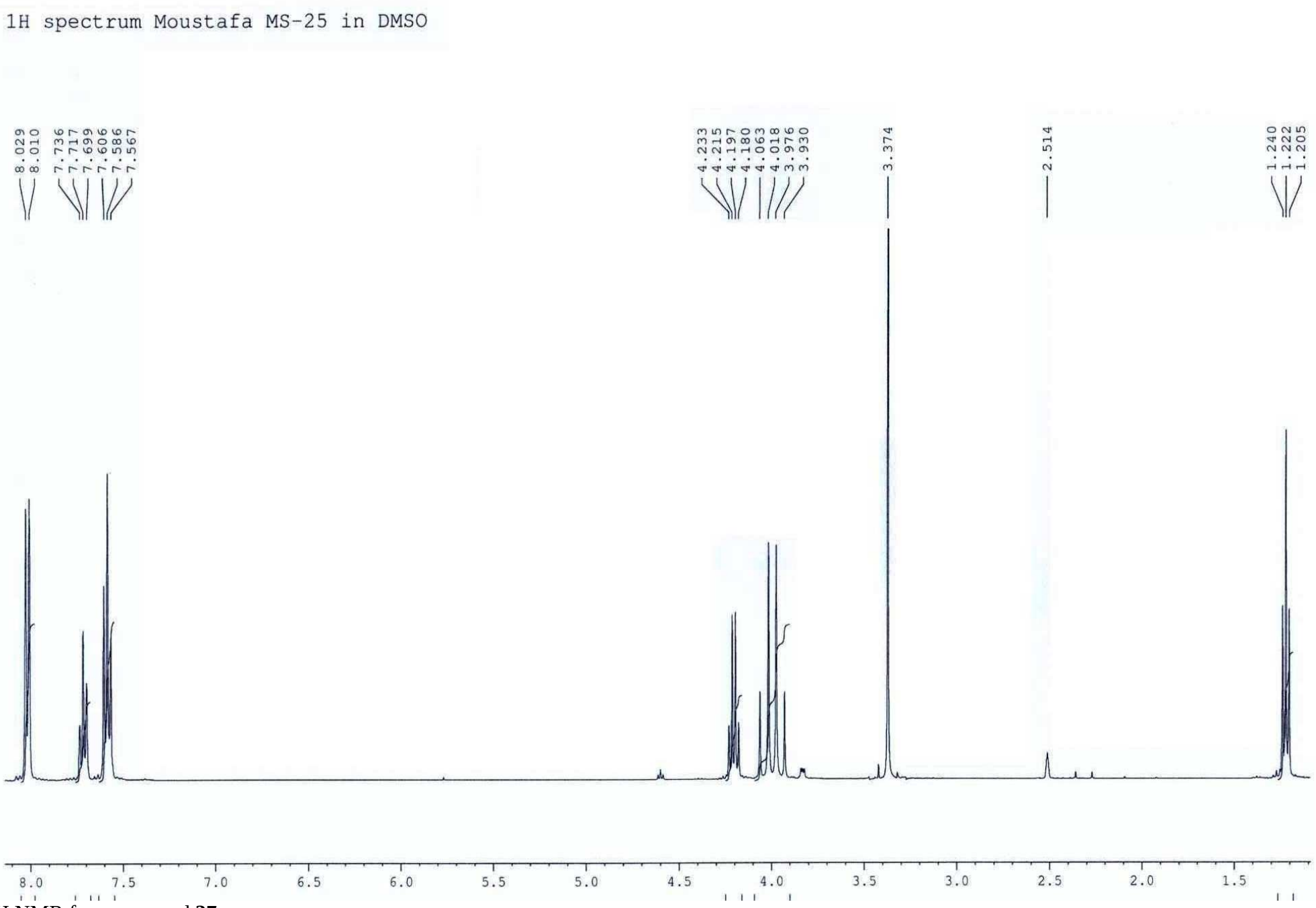
^{13}C NMR for compound **33**



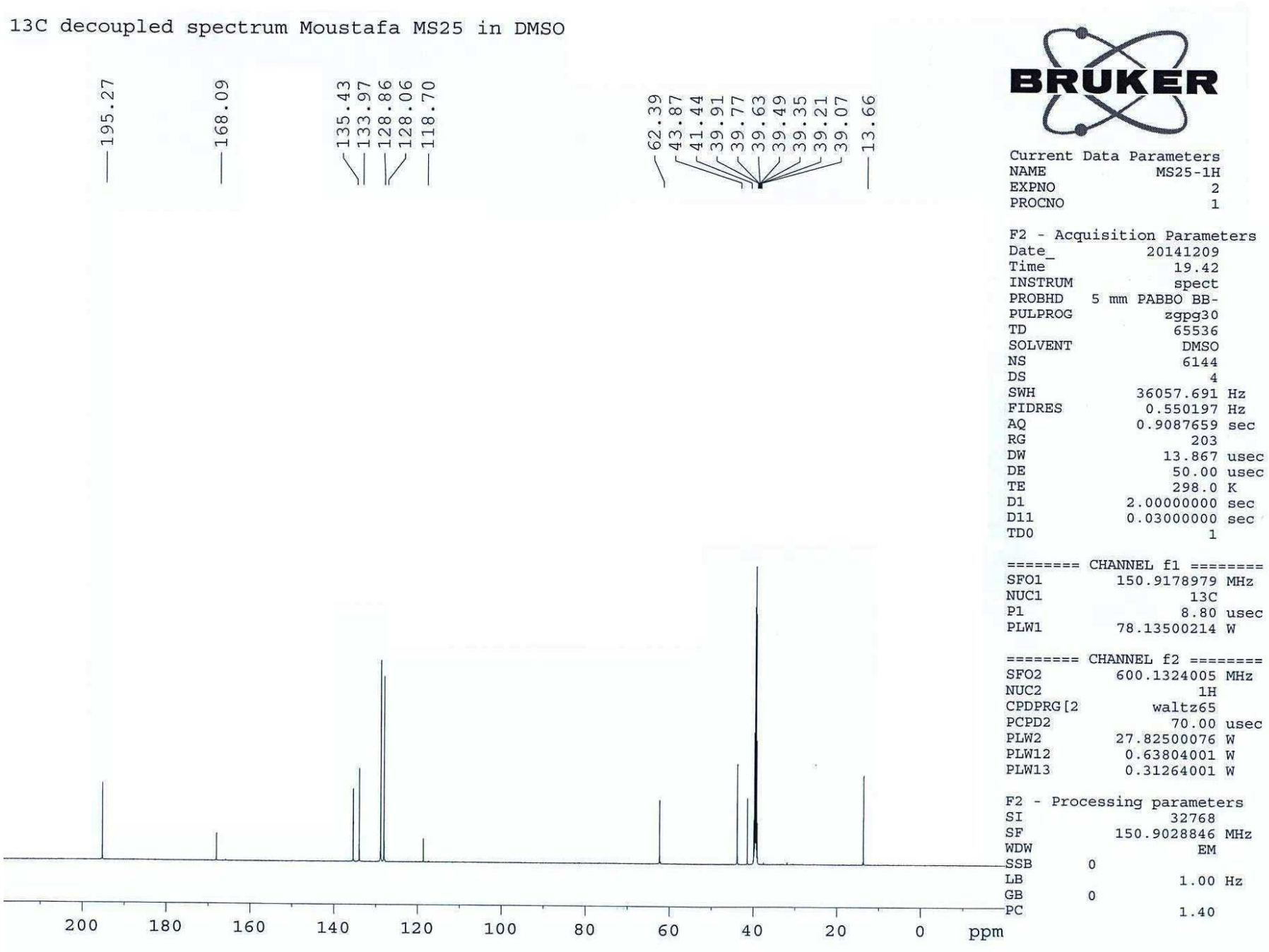
High resolution mass spectra for compound **33**



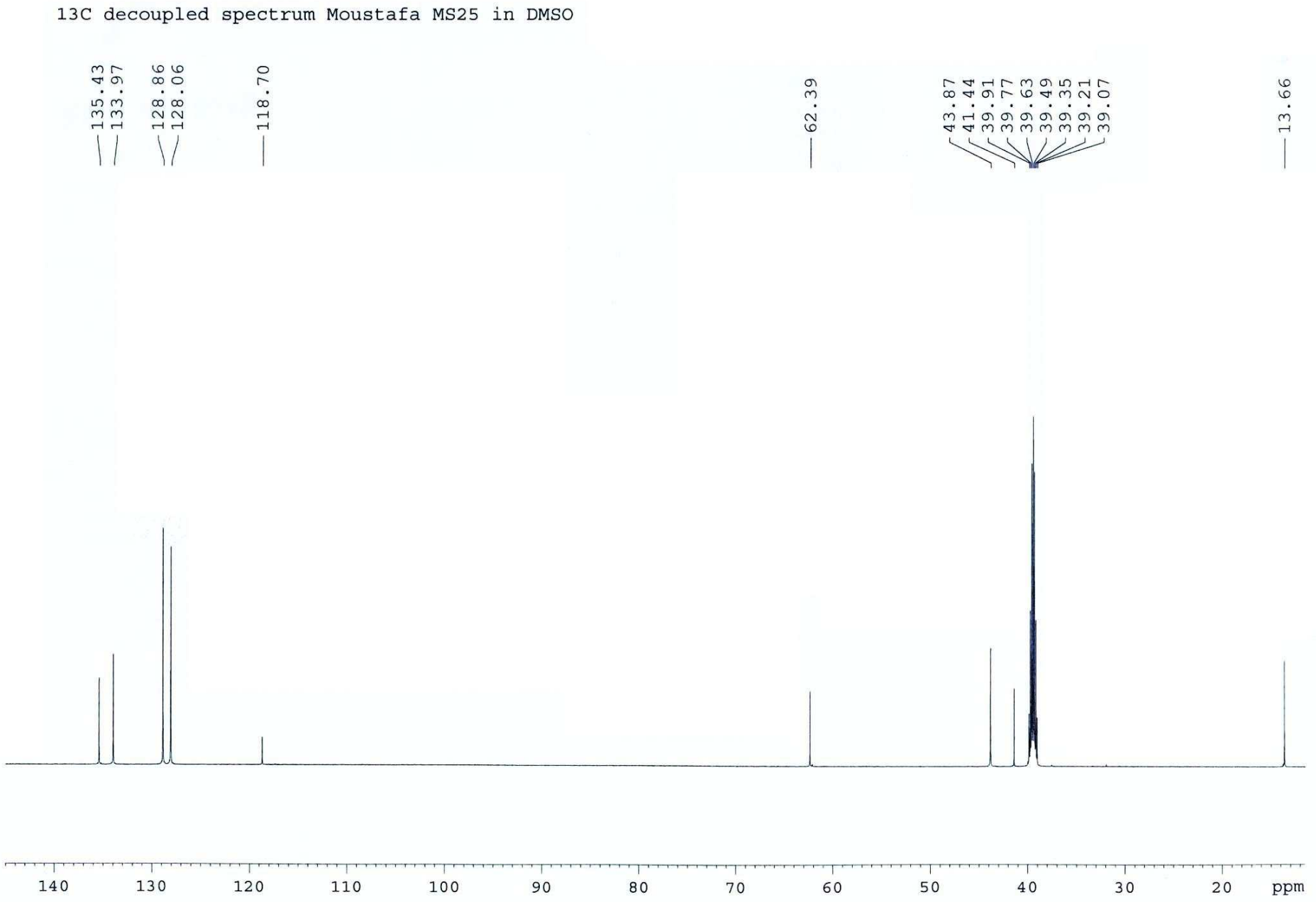
^{1}H NMR for compound **37**



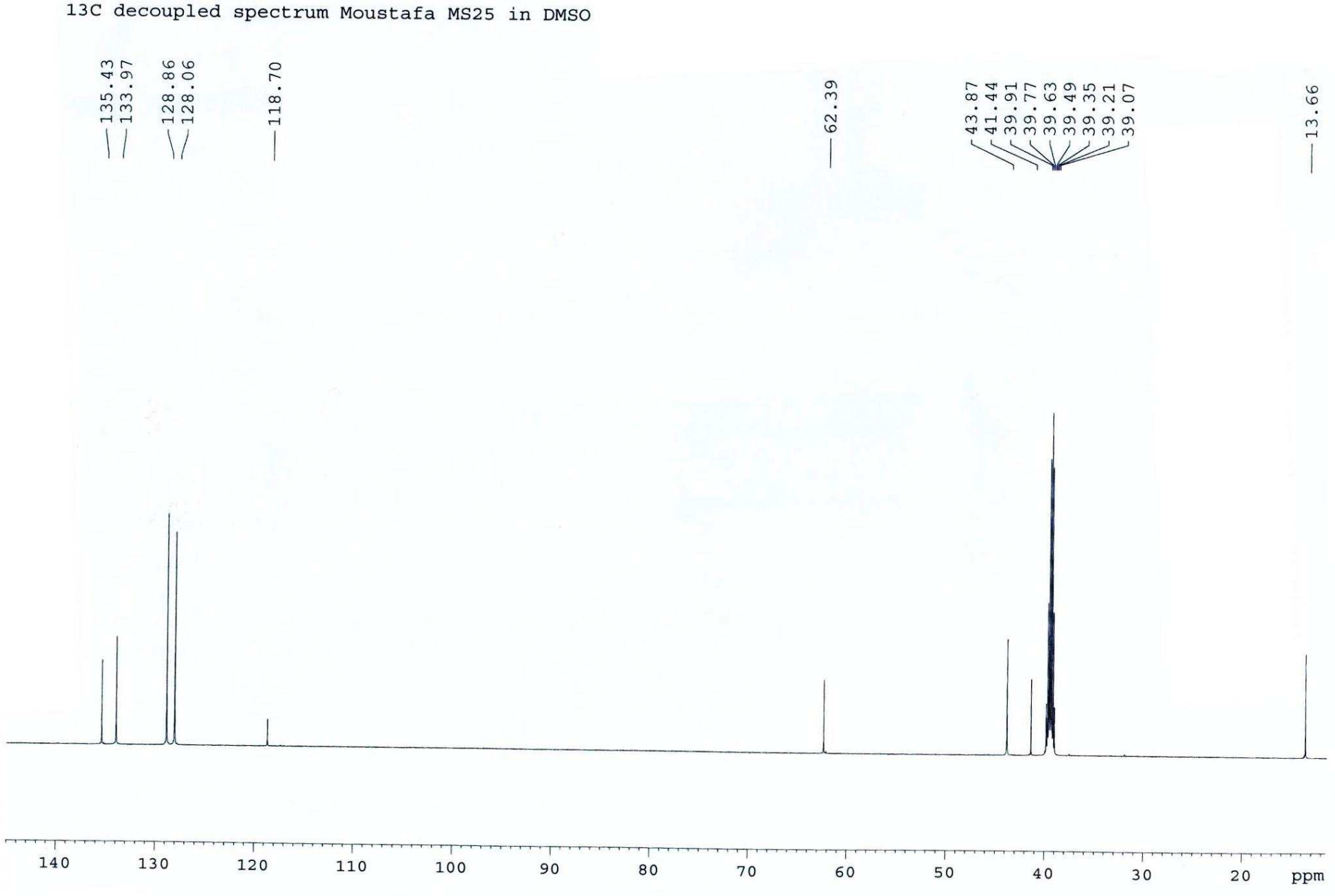
^{1}H NMR for compound **37**



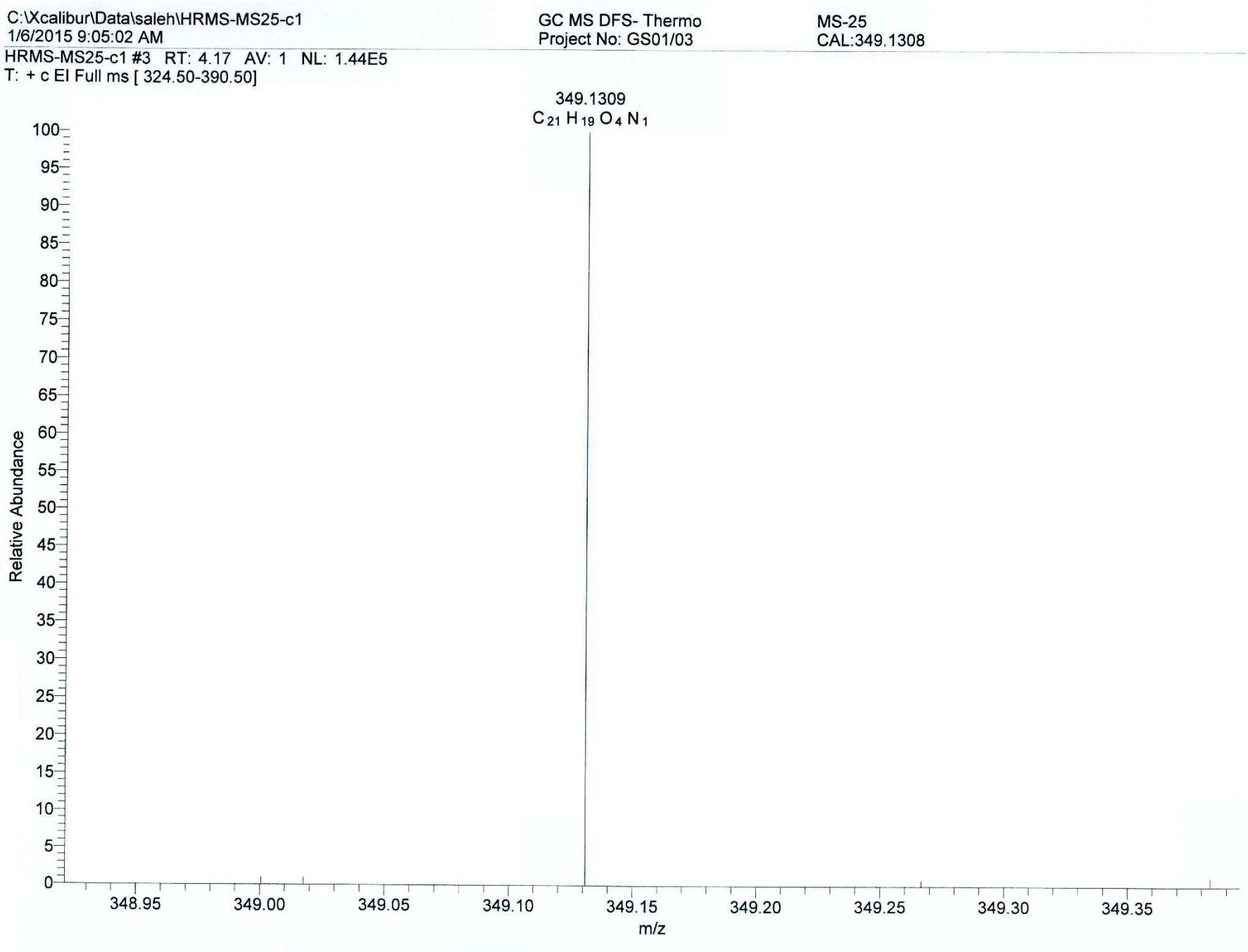
^{13}C NMR for compound **37**



^{13}C NMR for compound **37**



^{13}C NMR for compound **37**



High resolution mass spectra for compound **37**