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Synthesis of cross-reactive carbohydrate determinants fragments as tools for in vitro allergy diagnosis

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ABSTRACT

Four biotinylated tri and tetrasaccharide fragments of plant and invertebrate *N*-glycans were synthesized using methyl *tert*-butyl phenyl (MBP) thioglycosides donors in order to evaluate their involvement in cross-allergies as cross-reactive carbohydrate determinants (CCDs). Various levels of reactivity to anti-bee and anti-HRP antibodies and with sera from allergic patients were observed when the conjugates were coated on streptavidin microplates. The results showed the potential utility of these xylosylated and fucosylated oligosaccharide fragments in determining CCD antibody epitopes.

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1. Introduction

Health problems due to extreme allergic responses are a serious and growing health issue in the society at large. The increased prevalence of this type of disease and the aggravation of the cross-allergy phenomenon (allergy to apparently unrelated allergens) require the identification of the allergen structures involved. Cross-linking of cell-bound IgE on mast cells or basophils by allergenic glycoproteins causes the release of histamine and other mediators, which results in allergic symptoms. Allergen epitopes are not only peptides, but also can be carbohydrate moieties, called carbohydrate cross-reactive determinants (CCDs), which have been found in different allergens from plants (pollens, food, latex) or animals (insect venoms, seafood). *N*-Glycans containing α 1,3 fucose and β 1,2 xylose branches, specifically found in *N*-glycans from plants and invertebrate animals are most frequently recognised as CCD epitopes. This high degree of cross-reactivity has been explained by the conserved structure of *N*-glycans in plants and invertebrates, sharing several sequences that are not found in mammalian *N*-glycans (Fig. 1).

As it has been reported that both α 1,3 fucose and β 1,2 xylose moieties were involved in IgE binding,¹ the synthesis of xylosylated and fucosylated *N*-glycan fragments were required in order to study the respective involvement of these two features. The

fragments described therein were prepared in a biotinylated form, as previously done with *Candida albicans* cell wall oligomannosides.² The aim of this work is to determine the minimal epitopes of these CCDs, and thus to prepare standardised tools for diagnosis and follow-up of patients' treatment. Carbohydrate epitopes are usually of limited size (a tri- or tetrasaccharide) and thus we decided to focus on tri- and tetrasaccharidic fragments containing either xylose or fucose (Fig. 2). Compound **1** corresponds to a xylosylated fragment of both M0X and M0XF³, compound **2** is a xylosylated fragment of both MMX and MMXF³, compound **3** is the fucosylated core region of MMF³, M0XF³ and MMXF³, compound **4** is the fucosylated core of MMF³. These structures were then subject to preliminary immunogenic evaluations.

2. Results

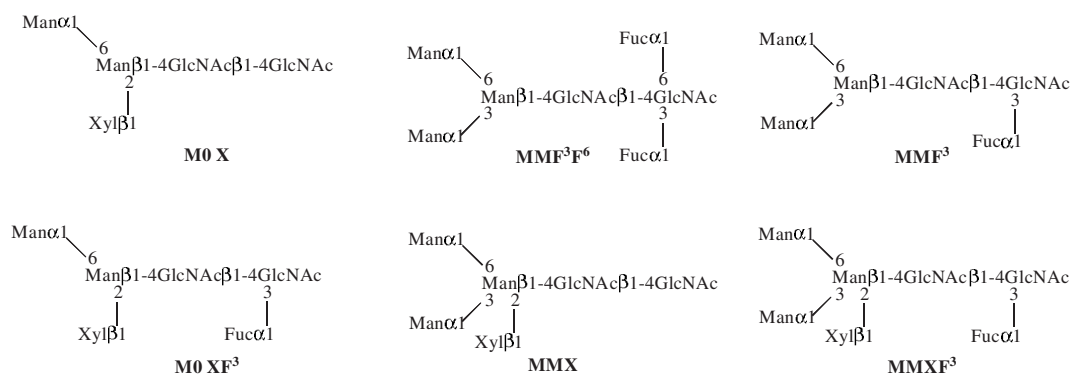
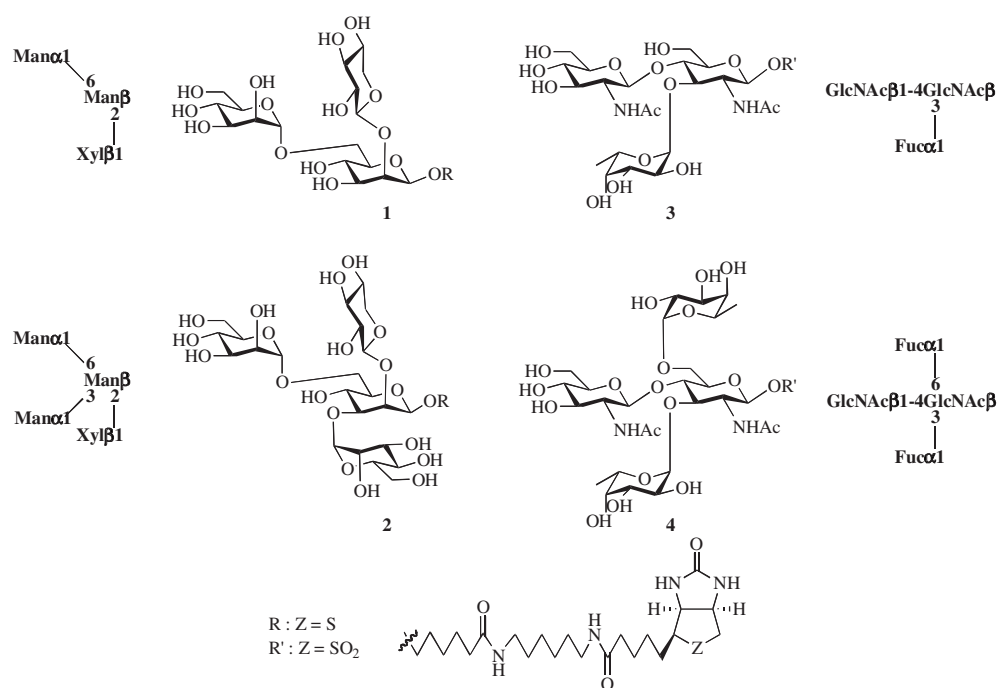
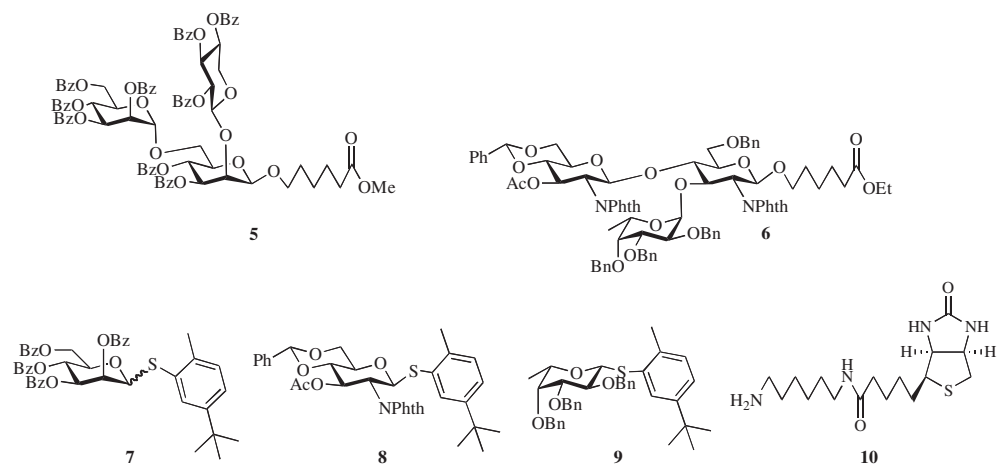
2.1. Chemical synthesis

The preparation of protected trisaccharides intermediates **5** and **6** (Fig. 3) was communicated recently by our group,³ using the efficient thioglycosides **7**, **8** and **9**, obtained from the odourless 2-methyl-5-*tert*-butylthiophenol. The *N*-glycan fragments herein synthesized were coupled to the previously described biotin derivative **10**.²

In the 1990's, A. Lipták and J.F.G. Vliegthart⁴ had previously explored the synthesis of xylosylated and fucosylated *N*-glycans

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**Figure 1.** Structures of some of the most common CCDs.**Figure 2.** Synthetic targets.**Figure 3.** Starting blocks: trisaccharides **5** and **6**; thioglycosides **7**, **8** and **9** and biotin block **10**.³

and described the difficulties encountered during the construction of these structures. Unfortunately, there have been no reports on the biological evaluation of these structures following their syntheses.

2.2. Synthesis of biotinylated xylosylated fragments

The synthesis of the xylosylated tetrasaccharide (Scheme 1) began with the acetalisation of known **11**³ to give **12**. In a first approach, the regioselective opening of **12** was attempted in order to obtain the diol **13** which after dimannosylation would have led to the tetrasaccharide **17** more directly. Likely due to the presence of a free hydroxyl in position 3, the selective reduction step⁵ was unsuccessful. Alternatively compound **12** was first mannosylated at position 3 in an excellent yield to give trisaccharide **14**. The reduction of benzylidene was then achieved in a good yield to give two regioisomers **15** and **16** (in an 8:2 ratio). Compound **15** was finally mannosylated to provide **17** in a moderate yield (46%) with a reduced efficiency attributed to the steric hindrance generated by the benzoylated mannoside and xyloside present on the upper face of the β mannoside of this highly branched structure.

Trisaccharide **5** and tetrasaccharide **17** were then deprotected and acetylated to give acids **19** and **23**. The hydrolysis (Water/THF) of the mixed anhydride formed during the acetylation of **18** and **21** was found to be important in order to ensure the coupling reaction with **10**. After coupling of **19** and **23** to the biotinylating agent **10**, the acetate protecting groups were removed to finally give **1** and **2**, respectively (Schemes 2 and 3).

2.3. Synthesis of biotinylated fucosylated fragments

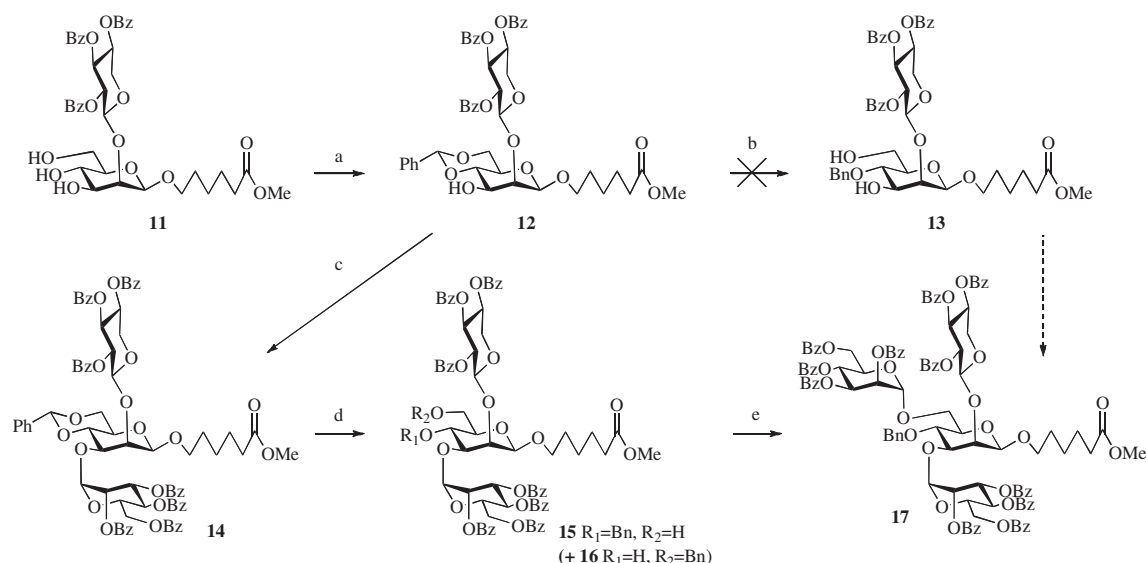
The synthesis of fucosylated fragments was undertaken next. In our first approach, we planned to introduce the two fucoses in one step onto the glucosamine moiety and then complete the synthesis by the glycosylation of the second glucosamine unit (Scheme 4).

This scheme proved unsuccessful as the regioselective opening of **26** (prepared from **25**³) failed to give any expected diol despite the use of different reduction systems such as DIBAL-H,⁶ TMSCl/NaBH₃CN,⁷ Et₃SiH/PhBCl₂⁵ and NEt₃BH₃/AlCl₃.⁸ We had already contemplated an alternative route, because—as described from the work of Lipták and co-workers and more recently from Crich's studies⁹—the glycosylation of position 4 of glucosamine

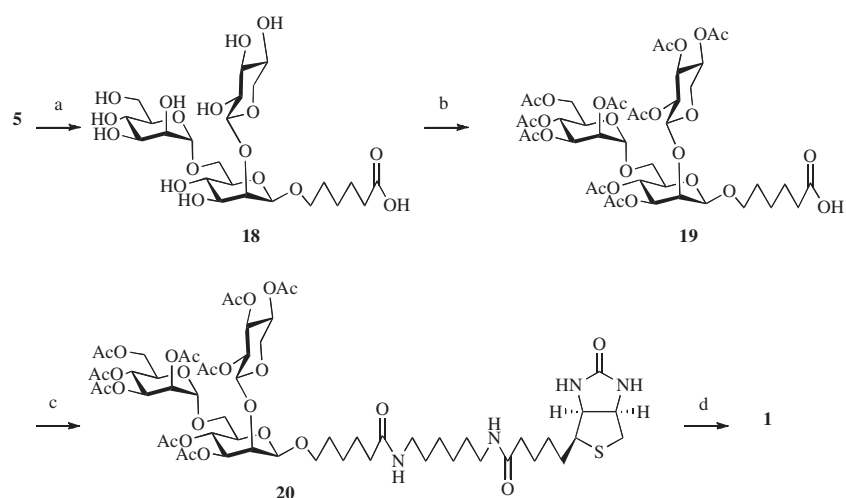
derivatives can be difficult; therefore, the preparation of a chitobiose intermediate during the early steps was examined as a potential approach to circumvent these problems. Using this plan, a regioselective glycosylation between the glucosaminyl donor **30** and acceptor **27** (obtained after selective protection of **25**) was attempted (Scheme 5). The yield of this glycosylation was low and suffered from a poor regioselectivity, in contrast with other related glycosylations.¹⁰ It was then clear that protection of the 3-hydroxyl was necessary for an efficient glycosylation and *tert*-butyl dimethyl silyl (TBS) was chosen at this point to provide this (Scheme 6).

To begin the new strategy, ethyl-6-hydroxyhexanoate was glycosylated with previously described intermediate **31**³ in good yield to give **32**. After quantitative benzylidene reduction and protection of position 6 as a TBS ether, **34** was obtained and was glycosylated with donor **8** to provide the chitobiose derivative **35** in a satisfactory yield (61%). The removal of the two TBS groups (**35**+**36**) was achieved using NH₄F in DMF¹¹ as other conditions were not effective: TBAF/THF at room temperature was found to not be reactive enough, and either warming the reaction to 70 °C or using acetic acid in combination led to the cleavage of the acetate groups. The fucosylation of diol **36** by fucosyl donor **9** was then examined under various conditions. In dichloromethane, a mixture of tetrasaccharides **37** and **38** was obtained in a 57% yield, with fucose in position 3 appearing only as an α -linkage, while the fucosylation of position 6 had low stereoselectivity (α/β , 3:1). The addition of diethyl ether to dichloromethane (1:1 mixture) strongly improved the yield (91%) and slightly improved the stereoselectivity (α/β : 3.5:1) (Scheme 6). Compounds **37** and **38** were then used as a mixture of isomers in the next steps to eventually recover compound **43** in a 53% yield.

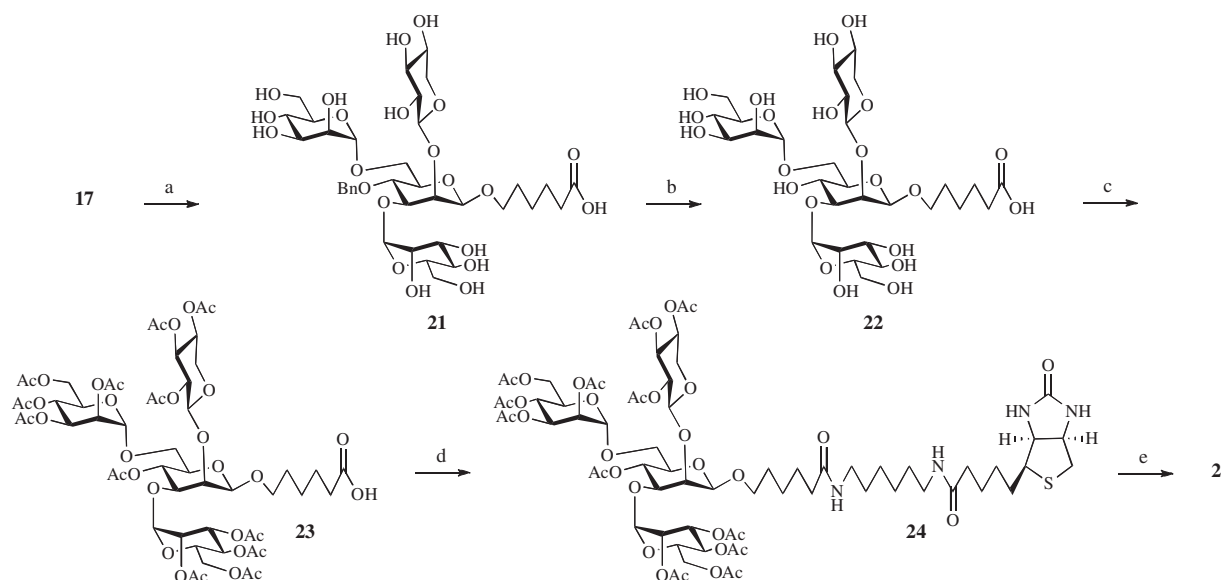
As the presence of non-participating benzyl protecting groups was necessary to achieve α -fucosylation in good selectivity, we chose to convert the biotin thioether function to a sulfone function. We have used this strategy previously² as the biotin does not interfere with the palladium hydrogenolysis catalyst when oxidised to sulfone, and biotin sulfone still presents a strong affinity to streptavidin. Phthalimido groups were removed and the amino functions were acetylated to give **39** and **43**. Ethyl esters were saponified and the acids were then coupled to **10** to give the biotin conjugates **40** and **44**. Oxidation to sulfones **42** and **45** (using *meta*-chloroperbenzoic acid), followed by hydrogenolysis of these latter, afforded the final conjugates **3** and **4** (Scheme 7).



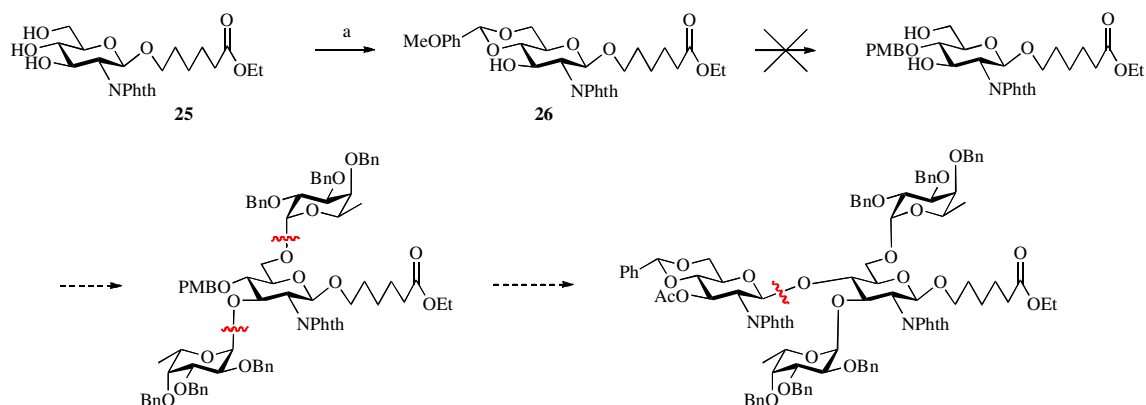
Scheme 1. Synthesis of **17**. Reagents and conditions: (a) dimethyl benzaldehyde acetal, CSA, CH₃CN, 89%; (b) Et₃SiH, PhBCl₂, 4 Å molecular sieves, CH₂Cl₂; (c) **7**, NIS, TfOH, 4 Å molecular sieves, CH₂Cl₂, 95%; (d) Et₃SiH, PhBCl₂, 4 Å molecular sieves, CH₂Cl₂, −78 °C 88%, **15**:**16**, 8:2 ratio; (e) **7**, NIS, TfOH, 4 Å molecular sieves, CH₂Cl₂, 46%.



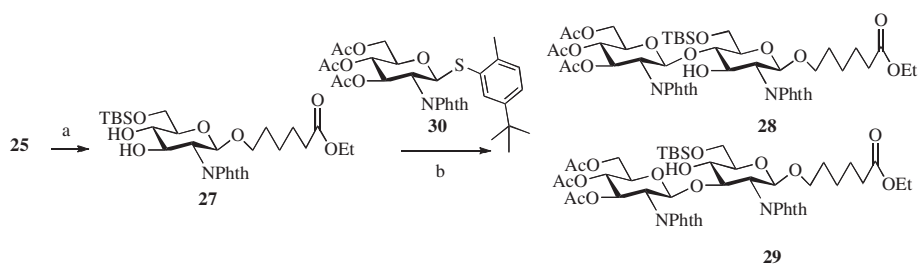
Scheme 2. Synthesis of **1**. Reagents and conditions: (a) MeONa, MeOH, then NaOH, H₂O, 70 °C, 98%; (b) Ac₂O, pyridine then H₂O/THF (v/v: 1:2); (c) **10**, EDC, DMAP, DMF, 60 °C (49% two steps); (d) MeONa, MeOH, 94%.



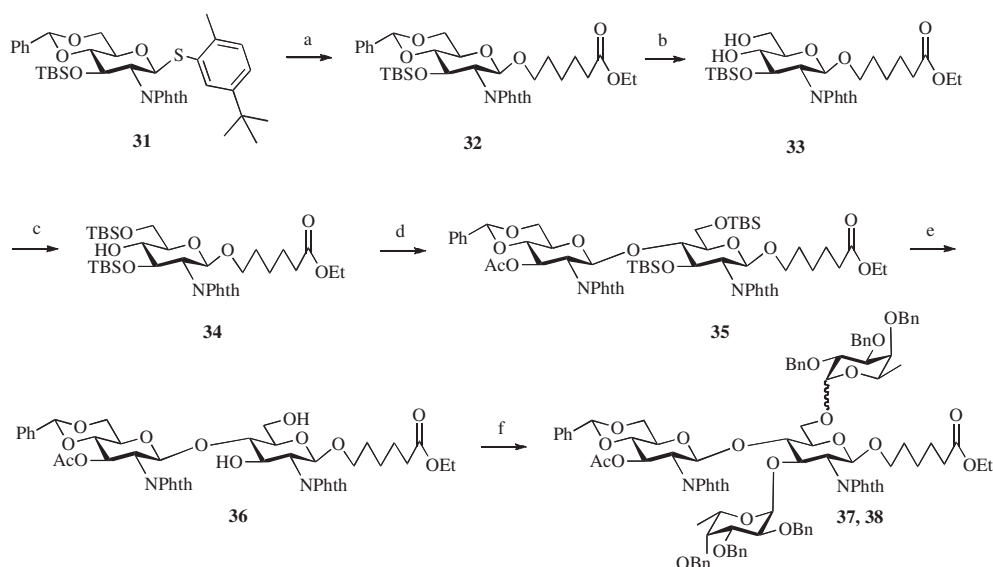
Scheme 3. Synthesis of **2**. Reagents and conditions: (a) MeONa, MeOH, then NaOH, H₂O; (b) H₂, Pd black, Pd(OH)₂/C; (c) Ac₂O, pyridine; then H₂O/THF; (d) **10**, EDC, DMAP, DMF, 70 °C, 30% overall yield; (e) MeONa, MeOH, 62%.



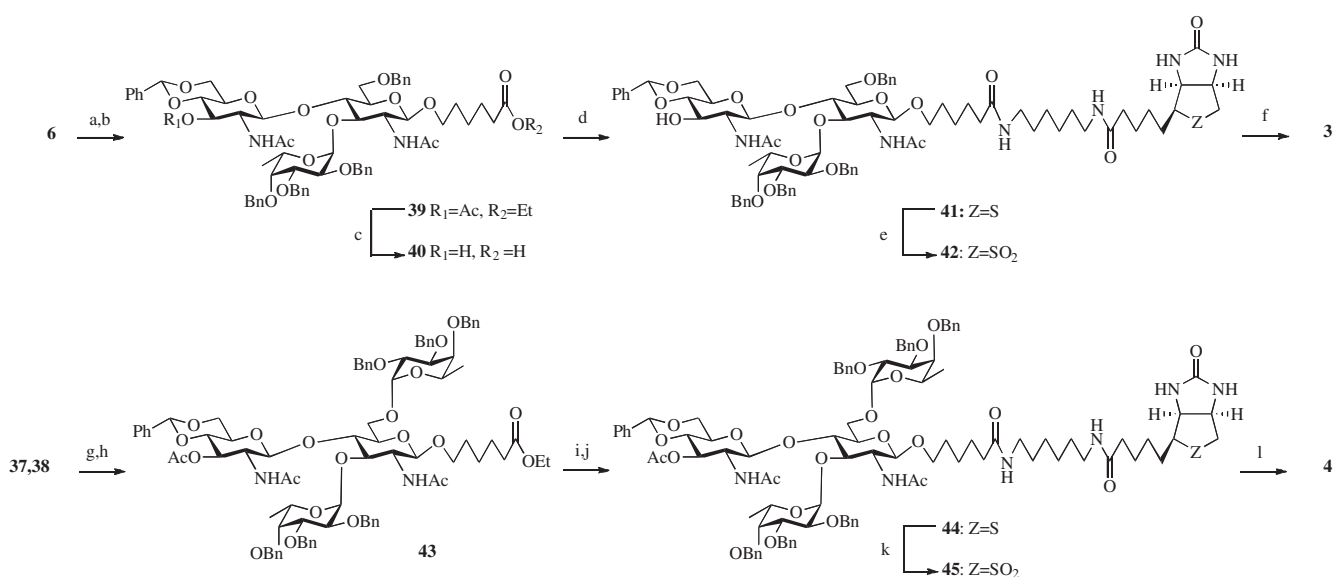
Scheme 4. Reagents and conditions: Benzaldehyde dimethyl acetal, CSA, CH₃CN, 81%.



Scheme 5. Reagents and conditions: (a) TBSCl, pyridine, DMAP, 56%; (b) NBS, TFOH, 4 Å molecular sieves, CH₂Cl₂, 21%, (28/29: 2:1).



Scheme 6. Reagents and conditions: (a) ethyl 6-hydroxyhexanoate, NIS, TFOH, 4 Å molecular sieves, CH₂Cl₂, 90%; (b) H₂, Pd/C, AcOEt, 100%; (c) TBSCl, DMAP, pyridine, 90%; (d) 8, NIS, TFOH, 4 Å molecular sieves, CH₂Cl₂, 61%; (e) NH₄F, DMF, 100 °C, 80%; (f) 9, NIS, TFOH, 4 Å molecular sieves, Et₂O/CH₂Cl₂, 91%, (β/α: 1:3.5).

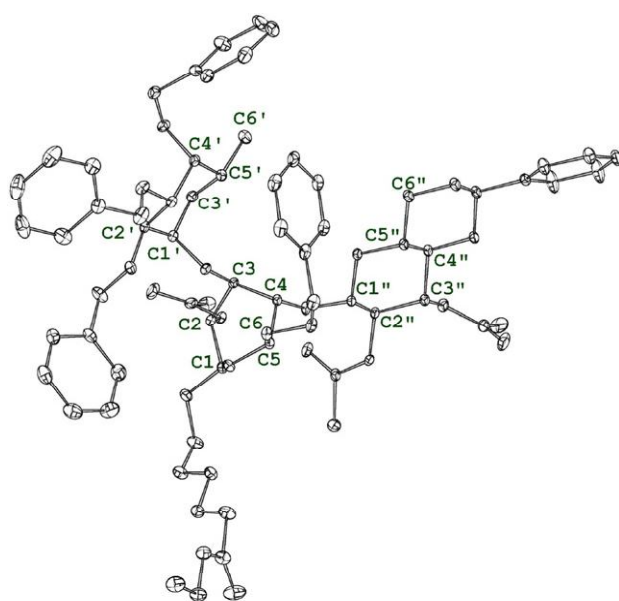


Scheme 7. Synthesis of **3** and **4**. Reagents and conditions: (a) N₂H₄·H₂O, EtOH, 90 °C; (b) Ac₂O, pyridine, 89% (two steps); (c) aq 10 M NaOH, THF, 75 °C, 100%; (d) **10**, DMAP, EDC, DMF, 70 °C, 54%; (e) mCPBA, CH₂Cl₂, 84%; (f) H₂, Pd/C, methanol, H₂O, 87%; (g) N₂H₄·H₂O, EtOH, 90 °C; (h) Ac₂O, pyridine, 58%; (i) aq 10 M NaOH, THF, 75 °C; (j) **10**, EDC, DMAP, DMF, 70 °C, 51%; (k) mCPBA, CH₂Cl₂, 84%; (l) H₂, Pd/C, methanol, H₂O, 100%.

2.4. Strain in branched chitobiosides: Analysis of the X-ray structure

An X-ray structure of crystalline **39** could be obtained (see Fig. 4) and an unexpected conformation could be evidently seen. The first glucosamine was distorted and adopts an unusual ${}^0S_4$ conformation. The conformation adopted by the core glucosamine could be explained by the steric hindrance induced by the adjacent fucosyl and glucosaminyl moieties (bearing bulky protecting groups), respectively, on position 3 and 4.

Figure 5 obtained from the crystal structure of **39**, clearly depicts an anti parallel conformation of position 3 and 4 of the core glucosamine. By analogy this gives for compound **6** a possible explanation for the poor reactivity or accessibility of the position 4 of the core glucosamine during our attempted glycosylations.



2.5. Biological evaluation

2.5.1. Reactivity with anti-bee venom and anti-horseradish peroxidase

As a first evaluation of the synthesized conjugates (**1–4**), an ELISA using anti-bee venom and anti-horseradish peroxidase rabbit antibodies was performed (Fig. 6) as these antisera are known to cross-react with fucosylated and/or xylosylated *N*-glycans.¹² The results showed that the xylose-containing conjugates (compounds **1** and **2**) bind particularly well to anti-HRP, but that the fucose-containing ones bind only weakly (the difucosylated compound **4** binds weakly to anti-bee venom, whereas both compounds **3** and **4**, respectively, bound more significantly to anti-HRP). The weaker binding to the fucosylated samples was expected from previous data with exoglycosidase-treated *N*-glycans;¹²

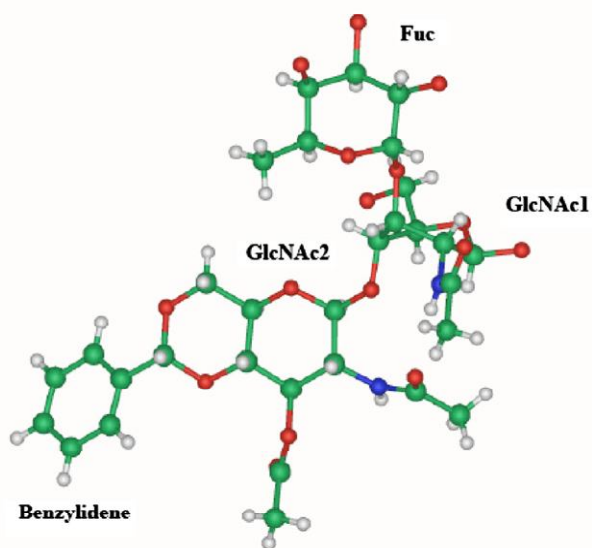


Figure 4. X-ray structure of **39** (left), **39** represented without the benzyl groups and aglycon (right).

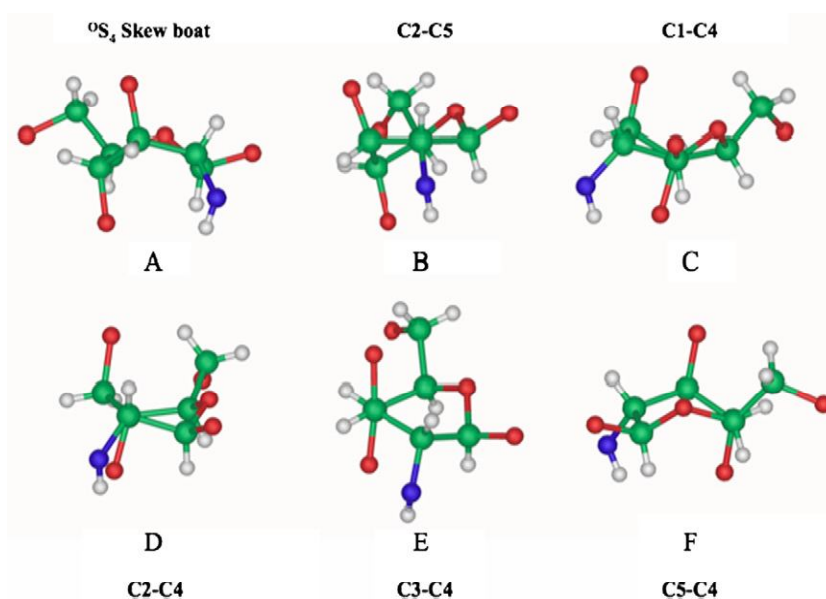


Figure 5. ${}^0S_4$ conformational observations of the core glucosamine (from crystal structure of **39**). (A) Side view, (B) in C2–C5 axis, (C) in C1–C4 axis, (D) in C2–C4 axis, (E) in C3–C4 axis, (F) in C5–C4 axis. The analysis were made with iMol version 0.40 Copyright © 2002–2007 Piotr Rotkiewicz.

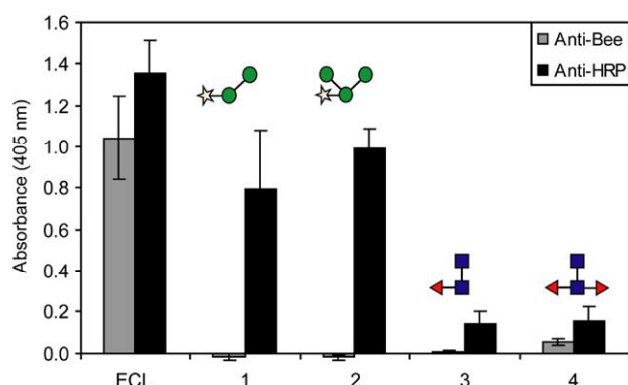


Figure 6. ELISA with anti-bee venom and anti-horseradish peroxidase antisera. Microtitre wells were coated with streptavidin followed by biotinylated *Erythrina cristagalli* lectin (ECL, as a positive control) or compounds **1** (MOX fragment), **2** (MMX fragment), **3** (monofucosylated F³ core fragment) and **4** (difucosylated F³F⁶ core fragment) at 5 µg/mL. 'Blank corrected' results of the average of two independent duplicate assays are presented (total $n = 4$, with standard deviations); structures of the oligosaccharide fragments are shown according to the nomenclature of the Consortium for Functional Glycomics. BSA-MOXF³ was used to coat one set of lanes as a positive control, whereas biotinylated ECL was shown not to bind BSA-blocked plates unless streptavidin was used to coat the wells (data not shown).

biotinylated *Erythrina cristagalli* lectin was used as a positive control since this plant lectin contains MMXF-type glycans.¹³

2.5.2. Reactivity with patients' sera

Fourteen sera (1–14) from multiple pollen sensitised patients' containing IgE antibodies reactive towards bromelain, as detected by ImmunoCAP, were selected for the study (Fig. 7). With exception of serum 9 and serum 11, all sera also contained IgE cross-reacting with HRP and *E. cristagalli* lectin (ECL). Controls consisted of sera from two non atopic subjects. The synthetic glycoconjugates were then tested for IgE binding in an ELISA assay. Three out of fourteen sera displayed additional IgE binding to xylosylated compound **2**, two to xylosylated compound **3** and two to fucosylated compounds **3** and **4**. Testing streptavidin as negative control gave no results in any of the sera tested. This weak reactivity with patients' sera was rather unexpected and may indicate that longer fragments are required for a better IgE binding.

3. Conclusion

Four biotinylated *N*-glycan fragments potentially involved in cross-allergies have been synthesized using exclusively MBP thio-glycosides donors. The results highlighted the difficulty of constructing branched oligosaccharides in particular chitobiosides. When the biotinylated *N*-glycan fragments were coated on streptavidin microplates, various levels of reactivity to anti-carbohydrate antibodies and patients' sera were observed. These preliminary studies showed the potential utility of xylosylated and fucosylated oligosaccharide fragments in determining CDD antibody epitopes.

4. Experimental part

4.1. Immunological evaluation

4.1.1. IgG ELISA

Microtitre plates (MaxiSorp Immuno Plate, Nalge Nunc International, Roskilde, Denmark) were coated with streptavidin (5 µg/mL) in sodium carbonate buffer, except for where BSA-MOXF³ was applied as the sole antigen. The plates were blocked with BSA to prevent non-specific interactions. Streptavidin-coated wells were then incubated with compounds **1**, **2**, **3** or **4** or with bio-

tinylated *E. cristagalli* lectin at 5 µg/mL. Then rabbit anti-bee venom (1:3000) or rabbit anti-HRP (1:10,000) were applied. Finally, alkaline-phosphatase-conjugated anti-rabbit antiserum (1:10,000) was used and *p*-nitrophenyl-phosphate was the chromogenic substrate (results in terms of absorbance at 405 nm after an enzymatic reaction time of 15 min at 37 °C are shown).

4.1.2. Patients' sera

Fourteen sera (1–14) from multiple pollen sensitised patients' containing IgE antibodies directed against bromelain, as detected by ImmunoCAP, have been selected for the study. With exception of patients' sera Nos. 9 and 11, all sera also contained HRP-specific IgE. Controls consisted of sera from two non atopic subjects.

4.1.3. IgE ELISA

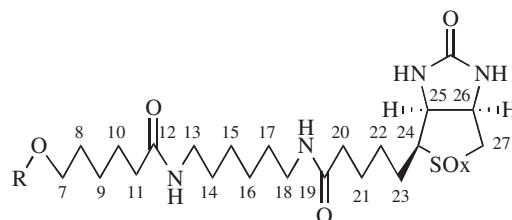
Microtitre plates, pre-coated as appropriate with streptavidin, were coated with 0.5 µg antigen (biotinylated compounds **1**, **2**, **3** or **4** with biotinylated *E. cristagalli* lectin and HRP as positive controls and streptavidin as negative control) per well overnight at 4 °C. After blocking with Tris-buffered saline (TBS), 0.05% (v/v) Tween 20 and 3% (w/v) milk powder, 1:7 diluted sera were applied onto the coated plates and incubated overnight at 4 °C. After washing, the plates were incubated with a 1:1000 diluted alkaline phosphatase-conjugated mouse anti-human IgE antibody (BD Pharmingen, San Diego, CA, USA) for 2 h at room temperature. Colour development was performed using 0.1% (w/v) disodium *p*-nitrophenyl phosphate substrate (Sigma–Aldrich, Steinheim, Germany) and the optical density (OD) was measured at 405 nm (550 nm as reference wavelength) after 30 min. Sera of two non-allergic subjects were used as negative controls and OD values were counted positive when they exceeded the mean OD of the negative controls by more than three standard deviations.

4.2. Chemical synthesis

4.2.1. General procedures

All compounds were homogeneous by TLC analysis and had spectral properties consistent with their assigned structures. Melting points were determined in capillary tubes in a Büchi 510 apparatus, and are uncorrected. Optical rotations were measured with a Perkin–Elmer Model 241 digital polarimeter at 22 ± 3 °C. Compound purity was checked by TLC on Silica Gel 60 F₂₅₄ (E. Merck) with detection by charring with sulfuric acid. Column chromatography was performed on Silica Gel 60 (E. Merck). ¹H NMR spectra were recorded with Brüker AM 250, AM 400 instruments. Chemical ionisation and FAB mass spectrometry were recorded with Jeol MS700: CI (gas: ammonia); FAB (matrix: NBA, NaI).

Chain numbering of biotin:



4.2.2. 5-Carboxypentyl 2-O-(β-D-xylopyranosyl)-6-O-(α-D-mannopyranosyl)-β-D-mannopyranoside biotin conjugate (**1**)

To a mixture of **18** (0.341 g, 0.579 mmol) and DMAP (0.028 g, 0.229 mmol, 0.4 equiv) in anhydrous pyridine, was added under argon acetic anhydride (2.50 mL, 26.47 mmol, 45 equiv). The mixture was stirred overnight at room temperature and concentrated. A

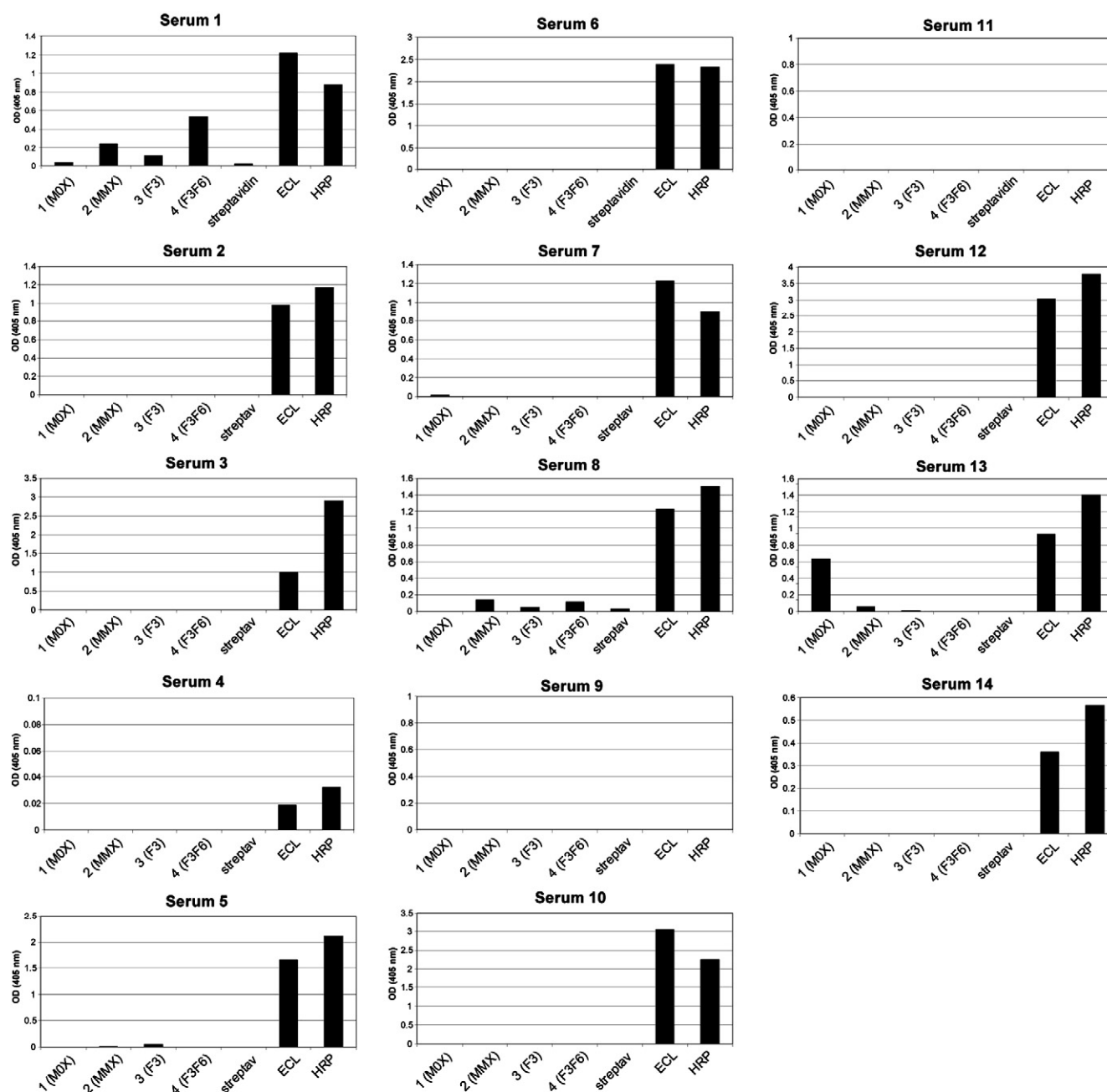


Figure 7. IgE ELISA with selected human sera. Reactivity to compounds **1–4** or ECL on streptavidin-coated microtitre plates was tested similarly as for the IgG reactivity; HRP was introduced as a second positive control.

solution of the residue was stirred in THF (4 mL) and water (1 mL) until disappearance of the mixed anhydride (TLC control: $\text{CH}_2\text{Cl}_2/\text{methanol}$: 9:1). A solution of the residues **19** and **10** (0.396 g, 1.158 mmol, 2 equiv), DMAP (0.084 g, 0.694 mmol, 1.2 equiv) and EDC (0.165 g, 0.868 mmol, 1.5 equiv) in anhydrous DMF (8 mL) was stirred overnight at 70 °C. Another portion of EDC (0.055 g, 0.289 mmol, 0.5 equiv) was added to complete the reaction and after 2 h, the solution was concentrated. The residue was extracted with CH_2Cl_2 and washed with water. The organic layer was dried over MgSO_4 , filtered and concentrated. The residue was purified by column chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{methanol}$: 95:5) to give 0.366 g of **20** (49%) as a syrup. R_f : 0.43 ($\text{CH}_2\text{Cl}_2/\text{methanol}$: 9:1). $[\alpha]_{\text{D}}^{25}$ –24 (c 0.3, CHCl_3). MS FAB+–HRMS m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{57}\text{H}_{86}\text{O}_{27}\text{N}_4\text{SNa}$ 1313.5097, found 1313.5099. Compound **20** (0.360 g, 0.279 mmol) was dissolved in methanol (6 mL) and sodium

(0.032 g, 1.391 mmol, 5 equiv) was added. The solution was stirred at room temperature overnight and neutralised ($\text{IR } 120 \text{ H}^+$), filtered and concentrated. The residue was purified on a G15 column to give, after lyophilisation, 240 mg of **1** (94%) as a white powder. $[\alpha]_{\text{D}}^{25} +0.3$ (c 5, $\text{H}_2\text{O}/\text{MeOH}$ (1:1)). ^1H NMR (400 MHz, D_2O) δ : 4.79 (s, 1H, H_{11}), 4.64 (s, 1H, H_{11}), 4.51 (m, 1H, H_{26}), 4.41 (d, 1H, $J_{\text{H}1'-\text{H}2'} = 7.2 \text{ Hz}$, $\text{H}_{1'}$), 4.32 (m, 1H, H_{25}), 4.04 (s, 1H, H_2), 3.89–3.64 (m, 8H, H_{27} , H_{13} , H_{18}), 2.89 (m, 1H, H_{27}), 2.68 (d, 1H, $J_{\text{gem}} = 13.0 \text{ Hz}$, H_{27}), 2.13 (m, 4H, H_{11} , H_{20}), 1.66–1.23 (m, 20H, H_8 , H_9 , H_{10} , H_{14} , H_{15} , H_{16} , H_{17} , H_{21} , H_{22} , H_{23}). ^{13}C NMR (100 MHz, D_2O) δ : 176.9 (CONH), 176.7 (CONH), 165.5 (CO urea), 104.7 ($\text{C}_{1'}$), 100.5 (C_1), 99.9 (C_1), 78.9 (C_2), 75.8 (C_3), 74.8, 73.7 (C_2), 73.0, 72.5, 70.9 (C_2), 70.2 (C_6), 70.2, 69.6, 67.5, 67.0, 66.1 (C_6), 65.5 (C_5), 62.4 (C_{25}), 61.2 (C_7), 60.6 (C_{26}), 55.8 (C_{24}), 40.1 (C_{27}), 39.5 (C_{13} , C_{18}), 36.1 (C_{11} or

C₂₀), 35.9 (C₁₁ or C₂₀), 28.8, 28.7, 28.6, 28.3, 28.1, 26.1, 25.6, 25.6, 25.1, 24.3. MS FAB+–HRMS *m/z* [M+Na]⁺ calcd for C₃₉H₆₈O₁₈N₄SNa 935.4147, found 935.4131.

4.2.3. 5-Carboxypentyl 2-O-(β-D-xylopyranosyl)-3-O-(α-D-mannopyranosyl)-6-O-(α-D-mannopyranosyl)-β-D-mannopyranoside biotin conjugate (2)

Compound **17** (0.300 g, 0.150 mmol) was dissolved in THF (2 mL) and methanol (5 mL) and sodium (0.034 g, 1.500 mmol, 10 equiv) was added. The mixture was degassed with stirring and NaOH (10 M, 0.3 mL, 3.000 mmol, 20 equiv) was added. The mixture was stirred overnight at room temperature and was then neutralised (IR 120 H⁺), filtered and concentrated. The crude product **21** was dissolved in methanol (10 mL) and water (HPLC grade, 2 mL) and Pd Black (20 mg) and Pd(OH)₂/C (20%, 50 mg) were added. Vacuum and H₂ were alternated and the mixture was stirred at room temperature under H₂ overnight. The mixture was filtered off through Celite and concentrated. The residue was dissolved in water and filtered through a 0.45 μm syringe filter and concentrated. The residue **22** was dissolved in anhydrous pyridine (4 mL) and DMAP (22 mg), acetic anhydride (0.7 mL) were added under argon. The mixture was stirred for 2 days at room temperature. Concentrated and the residue was extracted with CH₂Cl₂ and washed with water. The organic layer was dried over MgSO₄, filtered and concentrated. The crude product **23** was dissolved in anhydrous DMF (6 mL) and were added under argon: **10** (0.256 g, 0.750 mmol, 5 equiv), DMAP (0.020 g, 0.160 mmol, 1.1 equiv) and EDC (0.057 g, 0.300 mmol, 2 equiv). The solution was stirred for 3 h at 70 °C. EDC (0.057 g, 0.300 mmol, 2 equiv) was added to complete the reaction and after over night stirring, concentrated. The residue was extracted with CH₂Cl₂ and washed with water. The organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (CH₂Cl₂/methanol: 95:5) to give 70 mg of **24** (30% over 4 steps) as a syrup. **24** (0.067 mg, 0.042 mmol) was dissolved in methanol (5 mL) and sodium (0.030 g, 1.304 mmol, 30 equiv) was added. The mixture was degassed with stirring and was stirred overnight. The mixture was neutralised (IR 120 H⁺), filtered and concentrated. The residue was purified on a G15 column to give, after lyophilisation, 28 mg of **2** (62%) as a white powder. [α]_D²⁵ +19 (c 1.5, MeOH/H₂O (1:1)). ¹H NMR (400 MHz, D₂O) δ: 5.04 (s, 1H, 1H₁), 4.79 (s, 1H, 1H₁), 4.66 (s, 1H, 1H₁), 4.50 (dd, 1H, J_{H26–H27} = 5.0 Hz, J_{H26–H25} = 7.8 Hz, H₂₆), 4.39 (d, 1H, J_{H1′–H2′} = 7.4 Hz, H_{1′}), 4.32 (dd, 1H, J_{H25–H24} = 4.4 Hz, H₂₅), 4.08 (s, 1H, 1H₂), 3.94–3.45 (m, 21H), 3.36 (m, 2H), 3.22 (m, 1H, H₂₄), 3.14 (t, 1H, J = 11.0 Hz, 1H₆), 3.10–3.05 (m, 4H, H₁₃, H₁₈), 2.89 (dd, 1H, J_{gem} = 13.0 Hz, H₂₇), 2.68 (d, 1H, J_{gem} = 13.0 Hz, H₂₇), 2.14 (m, 4H, H₁₁, H₂₀), 1.65–1.20 (m, 20H, H₈, H₉, H₁₀, H₁₄, H₁₅, H₁₆, H₁₇, H₂₁, H₂₂, H₂₃). ¹³C NMR (100 MHz, D₂O) δ: 177.0 (CO NH), 176.6 (CO NH), 165.6 (CO urea), 105.6 (C_{1′}), 102.3 (1C₁), 100.4 (1C₁), 99.8 (1C₁), 80.2, 77.7 (2C), 75.8, 74.6, 73.9, 73.7, 73.0, 70.9, 70.6, 70.4, 70.3 (C₇), 70.2, 69.6, 67.1, 67.0, 65.7 (1C₆), 65.3 (1C₆), 62.4 (C₂₅), 61.4 (C₅, 1C), 61.2 (C₅, C₆), 60.6 (C₂₆), 55.8 (C₂₄), 40.0 (C₂₇), 39.5 (C₁₃, C₁₈), 36.1 (C₁₁ or C₂₀), 35.8 (C₁₁ or C₂₀), 28.0–24.0 (C₈, C₉, C₁₀, C₁₄, C₁₅, C₁₆, C₁₇, C₂₁, C₂₂, C₂₃). MS FAB+–HRMS *m/z* [M+Na]⁺ calcd for C₄₅H₇₈O₂₃N₄SNa 1097.4675, found 1097.4645.

4.2.4. 5-Carboxypentyl 4-O-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-3-O-(α-L-fucopyranosyl)-2-acetamido-2-deoxy-β-D-glucopyranoside oxidised biotin conjugate (3)

To a solution of **42** (0.100 mg, 0.067 mmol) in methanol (4 mL) and water (HPLC grade, 1 mL) was added Pd/C (10%) (50 mg, 0.5 g per g of substrate). Vacuum and H₂ were alternated and then the mixture was stirred at room temperature under H₂ overnight. The mixture was filtered off through Celite and concentrated. The residue was dissolved in water (HPLC grade) and washed with

CH₂Cl₂ (3 times). The aqueous layer was evaporated and the residue was purified on a G15 column to give, after lyophilisation, 60 mg of **3** (87%) as a white powder. [α]_D²⁵ –26 (c 2, MeOH/H₂O (1:1)). ¹H NMR (400 MHz, D₂O) δ: 5.00 (d, 1H, J_{H1′–H2′} = 4.0 Hz, H_{1′}), 4.74–4.65 (m, 3H, H₂₅, H₂₆, H_{5′}), 4.46 (d, 1H, J_{H1–H2} = 8.4 Hz, 1H₁), 4.41 (d, 1H, J_{H1–H2} = 8.0 Hz, 1H₁), 3.91–3.73 (m, 8H), 3.70–3.61 (m, 3H), 3.56–3.34 (m, 7H), 3.29 (d, 1H, J_{gem} = 14.9 Hz, H₂₇), 3.19–3.07 (m, 5H), 2.21 (t, 2H, H₁₁ or H₂₀), 2.15 (t, 2H, H₁₁ or H₂₀), 1.98 (s, 3H, CH₃ NHAc), 1.94 (s, 3H, CH₃ NHAc), 1.88–1.81 (m, 1H), 1.75–1.57 (m, 3H), 1.57–1.41 (m, 10H), 1.30–1.21 (m, 6H), 1.19 (d, 3H, J_{H6′–H5′} = 6.6 Hz, 1H_{6′}). ¹³C NMR (100 MHz, D₂O) δ: 177.0 (CONH), 176.7 (CONH), 174.9 (CONH), 174.5 (CONH), 164.4 (CO urea), 101.3 (1C₁), 100.7 (1C₁), 98.8 (C_{1′}), 76.3, 75.7, 75.3, 74.0, 73.9, 72.4, 71.1, 70.7 (C₇), 69.5, 68.0, 67.0 (C_{5′}), 61.9 (1C₆), 60.7 (C₂₄), 60.3 (1C₆), 56.1 (1C₂), 56.0 (1C₂), 54.5 (C₂₅ or C₂₆), 54.1 (C₂₇), 50.1 (C₂₅ or C₂₆), 39.6 (C₁₃ or C₁₈), 39.5 (C₁₃ or C₁₈), 36.1 (C₁₁ or C₂₀), 35.8 (C₁₁ or C₂₀), 28.6 (2C), 28.5, 26.0 (2C), 25.5 (2C), 25.4, 25.0, 22.6 (CH₃ NHAc), 22.4 (CH₃ NHAc), 21.2, 15.8 (C_{6′}). MS FAB+–HRMS *m/z* [M+Na]⁺ calcd for C₄₄H₇₆N₆O₂₀SNa 1063.4732, found 1063.4768.

4.2.5. 5-Carboxypentyl 3,6-di-O-(α-L-fucopyranosyl)-4-O-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-2-acetamido-2-deoxy-β-D-glucopyranoside oxidised biotin conjugate (4)

To a solution of **45** (0.190 g, 0.104 mmol) in methanol (4 mL) and water (HPLC grade, 1 mL) was added Pd/C (10%) (95 mg, 0.5 g per g of substrate). Vacuum and H₂ were alternated and the mixture was stirred at room temperature under H₂ overnight. The mixture was filtered off through Celite and concentrated. The residue was dissolved in water (HPLC grade) and washed with CH₂Cl₂ (3 times). The aqueous layer was evaporated and the residue was purified on a G15 column to give, after lyophilisation, 123 mg of **4** (100%) as a white powder. [α]_D²⁵ –55 (c 2, MeOH/H₂O (1:1)). ¹H NMR (400 MHz, D₂O) δ: 5.02 (d, 1H, J_{H1–H2} = 3.9 Hz, 1H₁ fucose), 4.84 (d, 1H, J_{H1–H2} = 3.8 Hz, 1H₁ fucose), 4.70–4.61 (m, 3H, H₂₅, H₂₆, 1H₅ fucose), 4.55 (d, 1H, J_{H1–H2} = 8.4 Hz, 1H₁), 4.38 (d, 1H, J_{H1–H2} = 8.0 Hz, 1H₁), 4.05 (q, 1H, J_{H5–H6} = 6.6 Hz, 1H₅ fucose), 3.92 (t, 1H, J = 9.0 Hz, 1H), 3.87–3.80 (m, 4H), 3.78–3.58 (m, 9H), 3.52–3.23 (m, 8H), 3.15–3.04 (m, 5H, H₁₃, H₁₈, 1H), 2.17 (t, 2H, J = 7.2 Hz, H₁₁ or H₂₀), 2.12 (t, 2H, J = 7.3 Hz, H₁₁ or H₂₀), 1.94 (s, CH₃ NHAc), 1.91 (s, CH₃ NHAc), 1.85–1.77 (m, 1H, 1H₂₃), 1.69–1.53 (m, 3H), 1.52–1.39 (m, 10H), 1.27–1.20 (m, 6H), 1.17 (d, 3H, J_{H6–H5} = 6.6 Hz, CH₃ fucose), 1.12 (d, 3H, J_{H6–H5} = 6.6 Hz, CH₃ fucose). ¹³C NMR (100 MHz, D₂O) δ: 176.9 (CO NH), 176.6 (CO NH), 174.9 (CO NH), 174.4 (CO NH), 164.4 (CO urea), 101.2 (1C₁), 100.4 (1C₁), 99.3 (1C₁ fucose), 98.9 (1C₁ fucose), 76.2, 75.3, 74.3, 73.9, 73.6, 72.4, 72.2, 71.1, 70.4 (C₇), 69.9, 69.5, 68.5, 68.0, 67.1, 67.0, 66.4 (1C₆), 62.0 (1C₆), 60.7 (C₂₄), 56.2 (1C₂), 56.0 (1C₂), 54.5 (C₂₅ or C₂₆), 54.1 (C₂₇), 50.0 (C₂₅ or C₂₆), 39.5 (C₁₂, C₁₈), 36.0 (C₁₁ or C₂₀), 35.7 (C₁₁ or C₂₀), 28.6, 28.5 (2C), 26.0, 25.5 (3C), 25.0, 22.6 (CH₃ NHAc), 22.5 (CH₃ NHAc), 21.3 (C₂₃), 15.8 (1C₆ fucose), 15.7 (1C₆ fucose). MS FAB+–MS *m/z* [M][–] calcd for C₅₀H₈₅N₆O₂₄Na 1185.5, found 1185.7.

4.2.6. 5-Carboxymethylpentyl 2-O-(2,3,4-tri-O-benzoyl-β-D-xylopyranosyl)-4,6-O-benzylidene-β-D-mannopyranoside (12)

Compound **11** (0.560 g, 0.744 mmol) was dissolved in anhydrous acetonitrile (5 mL). Dimethyl benzaldehyde acetal (0.224 mL, 1.489 mmol, 2 equiv), camphorsulfonic acid (0.051 g, 0.223 mmol, 0.3 equiv) were added under argon and the mixture was stirred at room temperature overnight. A saturated NaHCO₃ solution was added and the product was extracted with CH₂Cl₂. The organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (cyclohexane/EtOAc: 7:3–5:5) to give 0.558 g of **12** (89%) as a white solid. R_f: 0.19 (cyclohexane/EtOAc: 7:3). [α]_D²⁵ –77 (c 2, CHCl₃). Mp:

146–147 °C. ¹H NMR (400 MHz, CDCl₃) δ: 8.07–8.00 (m, 6H, H Ar), 7.60–7.35 (m, 14H, H Ar), 5.83 (t, 1H, $J_{H3'-H2'} = J_{H3'-H4'} = 7.4$ Hz, H_{3'}), 5.38–5.34 (m, 2H, H benzyldiene, H_{4'}), 5.29 (d, 1H, H_{1'}), 5.01 (dd, 1H, $J_{H2'-H1'} = 5.6$ Hz, H_{2'}), 4.64 (dd, 1H, $J_{H5'-H4'} = 12.1$ Hz, $J_{H5'-H6'} = 4.4$ Hz, 1H_{5'}), 4.45 (s, 1H, H₁), 4.22 (d, 1H, $J_{H2-H3} = 3.2$ Hz, H₂), 4.13 (m, 1H, 1H₆), 3.84–3.67 (m, 6H, H₃, H₄, 1H_{5'}, CH₃ OMe), 3.59–3.52 (m, 2H, 1H₆, 1H₇), 3.30 (td, 1H, $J_{gem} = 9.4$ Hz, $J_{H7-H8} = 6.8$ Hz, 1H₇), 3.23 (td, 1H, $J_{H5-H4} = 9.7$ Hz, $J_{H5-H6} = 4.8$ Hz, H₅), 2.94 (d, 1H, $J_{OH-H3} = 8.0$ Hz, OH), 2.28 (t, 2H, $J_{H11-H10} = 7.4$ Hz, H₁₁), 1.59 (m, 2H, H₁₀), 1.46 (m, 2H, H₈), 1.27 (m, 2H, H₉). ¹³C NMR (100 MHz, CDCl₃) δ: 174.4 (CO COOMe), 165.9 (CO Bz), 165.7 (CO Bz), 165.5 (CO Bz), 137.0–126.0 (C Ar), 102.3 (C benzyldiene), 101.5 (C₁), 100.7 (C_{1'}), 79.4 (C₄), 77.3 (C₂), 70.5 (C_{2'}), 70.5 (C_{3'}), 70.4 (C₃), 70.0 (C₇), 69.6 (C_{4'}), 68.8 (C₆), 67.5 (C₅), 61.7 (C_{5'}), 51.9 (CH₃ OMe), 34.2 (C₁₁), 29.4 (C₈), 25.9 (C₉), 25.0 (C₁₀). MS FAB+–HRMS *m/z* [M+Na]⁺ calcd for C₄₆H₄₈O₁₅Na 863.2891, found 863.2871.

4.2.7. 5-Carboxymethylpentyl 2-O-(2,3,4-tri-O-benzoyl-β-D-xyllopyranosyl)-3-O-(2,3,4,6-tetra-O-benzoyl-α-D-mannopyranosyl)-4,6-O-benzylidene-β-D-mannopyranoside (14)

To a mixture of **12** (0.320 g, 0.318 mmol), **7** (0.290 g, 0.382 mmol, 1.2 equiv) and 4 Å molecular sieves (500 mg) in anhydrous CH₂Cl₂ (4 mL), were added under argon: NIS (0.143 g, 0.636 mmol, 2 equiv) and TfOH (0.003 mL, 0.031 mmol, 0.1 equiv). After 20 min the mixture was filtered, extracted with CH₂Cl₂ and washed with saturated NaHCO₃ and Na₂S₂O₃ solutions. The organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (cyclohexane/EtOAc: 8:2) to give 430 mg of **14** (95%) as a white solid. *R*_f: 0.38 (cyclohexane/EtOAc: 7:3). [α]_D²⁵ –72 (c 1, CHCl₃). Mp: 102–103 °C. ¹H NMR (400 MHz, CDCl₃) δ: 8.36 (d, 2H, $J = 7.1$ Hz, H Ar), 8.15–8.10 (m, 6H, H Ar), 8.06 (d, 2H, $J = 7.1$ Hz, H Ar), 8.01 (d, 2H, $J = 7.1$ Hz, H Ar), 7.86 (d, 2H, $J = 7.2$ Hz, H Ar), 7.70–7.25 (m, 26H, H Ar), 6.24–6.17 (m, 2H, H_{3''}, H_{4''}), 6.01 (t, 1H, $J_{H2''-H1''} = 2.0$ Hz, H_{2''}), 5.71 (t, 1H, $J_{H3''-H2''} = 3.4$ Hz, H_{3''}), 5.66–5.63 (m, 3H, H_{1'}, H_{2'}, H_{1''}), 5.57 (d, 1H, $J = 2.6$ Hz, H_{4'}), 5.35 (dd, 1H, $J_{gem} = 12.5$ Hz, $J_{H5'-H4'} = 1.8$ Hz, 1H_{5'}), 4.85 (m, 2H, 1H_{6''}, H benzyldiene), 4.73 (m, 1H, 1H_{5''}), 4.56 (dd, 1H, $J_{gem} = 12.1$ Hz, $J_{H6''-H5''} = 4.7$ Hz, 1H_{6''}), 4.38 (m, 2H, H₁, H₂), 4.32 (dd, 1H, $J_{gem} = 12.5$ Hz, $J_{H5'-H4'} = 1.5$ Hz, H_{5'}), 4.16 (dd, 1H, $J_{gem} = 10.3$ Hz, $J_{H6-H5} = 4.8$ Hz, 1H₆), 4.06 (dd, 1H, $J_{H3-H4} = 10.0$ Hz, $J_{H3-H2} = 3.1$ Hz, H₃), 3.81 (m, 2H, H₄, 1H₇), 3.65 (s, 3H, CH₃ OMe), 3.44 (t, 1H, $J_{H6-H5} = J_{gem} = 10.3$ Hz, 1H₆), 3.32 (td, 1H, $J_{gem} = 9.1$ Hz, $J_{H7-H8} = 6.4$ Hz, 1H₇), 3.19 (td, 1H, $J_{H5-H4} = 9.6$ Hz, H₅), 2.18 (t, 2H, $J_{H11-H10} = 7.4$ Hz, H₁₁), 1.60–1.49 (m, 4H, H₈, H₁₀), 1.38 (m, 2H, H₉). ¹³C NMR (100 MHz, CDCl₃) δ: 174.4 (CO ester), 166.4–165.0 (Cq Ar), 137.3–126.2 (C Ar), 102.0 (C₁), 101.0 (C benzyldiene), 99.4 (C_{1'} or C_{1''}), 98.6 (C_{1'} or C_{1''}), 78.3 (C₄), 75.7 (C₃), 75.7 (C₂), 70.6 (C_{2''}), 70.1 (C₇), 69.9 (C_{5''}), 69.8 (C_{3''}), 68.9 (C₆), 68.5 (C_{4'}), 67.6 (C₅, C_{2'}), 67.5 (C_{4'}), 67.2 (C_{3'}), 63.3 (C_{6''}), 59.7 (C_{5'}), 51.8 (CH₃ OMe), 34.1 (C₁₁), 29.5 (C₈ or C₁₀), 26.0 (C₉), 25.0 (C₈ or C₁₀). MS FAB+–HRMS *m/z* [M+Na]⁺ calcd for C₈₀H₇₄O₁₂₄Na 1441.4468, found 1441.4496.

4.2.8. 5-Carboxymethylpentyl 2-O-(2,3,4-tri-O-benzoyl-β-D-xyllopyranosyl)-3-O-(2,3,4,6-tetra-O-benzoyl-α-D-mannopyranosyl)-4-O-benzyl-β-D-mannopyranoside (15) and 5-carboxymethylpentyl 2-O-(2,3,4-tri-O-benzoyl-β-D-xyllopyranosyl)-3-O-(2,3,4,6-tetra-O-benzoyl-α-D-mannopyranosyl)-6-O-benzyl-β-D-mannopyranoside (16)

To a mixture of **14** (0.890 g, 0.627 mmol), 4 Å molecular sieves (1 g), triethylsilane (0.303 mL, 1.881 mmol, 3 equiv) in anhydrous CH₂Cl₂ (10 mL) was added under argon at –78 °C, dichlorophenylborane (0.277 mL, 1.231 mmol, 3.4 equiv). The mixture was stirred for 15 min and triethylamine (4 mL) and methanol (4 mL) were added dropwise. The mixture was allowed to warm up to room temperature, filtered and concentrated. The crude product was extracted with CH₂Cl₂ and washed with water. The organic layer was

dried over MgSO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (cyclohexane/EtOAc: 7:3) to give 0.792 g (88%) of a syrup containing two regioisomers (NMR determination: 8:2: **15/16**). *R*_f: 0.54 (cyclohexane/EtOAc: 5:5). ¹H NMR (400 MHz, CDCl₃) δ: 8.12–7.25 (m, 40H, H Ar), 6.20 (m, 2H, H_{3''}, H_{4''}), 5.96 (m, 1H, H_{2''}), 5.91 (t, 1H, $J_{H3''-H2''} = J_{H3''-H4''} = 7.7$ Hz, H_{3''}), 5.74 (dd, 1H, $J_{H2''-H1''} = 5.8$ Hz, H_{2''}), 5.65 (ddd, 1H, $J_{H4''-H5'a} = 4.4$ Hz, $J_{H4''-H5'b} = 11.7$ Hz, H_{4''}), 5.46 (d, 1H, $J_{H1''-H2''} = 1.4$ Hz, H_{1''}), 5.35 (d, 1H, H_{1'}), 5.01 (m, 1H, H_{5''}), 4.96 (d, 1H, $J_{gem} = 10.6$ Hz, CHPh), 4.85 (dd, 1H, $J_{gem} = 12.1$ Hz, $J_{H6''-H5''} = 2.9$ Hz, 1H_{6''}), 4.77 (dd, 1H, $J_{gem} = 12.1$ Hz, $J_{H5'-H4'} = 4.4$ Hz, 1H_{5'}), 4.68 (d, 1H, CHPh), 4.55 (dd, 1H, $J_{H6''-H5''} = 4.5$ Hz, 1H_{6''}), 4.31 (s, 1H, H₁), 4.24 (d, 1H, $J_{H2-H1} = 2.8$ Hz, H₂), 4.08 (t, 1H, $J_{H4-H3} = J_{H4-H5} = 9.5$ Hz, H₄), 3.90 (m, 1H, H_{5'}), 3.84–3.81 (m, 2H, H₃, 1H₆), 3.70 (s, 3H, OMe), 3.61 (m, 1H, 1H₆), 3.36 (m, 1H, 1H₇), 3.21 (m, 1H, H₅), 3.10 (m, 1H, 1H₇), 2.59 (s, 1H, OH (C₆)), 2.30 (t, 2H, $J = 7.8$ Hz, H₁₁), 1.61–1.19 (m, 6H, H₈, H₉, H₁₀). ¹³C NMR (100 MHz, CDCl₃) δ: 174.5 (CO COOMe), 166.0–165.0 (Cq Ar), 136.0–128.0 (C Ar), 101.4 (C_{1'}), 100.9 (C₁), 100.6 (C_{1''}), 81.4 (C₃), 77.2 (C₂), 76.2 (CH₂Ph), 76.1 (C₅), 74.6 (C₄), 71.5 (C_{2'}), 71.2 (C_{3'}), 71.0 (C_{2''}), 70.2 (C_{4'}, C_{3''}), 70.0 (C₇), 69.6 (C_{5''}), 67.9 (C_{4''}), 63.6 (C_{5'}), 62.2 (C₆, C_{6''}), 51.9 (CH₃ OMe), 34.2 (C₁₁), 29.4 (C₈), 25.8 (C₉), 25.0 (C₁₀). MS FAB+–HRMS *m/z* [M+Na]⁺ calcd for C₈₀H₇₆O₂₄Na 1443.4624, found 1443.4628.

4.2.9. 5-Carboxymethylpentyl 2-O-(2,3,4-tri-O-benzoyl-β-D-xyllopyranosyl)-3-O-(2,3,4,6-tetra-O-benzoyl-α-D-mannopyranosyl)-6-O-(2,3,4,6-tetra-O-benzoyl-α-D-mannopyranosyl)-4-O-benzyl-β-D-mannopyranoside (17)

To a mixture of **15** (0.090 g, 0.063 mmol), **7** (0.057 g, 0.075 mmol, 1.2 equiv) and 4 Å molecular sieves (100 mg) in anhydrous CH₂Cl₂ (2 mL), were added under argon: NIS (0.028 g, 0.126 mmol, 2 equiv) and TfOH (1 μL, 0.010 mmol, 0.17 equiv). The mixture was allowed to stir for 20 min and was then filtered, extracted with CH₂Cl₂ and washed with saturated NaHCO₃ and Na₂S₂O₃ solutions. The organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (cyclohexane/EtOAc: 7:3) to give 58 mg of **17** (46%) as a white solid. *R*_f: 0.24 (cyclohexane/EtOAc: 7:3). [α]_D²⁵ –59 (c 2, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ: 8.16–7.80 (m, 22H, H Ar), 7.70–7.25 (m, 38H, H Ar), 6.20 (t, 1H, $J_{H4''-H3''} = J_{H4''-H5''} = 10.2$ Hz, H_{4''}), 6.18 (m, 1H, H_{3''}), 6.13 (t, 1H, $J_{H4''-H3''} = J_{H4''-H5''} = 10.1$ Hz, H_{4''}), 5.91 (m, 1H, H_{2''}), 5.86 (dd, 1H, $J_{H3''-H2''} = 3.2$ Hz, $J_{H3''-H4''} = 10.1$ Hz, H_{3''}), 5.79 (t, 1H, $J_{H3''-H2''} = J_{H3''-H4''} = 6.3$ Hz, H_{3''}), 5.72 (dd, 1H, $J_{H2''-H1''} = 4.6$ Hz, H_{2''}), 5.63 (dd, 1H, $J_{H2''-H1''} = 1.8$ Hz, $J_{H2''-H3''} = 3.2$ Hz, H_{2''}), 5.58 (dt, 1H, $J_{H4''-H5'a} = 3.9$ Hz, $J_{H4''-H5'b} = J_{H4''-H3''} = 6.3$ Hz, H_{4''}), 5.48 (d, 1H, H_{1'}), 5.42 (d, 1H, $J_{H1''-H2''} = 1.3$ Hz, H_{1''}), 4.99 (m, 1H, H_{5''}), 4.93–4.84 (m, 4H, H_{1''}, 1H_{6''}, 1H_{5'}, CHPh), 4.69 (dd, 1H, $J_{gem} = 12.4$ Hz, $J_{H6''-H5''} = 2.3$ Hz, 1H_{6''}), 4.57–4.49 (2dd, 2H, 1H_{6''}, 1H_{6''}), 4.45–4.40 (m, 2H, H_{5''}, CHPh), 4.38 (s, 1H, H₁), 4.29 (d, 1H, $J_{H2-H1} = 2.8$ Hz, H₂), 4.03 (dd, 1H, $J_{gem} = 12.2$ Hz, $J_{H5'-H4'} = 6.0$ Hz, 1H_{5'}), 3.82–3.76 (m, 2H, H₃, 1H₇), 3.70 (d, 1H, $J_{gem} = 9.5$ Hz, 1H₆), 3.62 (s, 3H, OMe), 3.58 (t, 1H, $J_{H4-H3} = J_{H4-H5} = 9.5$ Hz, H₄), 3.50–3.39 (m, 2H, H₅, 1H₆), 3.34 (td, 1H, $J = 6.9$ Hz and 6.8 Hz, 1H₇), 2.16 (t, 2H, $J = 7.4$ Hz, H₁₁), 1.76–1.20 (m, 6H, H₈, H₉, H₁₀). ¹³C NMR (100 MHz, CDCl₃) δ: 174.4 (CO COOMe), 166–165 (Cq Ar), 133–128 (C Ar), 100.8 (C₁), 100.5 (C_{1''}), 100.3 (C_{1'}), 97.7 (C_{1''}), 81.6 (C₃), 76.5 (C₂), 76.0 (CH₂Ph), 75.8 (C₄), 75.3 (C₅), 70.9 (C_{2''}), 70.7 (C_{2''}), 70.4 (C_{3''}), 70.2 (C_{3'}, C_{3''}), 70.0 (C_{2'}, C₇), 69.8 (C_{5''}), 69.5 (C_{4'}), 69.3 (C_{5''}), 68.2 (C₆), 67.6 (C_{4''}), 67.1 (C_{4''}), 63.5 (C_{6''}), 62.9 (C_{6''}), 61.4 (C_{5'}), 51.7 (CH₃ OMe), 34.1 (C₁₁), 29.6 (C₈), 26.0 (C₉), 25.1 (C₁₀). MS FAB+–HRMS *m/z* [M+Na]⁺ calcd for C₁₁₄H₁₀₂O₃₃Na 2021.6201, found 2021.6230.

4.2.10. 5-Carboxypentyl 2-O-(β-D-xyllopyranosyl)-6-O-(α-D-mannopyranosyl)-β-D-mannopyranoside (18)

Compound **5** (1.00 g, 0.650 mmol) was dissolved in anhydrous methanol (20 mL) and sodium (0.100 g, 4.347 mmol, 6.7 equiv)

was added. The mixture was stirred overnight at rt. A NaOH solution (10 M, 3.00 mL, 30 mmol, 46 equiv) was added and the mixture was heated at 70 °C overnight. The cooled mixture was neutralised (IR 120 H⁺), filtered and concentrated. The residue was purified on a G15 column to give, after lyophilisation, 375 mg of **18** (98%) as a white powder. $[\alpha]_D^{25}$ –19 (c 1, D₂O). ¹H NMR (400 MHz, D₂O) δ : 4.75 (s, 1H, 1H₁), 4.61 (s, 1H, 1H₁), 4.37 (d, 1H, $J_{H1'-H2'} = 7.5$ Hz, H_{1'}), 4.02 (d, 1H, $J_{H2-H3} = 2.5$ Hz, 1H₂), 3.85 (m, 1H, 1H₂), 3.83–3.60 (m, 7H, 1H₃, 1H₇, 5H), 3.53–3.46 (m, 6H, 1H₃, H_{4'}, 1H₇, 3H), 3.44–3.36 (m, 1H), 3.30 (t, 1H, $J_{H3'-H4'} = 8.9$ Hz, H_{3'}), 3.23 (dd, 1H, H_{2'}), 3.12 (t, 1H, $J_{gem} = J_{H6-H5} = 10.9$ Hz, 1H₆), 2.27 (t, 2H, $J_{H11-H10} = 7.3$ Hz, H₁₁), 1.53–1.46 (m, 4H, H₈, H₁₀), 1.30–1.23 (m, 2H, H₉). ¹³C NMR (100 MHz, D₂O) δ : 179.4 (CO COOH), 104.6 (C_{1'}), 100.5 (1C₁), 99.8 (1C₁), 78.8 (1C₂), 75.7 (C_{3'}), 74.7, 73.6 (C_{2'}), 72.9, 72.4, 70.8, 70.2 (1C₂), 70.1 (C_{5'}), 69.5, 67.5, 66.9, 66.1 (C₇), 65.4 (1C₆), 61.2 (1C₆), 34.0 (C₁₁), 28.7 (C₈ or C₁₀), 25.1 (C₉), 24.2 (C₈ or C₁₀). MS DCI+–HRMS m/z [M+NH₄]⁺ calcd for C₂₃H₄₄O₁₇N 606.2609, found 606.2584.

4.2.11. 5-Carboxyethylpentyl 4,6-O-*para*-methoxybenzylidene-2-deoxy-2-phthalimido- β -D-glucopyranoside (**26**)

Compound **25** (1.452 g, 3.215 mmol) was dissolved in anhydrous acetonitrile (40 mL) under argon. To the solution were added successively: dimethyl *para*-methoxybenzaldehyde acetal (1.11 mL, 6.430 mmol, 2 equiv) and camphorsulfonic acid (0.223 g, 0.964 mmol, 0.3 equiv). After 2 h, a saturated NaHCO₃ solution was added and the product was extracted with CH₂Cl₂. The organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (cyclohexane/EtOAc: 7:3) to give 1.495 g of **26** (81%) as a white foam. R_f : 0.15 (cyclohexane/EtOAc: 7:3). $[\alpha]_D^{25}$ –35 (c 2, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ : 7.86 (dd, 2H, $J = 3.1$ Hz, $J = 5.5$ Hz, H Ar Phth), 7.72 (dd, 2H, $J = 3.0$ Hz, $J = 5.2$ Hz, H Ar Phth), 7.42 (m, 2H, H Ar), 6.90 (m, 2H, H Ar), 5.53 (s, 1H, H benzylidene), 5.23 (d, 1H, $J_{H1-H2} = 8.4$ Hz, H₁), 4.59 (m, 1H, H₃), 4.36 (dd, 1H, $J_{gem} = 10.3$ Hz, $J_{H6-H5} = 4.3$ Hz, 1H₆), 4.21 (dd, 1H, $J_{H2-H3} = 10.4$ Hz, H₂), 4.06 (q, 2H, $J = 7.0$ Hz, CH₂ OEt), 3.84–3.78 (m, 5H, OMe, 1H₆, 1H₇), 3.63–3.53 (m, 2H, H₄, H₅), 3.43 (td, 1H, $J_{gem} = 9.8$ Hz, $J = 6.4$ Hz, 1H₇), 3.05 (d, 1H, $J = 3.8$ Hz, OH (C₃)), 1.99 (m, 2H, H₁₁), 1.50–1.33 (m, 4H, H₈, H₁₀), 1.22 (t, 3H, $J = 7.0$ Hz, CH₃ OEt), 1.17–1.06 (m, 2H, H₉). ¹³C NMR (100 MHz, CDCl₃) δ : 173.3 (CO ester), 160.1 (CO Phth), 134.0–113.0 (C Ar), 101.6 (C benzylidene), 98.7 (C₁), 82.0 (C₄), 69.5 (C₇), 68.5 (C₆), 68.4 (C₃), 66.0 (C₅), 60.0 (CH₂ OEt), 56.6 (C₂), 55.1 (OMe), 33.8 (C₁₁), 28.8 (C₈ or C₁₀), 25.1 (C₉), 24.2 (C₈ or C₁₀), 14.0 (CH₃ OEt). MS DCI+–HRMS m/z [M+1]⁺ calcd for C₃₀H₃₆NO₁₀ 570.2339, found 570.2346.

4.2.12. 5-Carboxyethylpentyl 6-O-*tert*-butyldimethylsilyl-2-deoxy-2-phthalimido- β -D-glucopyranoside (**27**)

To a solution of 5-carboxyethylpentyl 2-deoxy-2-phthalimido- β -D-glucopyranoside **25** (0.557 g, 1.235 mmol) in anhydrous pyridine (10 mL) were added under argon: DMAP (0.015 g, 0.123 mmol, 0.1 equiv) and TBSCl (0.204 g, 1.358 mmol, 1.1 equiv). The mixture was allowed to stir overnight. The solvent was evaporated and the product was extracted with CH₂Cl₂, washed with HCl (1 M) and neutralised with a saturated NaHCO₃ solution. The organic layer was dried over MgSO₄, filtered and the solvent was evaporated. The residue was purified by column chromatography on silica gel (cyclohexane/EtOAc: 95:5) to give 393 mg of **27** (56%) as syrup. R_f : 0.39 (cyclohexane/EtOAc: 95:5). $[\alpha]_D^{25}$ –26 (c 20, CHCl₃). ¹H NMR (250 MHz, CDCl₃) δ : 7.70–7.56 (m, 4H, H Phth), 5.03 (d, 1H, $J_{H1-H2} = 8.3$ Hz), 3.92 (m, 1H), 3.95–3.80 (m, 5H, CH₂ OEt, 3H), 3.64 (m, 1H, 1H₇), 3.50–3.26 (m, 3H, 1H₇), 1.85 (dt, 2H, $J = 2.6$ Hz, $J = 7.5$ Hz, H₁₁), 1.28 (m, 4H, H₈, H₁₀), 1.09 (t, 3H, $J = 7.1$ Hz, CH₃ OEt), 1.00 (m, 2H, H₉), 0.79 (s, 9H, CH₃ *t*Bu TBS), 0.00 (s, 3H, CH₃ TBS), –1.77 (s, 3H, CH₃ TBS).

4.2.13. 5-Carboxyethylpentyl 4-O-(3,4,6-O-acetyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-6-O-*tert*-butyldimethylsilyl-2-deoxy-2-phthalimido- β -D-glucopyranoside (**28**) and 5-carboxyethylpentyl 3-O-(3,4,6-O-acetyl-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-6-O-*tert*-butyldimethylsilyl-2-deoxy-2-phthalimido- β -D-glucopyranoside (**29**)

To a mixture of **27** (0.190 g, 0.336 mmol), **30** (0.241 g, 0.403 mmol, 1.2 equiv) and 4 Å molecular sieves (0.2 g) in anhydrous CH₂Cl₂ (4 mL), were added under argon: NBS (0.150 g, 0.840 mmol, 2.5 equiv) and TfOH (0.015 mL, 0.168 mmol, 0.5 equiv). After 20 min the mixture was filtered, extracted with CH₂Cl₂ and washed with saturated NaHCO₃ and Na₂S₂O₃ solutions. The organic layer was dried over MgSO₄, filtered and the solvent was evaporated. The residue was purified by column chromatography on silica gel (cyclohexane/EtOAc/acetone: 5:4:1) to give 42 mg of **28** (14%) as a syrup R_f : 0.44 (cyclohexane/EtOAc/acetone: 5:4:1), $[\alpha]_D^{25}$ –4 (c 2, CHCl₃) and 22 mg of **29** (7%) as a syrup R_f : 0.32 (cyclohexane/EtOAc/acetone: 5:4:1), $[\alpha]_D^{25}$ +13 (c 1, CHCl₃). The regioselectivity was demonstrated by addition of trichloroacetyl isocyanate and ¹H NMR analysis: **28**: ¹H NMR (400 MHz, CDCl₃) δ : 7.89–7.73 (m, 8H, H Ar), 5.85 (dd, 1H, $J_{H3-H4} = 9.0$ Hz, $J_{H3-H2} = 10.6$ Hz, H₃), 5.50 (d, 1H, $J_{H1-H2} = 8.5$ Hz, H₁), 5.14 (d, 1H, $J_{H1'-H2'} = 8.5$ Hz, H_{1'}), 5.09 (dd, 1H, $J_{H4-H5} = 9.9$ Hz, H₄), 4.36 (m, 2H, H₂, H_{3'}), 4.17 (m, 2H, 2H₆), 4.09–4.04 (m, 3H, CH₂ OEt, H_{2'}), 3.99 (m, 1H, H₅), 3.73–3.61 (m, 2H, H_{4'}, 1H₇), 3.47 (dd, 1H, $J_{gem} = 11.5$ Hz, $J_{H6'-H5'} = 1.4$ Hz, 1H_{6'}), 3.36 (m, 2H, H_{5'}, 1H₇), 3.28 (dd, $J_{H6'-H5'} = 4.4$ Hz, 1H_{6'}), 2.04 (m, 5H, CH₃ OAc, H₁₁), 1.93 (s, 3H, CH₃ OAc), 1.85 (s, 3H, CH₃ OAc), 1.42 (m, 4H, H₈, H₁₀), 1.22 (t, 3H, $J = 7.2$ Hz, CH₃ OEt), 1.12 (m, 2H, H₉), 0.81 (s, 9H, *t*Bu), –0.11 (s, 3H, CH₃ TBS), –0.15 (s, 3H, CH₃ TBS). ¹³C NMR (100 MHz, CDCl₃) δ : 173.4 (CO ester), 170.4 (CO OAc), 169.9 (CO OAc), 169.4 (CO OAc), 134.6–123.0 (C Ar), 98.6 (C₁), 97.5 (C_{1'}), 81.7 (C_{4'}), 74.3 (C_{5'}), 71.6 (C₅), 70.2 (C₃), 69.9 (C_{3'}), 68.8 (C₄), 68.7 (C₇), 62.0 (C₆), 61.4 (C_{6'}), 60.0 (CH₂ OEt), 55.9 (C_{2'}), 54.5 (C₂), 33.9 (C₁₁), 28.8 (C₈ or C₁₀), 25.7 (*t*Bu), 25.3 (C₉), 24.4 (C₈ or C₁₀), 20.5 (CH₃ OAc), 20.3 (CH₃ OAc), 20.2 (CH₃ OAc), 14.1 (CH₃ OEt), –5.3 (CH₃ TBS), –5.4 (CH₃ TBS). MS FAB+–HRMS m/z [M+Na]⁺ calcd for C₄₈H₆₂N₂O₁₈SiNa 1005.3665, found 1005.3679. Compound **29**: ¹H NMR (400 MHz, CDCl₃) δ : 7.70–7.00 (m, 8H, H Ar), 5.58 (dd, 1H, $J_{H3-H2} = 10.7$ Hz, $J_{H3-H4} = 9.0$ Hz, H₃), 5.43 (d, 1H, $J_{H1-H2} = 8.4$ Hz, H₁), 5.11 (dd, 1H, $J_{H4-H5} = 9.0$ Hz, H₄), 4.87 (d, 1H, $J_{H1'-H2'} = 8.5$ Hz, H_{1'}), 4.58 (dd, 1H, $J_{H3'-H4'} = 8.0$ Hz, $J_{H3'-H2'} = 10.7$ Hz, H_{3'}), 4.32 (dd, 1H, H₂), 4.25 (m, 2H, 2H₆), 4.09–4.01 (m, 4H, CH₂ OEt, H_{2'}, 1H_{6'}), 3.97 (ddd, 1H, $J_{H5-H6} = 10.3$ Hz, $J_{H5-H4} = 4.7$ Hz, H₅), 3.84 (dd, 1H, $J_{gem} = 11.3$ Hz, $J_{H6'-H5'} = 5.8$ Hz, 1H_{6'}), 3.71 (dt, 1H, $J_{gem} = 9.8$ Hz, $J = 6.1$ Hz, 1H₇), 3.56 (dd, 1H, $J_{H4'-H5'} = 8.0$ Hz, H_{4'}), 3.45 (m, 1H, H_{5'}), 3.25 (m, 1H, 1H₇), 2.16 (s, 3H, CH₃ OAc), 2.02 (s, 3H, CH₃ OAc), 1.89 (m, 2H, H₁₁), 1.75 (s, 3H, CH₃ OAc), 1.71 (s, 1H, OH (C₄)), 1.36–1.20 (m, 7H, CH₃ OEt, H₈, H₁₀), 0.95–0.87 (m, 11H, *t*Bu, H₉), 0.10 (s, 3H, CH₃ TBS), 0.09 (s, 3H, CH₃ TBS). ¹³C NMR (100 MHz, CDCl₃) δ : 173.3 (CO ester), 170.5 (CO OAc), 169.8 (CO OAc), 169.3 (CO OAc), 134.0–123.1 (C Ar), 98.1 (C₁), 97.7 (C_{1'}), 82.0 (C_{3'}), 76.4 (C_{5'}), 71.8 (C₅), 70.2 (C₃), 69.9 (C_{4'}), 68.8 (C₇), 68.6 (C₄), 63.0 (C_{6'}), 61.8 (C₆), 60.0 (CH₂ OEt), 55.1 (C_{2'}), 54.4 (C₂), 33.9 (C₁₁), 28.7 (C₈ or C₁₀), 25.8 (*t*Bu), 25.1 (C₉), 24.2 (C₈ or C₁₀), 20.5–20.1 (CH₃ OAc), –5.22 (CH₃ TBS), –5.25 (CH₃ TBS). MS FAB+–HRMS m/z [M+Na]⁺ calcd for C₄₈H₆₂N₂O₁₈SiNa 1005.3665, found 1005.3676.

4.2.14. 5-Carboxyethylpentyl 4,6-O-benzylidene-3-O-*tert*-butyldimethylsilyl-2-deoxy-2-phthalimido- β -D-glucopyranoside (**32**)

To a mixture of **31** (1.000 g, 1.483 mmol), ethyl 6-hydroxy-hexanoate (0.362 mL, 2.225 mmol, 1.5 equiv) and 4 Å molecular sieves (4 g) in anhydrous CH₂Cl₂ (15 mL) were added under argon: NIS (0.667 g, 2.966 mmol, 2 equiv) and TfOH (0.026 mL, 0.296 mmol, 0.2 equiv). The mixture was stirred for 3 h and was filtered, extracted with CH₂Cl₂ and washed with saturated Na₂S₂O₃ and NaHCO₃ solutions. The organic layer was dried over MgSO₄, filtered and

concentrated. The residue was purified by column chromatography on silica gel (cyclohexane/EtOAc: 8:2) to give 0.873 g of **32** (90%) as a white solid. R_f : 0.34 (cyclohexane/EtOAc: 8:2). $[\alpha]_D^{25}$ –22 (c 4, CHCl₃). Mp: 90 °C. ¹H NMR (400 MHz, CDCl₃) δ : 7.90–7.30 (m, 9H, H Ar), 5.56 (s, 1H, H benzylidene), 5.24 (d, 1H, J_{H1-H2} = 8.5 Hz, H₁), 4.65 (dd, 1H, J_{H3-H4} = 8.4 Hz, J_{H3-H2} = 10.2 Hz, H₃), 4.40 (dd, 1H, J_{gem} = 10.3 Hz, J_{H6-H5} = 4.6 Hz, 1H₆), 4.24 (dd, 1H, H₂), 4.09 (q, 2H, J = 7.0 Hz, CH₂ OEt), 3.83 (m, 2H, 1H₆, 1H₇), 3.66 (td, 1H, J_{H5-H4} = 9.4 Hz, H₅), 3.59 (dd, 1H, H₄), 3.44 (m, 1H, 1H₇), 2.01 (m, 2H, H₁₁), 1.50–1.38 (m, 4H, H₈, H₁₀), 1.24 (t, 3H, CH₃ OEt), 1.18–1.10 (m, 2H, H₉), 0.63 (s, 9H, *t*Bu TBS), –0.08 (s, 3H, CH₃ TBS), –0.24 (s, 3H, CH₃ TBS). ¹³C NMR (100 MHz, CDCl₃) δ : 173.3 (CO ester), 137.0–126.0 (C Ar), 101.8 (C benzylidene), 98.7 (C₁), 82.7 (C₄), 69.5 (C₃), 69.5 (C₇), 68.7 (C₆), 66.2 (C₅), 60.0 (CH₂ OEt), 57.7 (C₂), 33.9 (C₁₁), 28.9 (C₈ or C₁₀), 25.3 (*t*Bu TBS), 25.2 (C₉), 24.3 (C₈ or C₁₀), 17.6 (Cq *t*Bu TBS), 14.1 (CH₃ OEt), –4.2 (CH₃ TBS), –5.4 (CH₃ TBS). MS DCI+–HRMS m/z [M+NH₄]⁺ calcd for C₃₅H₅₁N₂O₉Si 671.3364, found 671.3356.

4.2.15. 5-Carboxyethylpentyl 3-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-phthalimido- β -D-glucopyranoside (**33**)

To a solution of **32** (0.775 g, 1.185 mmol) in ethyl acetate (9 mL) was added Pd/C (10%) (387 mg, 0.5 g per g of substrate). Vacuum and H₂ were alternated and then the mixture was stirred at room temperature under H₂ for 3 h. The mixture was filtered off through Celite and concentrated to give 670 mg of pure **33** (100%) as a syrup. R_f : 0.39 (cyclohexane/EtOAc: 5:5). $[\alpha]_D^{25}$ –1 (c 6, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ : 7.84–7.72 (m, 4H, H Ar), 5.16 (d, 1H, J_{H1-H2} = 8.5 Hz, H₁), 4.40 (dd, 1H, J_{H3-H4} = 8.4 Hz, J_{H3-H2} = 10.4 Hz, H₃), 4.09 (dd, 1H, H₂), 4.05 (q, 2H, J = 7.1 Hz, CH₂ OEt), 3.95 (dd, 1H, J_{gem} = 11.8 Hz, J_{H6-H5} = 3.3 Hz, 1H₆), 3.87 (dd, 1H, J_{H6-H5} = 4.2 Hz, 1H₆), 3.77 (td, 1H, J_{gem} = 9.8 Hz, J_{H7-H8} = 6.2 Hz, 1H₇), 3.62 (m, 1H, H₄), 3.50 (m, 1H, H₅), 3.40 (td, 1H, J_{H7-H8} = 6.4 Hz, 1H₇), 3.08 (d, 1H, J_{OH-H4} = 3.7 Hz, OH), 1.97 (m, 2H, H₁₁), 1.39 (m, 4H, H₈, H₁₀), 1.20 (t, 3H, CH₃ OEt), 1.07 (m, 2H, H₉), 0.67 (s, 9H, *t*Bu TBS), 0.05 (s, 3H, CH₃ TBS), –0.27 (s, 3H, CH₃ TBS). ¹³C NMR (100 MHz, CDCl₃) δ : 173.4 (CO ester), 134–122 (C Ar), 98.1 (C₁), 75.2 (C₅), 72.6 (C₃), 72.4 (C₄), 69.2 (C₇), 62.2 (C₆), 60.0 (CH₂ OEt), 57.1 (C₂), 33.8 (C₁₁), 28.8 (C₈ or C₁₀), 25.4 (*t*Bu TBS), 25.1 (C₉), 24.2 (C₈ or C₁₀), 17.6 (Cq *t*Bu TBS), 14.0 (CH₃ OEt), –4.1 (CH₃ TBS), –5.2 (CH₃ TBS). MS DCI+–HRMS m/z [M+NH₄]⁺ calcd for C₂₈H₄₇N₂O₉Si 583.3051, found 583.3043.

4.2.16. 5-Carboxyethylpentyl 3,6-di-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-phthalimido- β -D-glucopyranoside (**34**)

To a mixture of **33** (0.554 g, 0.980 mmol), DMAP (0.012 g, 0.098 mmol, 0.1 equiv) in anhydrous pyridine (3 mL) was added under argon TBSCl (0.441 g, 2.941 mmol, 3 equiv). The mixture turned cloudy and was stirred overnight. Concentrated and the product was extracted with CH₂Cl₂, washed with HCl (1 M) and neutralised with a saturated NaHCO₃ solution. The organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (cyclohexane/EtOAc: 8:2) to give 603 mg of **34** (90%) as syrup. R_f : 0.60 (cyclohexane/EtOAc: 7:3). $[\alpha]_D^{25}$ –9 (c 3, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ : 7.8–7.7 (m, 4H, H Ar), 5.08 (d, 1H, J_{H1-H2} = 8.6 Hz, H₁), 4.35 (dd, 1H, J_{H3-H4} = 7.9 Hz, J_{H3-H2} = 10.5 Hz, H₃), 4.04 (dd, 1H, H₂), 4.00 (q, 2H, J = 7.2 Hz, CH₂ OEt), 3.91 (dd, 1H, J_{gem} = 10.6 Hz, J_{H6-H5} = 4.9 Hz, 1H₆), 3.85 (dd, 1H, J_{H6-H5} = 5.3 Hz, 1H₆), 3.71 (td, 1H, J_{gem} = 9.8 Hz, J_{H7-H8} = 6.2 Hz, 1H₇), 3.50 (td, 1H, J_{H4-H5} = J_{H4-H3} = 7.9 Hz, J_{H4-OH} = 2.3 Hz, H₄), 3.44 (m, 1H, H₅), 3.33 (m, 1H, 1H₇), 3.15 (d, 1H, OH), 1.91 (m, 2H, H₁₁), 1.34 (m, 4H, H₈, H₁₀), 1.15 (t, 3H, CH₃ OEt), 1.04 (m, 2H, H₉), 0.86 (s, 9H, *t*Bu TBS), 0.60 (s, 9H, *t*Bu TBS), 0.06 (s, 3H, CH₃ TBS), 0.06 (s, 3H, CH₃ TBS),

0.01 (s, 3H, CH₃ TBS), –0.28 (s, 3H, CH₃ TBS). ¹³C NMR (100 MHz, CDCl₃) δ : 173.0 (CO ester), 168.0 (CO NPhth), 167.0 (CO NPhth), 133.0–122.0 (C Ar), 97.8 (C₁), 74.6 (C₄), 74.2 (C₅), 72.5 (C₃), 68.7 (C₇), 64.6 (C₆), 59.8 (CH₂ OEt), 56.8 (C₂), 33.7 (C₁₁), 28.7 (C₈ or C₁₀), 25.6 (*t*Bu TBS), 25.3 (*t*Bu TBS), 25.1 (C₉), 24.2 (C₈ or C₁₀), 18.0 (Cq *t*Bu TBS), 17.5 (Cq *t*Bu TBS), 14.0 (CH₃ OEt), –4.2 (CH₃ TBS), –5.4 (CH₃ TBS), –5.6 (2CH₃ TBS). MS DCI+–HRMS m/z [M+NH₄]⁺ calcd for C₃₄H₆₁N₂O₉Si₂ 697.3916, found 697.3922.

4.2.17. 5-Carboxyethylpentyl 4-*O*-(3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-3,6-di-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-phthalimido- β -D-glucopyranoside (**35**)

To a mixture of **34** (0.177 g, 0.260 mmol), **8** (0.234 g, 0.390 mmol, 1.5 equiv) and 4 Å molecular sieves (200 mg) in anhydrous CH₂Cl₂ (3 mL), was added under argon NIS (0.667 g, 2.966 mmol, 2.0 equiv). The mixture was stirred, cooled down to –25 °C and TFOH (0.002 mL, 0.026 mmol, 0.1 equiv) was added. The mixture was allowed to warm up to 0 °C over 1 h and was then filtered, extracted with CH₂Cl₂ and washed with saturated NaHCO₃ and Na₂S₂O₃ solutions. The organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (cyclohexane/EtOAc: 8:2) to give 0.178 g of **35** (61%) as a white solid. R_f : 0.29 (cyclohexane/EtOAc: 7:3). $[\alpha]_D^{25}$ –30 (c 1.5, CHCl₃). Mp: 87–88 °C. ¹H NMR (400 MHz, CDCl₃) δ : 7.92–7.35 (m, 13H, H Ar), 5.97 (dd, 1H, J = 9.5 Hz, J = 10.0 Hz, H₃'), 5.67 (d, 1H, $J_{H1'-H2'}$ = 8.4 Hz, H₁'), 5.55 (s, 1H, H benzylidene), 5.04 (d, 1H, J_{H1-H2} = 8.5 Hz, H₁), 4.42 (m, 2H, H₂, 1H₆), 4.28 (dd, 1H, J_{H3-H4} = 8.8 Hz, J_{H3-H2} = 10.0 Hz, H₃), 4.06 (m, 4H, CH₂ OEt, H₂, H₄), 3.82 (t, 1H, J = 9.9 Hz, 1H₆), 3.73 (m, 3H, 1H₆, H₄, H₅'), 3.64 (td, 1H, J_{gem} = 9.8 Hz, J_{H7-H8} = 6.3 Hz, 1H₇), 3.57 (dd, 1H, J_{gem} = 12.1 Hz, J_{H6-H5} = 2.5 Hz, 1H₆), 3.31 (td, 1H, J_{H7-H8} = 6.3 Hz, 1H₇), 3.11 (d, 1H, J = 9.4 Hz, H₅), 2.00 (td, 2H, J_{gem} = 7.4 Hz, $J_{H11-H10}$ = 4.6 Hz, H₁₁), 1.89 (s, 3H, CH₃ OAc), 1.38 (m, 4H, H₈, H₁₀), 1.22 (t, 3H, J = 7.0 Hz, CH₃ OEt), 1.08 (m, 2H, H₉), 1.01 (s, 9H, *t*Bu TBS), 0.79 (s, 9H, *t*Bu TBS), 0.25 (s, 3H, CH₃ TBS), 0.18 (s, 3H, CH₃ TBS), 0.15 (s, 3H, CH₃ TBS), –0.37 (s, 3H, CH₃ TBS). ¹³C NMR (100 MHz, CDCl₃) δ : 176.0 (CO), 173.0 (CO), 169.0 (CO), 167.0 (2CO), 134.0–123.0 (C Ar), 101.4 (C benzylidene), 97.8 (C₁), 96.6 (C₁'), 79.3 (C₄'), 74.9 (C₅), 74.1 (C₄), 70.7 (C₃), 69.7 (C₃'), 68.5 (C₆'), 68.1 (C₇), 65.9 (C₅'), 61.2 (C₆), 59.9 (CH₂ OEt), 57.5 (C₂), 55.1 (C₂'), 33.8 (C₁₁), 28.8 (C₈ or C₁₀), 25.7 (2*t*Bu TBS, CH₃ OEt), 25.2 (C₉), 24.2 (C₈ or C₁₀), 20.4 (CH₃ OAc), 18.2 (Cq *t*Bu TBS), 17.5 (Cq *t*Bu TBS), –3.0 (CH₃ TBS), –5.0 (CH₃ TBS), –5.2 (CH₃ TBS), –5.3 (CH₃ TBS). MS FAB+–HRMS m/z [M+Na]⁺ calcd for C₅₇H₇₆N₂O₁₆–Si₂Na 1123.4631, found 1123.4657.

4.2.18. 5-Carboxyethylpentyl 4-*O*-(3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido- β -D-glucopyranosyl)-2-deoxy-2-phthalimido- β -D-glucopyranoside (**36**)

To a solution of **35** (1.000 g, 0.908 mmol) in anhydrous DMF (10 mL) was added under argon ammonium fluoride (0.672 g, 18.16 mmol, 20 equiv). The mixture was stirred and heated at 100 °C overnight. Concentrated and the residue was extracted with CH₂Cl₂ and washed with water. The organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (cyclohexane/EtOAc: 5:5) to give a 0.666 g of **36** (80%) as white solid. R_f : 0.25 (cyclohexane/EtOAc: 5:5). Mp: 225–226 °C. $[\alpha]_D^{25}$ –26 (c 0.8, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ : 7.93–7.73 (m, 8H, H Ar), 7.45–7.41 (m, 2H, H Ar), 7.35 (m, 3H, H Ar), 5.91 (t, 1H, $J_{H3'-H2'}$ = $J_{H3'-H4'}$ = 9.1 Hz, H₃'), 5.63 (d, 1H, $J_{H1'-H2'}$ = 7.7 Hz, H₁'), 5.52 (s, 1H, H benzylidene), 5.15 (d, 1H, J_{H1-H2} = 7.5 Hz, H₁), 4.43–4.32 (m, 3H, H₂, 1H₆, H₃), 4.12–4.02 (m, 3H, CH₂ OEt, H₂), 3.96 (s, 1H, OH C₃), 3.89–3.69 (m, 5H, H₄, H₄, 1H₆, H₅, 1H₇), 3.46–3.34 (m, 3H, H₅, 1H₆, 1H₇), 3.20 (m,

1H, 1H₆), 1.98 (m, 2H, H₁₁), 1.90 (s, 3H, CH₃ OAc), 1.80 (br s, 1H, OH C₆), 1.43–1.33 (m, 4H, H₈, H₁₀), 1.20 (t, 3H, CH₃ OEt), 1.16–1.07 (m, 2H, H₉). ¹³C NMR (100 MHz, CDCl₃) δ: 173.9 (CO ester), 170.4 (CO Phth), 136.0–126.0 (C Ar), 102.1 (C benzylidene), 100.0 (C_{1'}), 98.6 (C₁), 81.8 (C₄ or C_{4'}), 79.0 (C₄ or C_{4'}), 74.4 (C₅), 70.1 (C_{3'}), 69.9 (C₃), 69.8 (C₇), 68.5 (1C₆), 66.6 (C₅), 61.1 (1C₆), 60.5 (CH₂ OEt), 56.3 (C₂), 55.6 (C_{2'}), 34.3 (C₁₁), 29.3 (C₈ or C₁₀), 25.6 (C₉), 24.7 (C₈ or C₁₀), 20.9 (CH₃ OAc), 14.6 (CH₃ OEt). MS FAB+–HRMS *m/z* [M+Na]⁺ calcd for C₄₅H₄₈N₂O₁₆Na 895.2902, found 895.2883.

4.2.19. 5-Carboxyethylpentyl 3,6-di-O-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-4-O-(3-O-acetyl-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-2-deoxy-2-phthalimido-β-D-glucopyranoside mixture (37,38)

To a mixture of **35** (0.100 g, 0.114 mmol), **9** (0.163 g, 0.273 mmol, 2.4 equiv) and 4 Å molecular sieves (300 mg) in anhydrous CH₂Cl₂ (1.5 mL) and anhydrous Et₂O (1.5 mL), were added under argon: NIS (0.102 g, 0.456 mmol, 4 equiv) and TfOH (1 μL, 0.011 mmol, 0.1 equiv). The mixture was stirred for 5 min at room temperature and was then filtered, extracted with CH₂Cl₂ and washed with saturated NaHCO₃ and Na₂S₂O₃ solutions. The organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (cyclohexane/EtOAc: 7:3) to give 177 mg of a syrup containing **37** and **38** (91%) (α/β: 3.5:1 estimated by ¹H NMR). R_f: 0.67 (cyclohexane/EtOAc: 5:5).

4.2.20. 5-Carboxyethylpentyl 4-O-(2-acetamido-3-O-acetyl-4,6-O-benzylidene-2-deoxy-β-D-glucopyranosyl)-3-O-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-2-acetamido-6-O-benzyl-2-deoxy-β-D-glucopyranoside (39)

Compound **6** (0.650 g, 0.471 mmol) was dissolved in ethanol (10 mL) and hydrazine monohydrate (0.230 mL, 4.713 mmol, 10 equiv) was added. The mixture was stirred at 90 °C overnight. The mixture was allowed to cool down to room temperature, filtered and concentrated. The residue was dissolved in anhydrous pyridine (5 mL) and acetic anhydride (2 mL) was added under argon. The mixture was stirred at room temperature overnight. Concentrated and the crude product was extracted with CH₂Cl₂, washed with an HCl solution (1 M) and neutralised with a saturated NaHCO₃ solution. The organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (cyclohexane/EtOAc: 5:5) to give 0.507 g of **39** (89%) as a syrup. R_f: 0.62 (CH₂Cl₂/methanol: 9:1). [α]_D²⁵ –90 (c 6, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ: 7.46–7.25 (m, 25H, H Ar), 6.73 (d, 1H, J_{NH–H2} = 9.0 Hz, NHAc), 5.99 (d, 1H, J_{NH–H2} = 9.1 Hz, NHAc), 5.48 (s, 1H, H benzylidene), 5.26 (d, 1H, J_{H1'–H2'} = 3.4 Hz, H_{1'}), 5.14 (t, 1H, J_{H3'–H2'} = J_{H3'–H4'} = 9.9 Hz, H_{3'}), 5.00 (d, 1H, J_{gem} = 11.6 Hz, CHPh), 4.88–4.83 (2d, 2H, J_{gem} = 12.1 Hz, J_{gem} = 11.5 Hz, 2CHPh), 4.77–4.68 (m, 3H, 3CHPh), 4.50–4.42 (m, 4H, H₁, H_{1''}, 2CHPh), 4.22 (dd, 1H, J_{gem} = 10.4 Hz, J_{H6–H5} = 4.8 Hz, 1H₆), 4.15–4.06 (m, 5H, H₂, H_{2'}, H_{2''}, CH₂ OEt), 3.95–3.89 (m, 3H, H_{5'}, 2H), 3.84–3.64 (m, 7H, 3H₆, 1H₇, H_{4''}, 2H), 3.58 (s, 1H), 3.40–3.34 (m, 2H, 1H₇, 1H), 2.25 (t, 2H, J_{H11–H10} = 7.6 Hz, H₁₁), 2.07 (s, 3H, CH₃ OAc), 2.02 (s, 3H, NHAc), 1.94 (s, 3H, NHAc), 1.61–1.48 (m, 4H, H₁₀, H₈), 1.30 (m, 2H, H₉), 1.25 (t, 3H, J = 7.1 Hz, CH₃ OEt), 1.10 (d, 3H, J_{H6'–H5'} = 6.3 Hz, 1H_{6'}). ¹³C NMR (100 MHz, CDCl₃) δ: 174.1 (CO), 172.0 (CO), 171.4 (CO), 170.5 (CO), 139.4 (Cq Ar), 139.1 (Cq Ar), 139.0 (Cq Ar), 138.3 (Cq Ar), 137.2 (Cq Ar), 128.0–126.0 (C Ar), 101.8 (C benzylidene), 100.9 (1C₁), 100.4 (1C₁), 96.6 (C_{1'}), 79.3, 78.5 (C_{4''}), 78.0, 76.8 (C_{2'}), 75.1 (CH₂Ph), 74.8, 74.6, 73.8 (CH₂Ph), 73.4 (CH₂Ph), 73.2, 72.8 (CH₂Ph), 71.7 (C_{3'}), 70.1 (1C₆), 69.2 (C₇), 68.8 (1C₆), 67.2, 66.7, 60.6 (CH₂ OEt), 55.0 (1C₂), 51.5 (1C₂), 34.6 (C₁₁), 29.5 (C₈ or C₁₀), 25.8 (C₉), 25.0 (C₈ or C₁₀), 23.8 (CH₃ NHAc), 23.5 (CH₃ NHAc), 21.3 (CH₃ OAc), 17.1 (C_{6'}), 14.6 (CH₃ OEt). MS FAB+–HRMS *m/z* [M+Na]⁺ calcd for C₆₇H₈₂O₁₈N₂Na 1225.5460, found 1225.5458.

4.2.21. 5-Carboxypentyl 4-O-(2-acetamido-4,6-O-benzylidene-2-deoxy-β-D-glucopyranosyl)-3-O-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-2-acetamido-6-O-benzyl-2-deoxy-β-D-glucopyranoside (40)

Compound **39** (0.500 g, 0.415 mmol) was dissolved in THF (5 mL) and NaOH (10 M, 500 μL, 4.150 mmol, 10 equiv) was added. The mixture was stirred at 75 °C overnight. The mixture was allowed to cool down to room temperature, neutralised (IR 120 H⁺), filtered and concentrated to give 0.470 g of **40** (100%) as a syrup. R_f: 0.47 (CH₂Cl₂/methanol: 9:1). [α]_D²⁵ –88 (c 2.5, MeOH). ¹H NMR (400 MHz, CD₃OD) δ: 8.24 (m, 1H, NHAc), 7.95 (m, 1H, NHAc), 7.50–7.25 (m, 27H, H Ar), 5.43 (s, 1H, H benzylidene), 5.35 (d, 1H, J_{H1'–H2'} = 3.6 Hz, H_{1'}), 5.00–4.77 (m, 3H), 4.69–4.56 (m, 5H, 1H₁, 4CHPh), 4.43 (d, 1H, J = 7.2 Hz, 1H₁), 4.35 (m, 1H, H_{5'}), 4.15 (m, 1H, 1H₆), 4.10–3.99 (m, 3H, H_{2'}, 1H₂, 1H), 3.94–3.90 (m, 2H, 1H₃, 1H), 3.84–3.74 (m, 5H, 1H₂, 2H₆, 2H), 3.66 (m, 1H), 3.56 (t, 1H, J = 10.0 Hz, 1H₆), 3.45–3.36 (m, 3H, 1H₃, 1H₄, 1H), 3.32 (m, 1H), 3.20 (dd, 1H, J = 5.0 Hz, J = 12.0 Hz, 1H₅), 2.27 (t, 2H, J = 7.4 Hz, H₁₁), 2.01 (s, 3H, CH₃ NHAc), 2.00 (s, 3H, CH₃ NHAc), 1.58 (m, 4H, H₈, H₁₀), 1.37 (m, 2H, H₉, 1H), 1.21 (d, 3H, J_{H6'–H5'} = 6.5 Hz, 1H_{6'}). ¹³C NMR (100 MHz, CD₃OD) δ: 172.8 (CO), 139.4–126.0 (C Ar), 101.8 (C benzylidene), 101.4 (1C₁), 100.8 (1C₁), 96.1 (C_{1'}), 81.9, 78.8, 78.7, 76.2, 75.7, 75.2 (CH₂Ph), 74.9, 73.6, 73.1 (CH₂Ph), 72.7 (CH₂Ph), 72.2 (CH₂Ph), 71.1, 69.3 (1C₆ and C₇), 68.6 (1C₆), 66.9 (C_{5'}), 66.5 (1C₅), 57.1 (1C₂), 54.8 (1C₂), 34.0 (C₁₁), 29.3 (C₈ or C₁₀), 25.6 (C₉), 24.8 (C₈ or C₁₀), 22.2 (CH₃ NHAc), 22.1 (CH₃ NHAc), 16.1 (C_{6'}). MS FAB+–HRMS *m/z* [M+Na]⁺ calcd for C₆₃H₇₆N₂O₁₇Na 1155.5042, found 1155.5156.

4.2.22. 5-Carboxypentyl 4-O-(2-acetamido-4,6-O-benzylidene-2-deoxy-β-D-glucopyranosyl)-3-O-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-2-acetamido-6-O-benzyl-2-deoxy-β-D-glucopyranoside biotin conjugate (41)

Compound **40** (0.400 g, 0.353 mmol) was dissolved in anhydrous DMF (5 mL) under argon with **10** (0.241 g, 0.706 mmol, 2 equiv), DMAP (0.051 g, 0.423 mmol, 1.2 equiv) and EDC (0.134 g, 0.706 mmol, 2 equiv). The solution was stirred for 3 h at 70 °C. EDC (0.067 g, 0.353 mmol, 1 equiv) was added to complete the reaction and after 2 h, concentrated. The residue was extracted with CH₂Cl₂ and washed with water. The organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (CH₂Cl₂/methanol: 9:1) to give 0.282 g of **41** (54%) as a syrup. R_f: 0.33 (CH₂Cl₂/methanol: 9:1). [α]_D²⁵ –49 (c 1, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ: 7.51–7.20 (m, 26H, H Ar, NHAc), 7.03 (d, 1H, J = 8.5 Hz, NHAc), 6.46 (t, 1H, J = 5.5 Hz, NH), 6.41 (t, 1H, J = 5.2 Hz, NH), 6.29 (s, 1H, NH urea), 5.54 (s, 1H, NH urea), 5.47 (s, 1H, H benzylidene), 5.28 (d, 1H, J_{H1'–H2'} = 3.2 Hz, H_{1'}), 4.98 (d, 1H, J_{gem} = 11.4 Hz, CHPh), 4.82 (m, 2H, 2CHPh), 4.71–4.64 (m, 3H, 3CHPh), 4.53–4.48 (m, 3H, 2H₁, CHPh), 4.40 (d, 1H, J_{gem} = 11.6 Hz, CHPh), 4.29 (m, 1H), 4.22 (m, 2H), 4.05 (m, 2H), 3.95 (m, 3H), 3.80–3.75 (m, 6H), 3.61 (t, 1H, J = 9.0 Hz), 3.55 (s, 1H), 3.50 (t, 1H, J = 8.1 Hz), 3.39–3.30 (m, 3H), 3.24–3.15 (m, 4H), 3.06 (m, 1H), 2.77 (dd, 1H, J_{gem} = 12.7 Hz, J_{H27–H26} = 4.2 Hz, H₂₇), 2.61 (d, 1H, J_{gem} = 12.7 Hz, 1H₂₇), 2.15 (m, 4H, H₁₁, H₂₀), 1.95 (s, 3H, CH₃ NHAc), 1.94 (s, 3H, CH₃ NHAc), 1.65–1.27 (m, 20H, H₈, H₉, H₁₀, H₁₄, H₁₅, H₁₆, H₁₇, H₂₁, H₂₂, H₂₃), 1.08 (d, 3H, J_{H6'–H5'} = 6.1 Hz, CH₃ H_{6'}). ¹³C NMR (100 MHz, CHCl₃) δ: 173.9 (CO), 173.7 (CO), 172.8 (CO), 170.7 (CO), 164.2 (CO), 139.3–137.5 (Cq Ar), 128.0–126.0 (C Ar), 102.2 (C benzylidene), 101.0 (1C₁), 98.8 (1C₁), 96.5 (C_{1'}), 82.0, 79.2 (2C), 78.2, 76.5, 75.4, 75.2 (CH₂Ph), 75.0, 73.8 (CH₂Ph), 73.4 (CH₂Ph), 72.8 (CH₂Ph), 71.5, 70.9 (1C₆), 69.3 (1C₆), 68.8 (C₇), 67.1, 66.6 (2C), 62.1 (C₂₅ or C₂₆), 60.4 (C₂₅ or C₂₆), 57.4, 55.9 (C₂₄), 40.9 (C₃₉), 39.3 (C₁₂ or C₁₈), 39.3 (C₁₂ or C₁₈), 37.0 (C₁₁ or C₂₀), 35.9 (C₁₁ or C₂₀), 28.0–25.0 (C₈, C₉, C₁₀, C₁₄, C₁₅, C₁₆, C₁₇, C₂₁, C₂₂, C₂₃), 23.8 (CH₃ NHAc),

23.0 (CH₃ NHAc), 17.1 (C_{6'}). MS FAB+-HRMS *m/z* [M+Na]⁺ calcd for C₇₉H₁₀₄N₆O₁₈SNa 1479.7026, found 1479.7040.

4.2.23. 5-Carboxypentyl 4-O-(2-acetamido-4,6-O-benzylidene-2-deoxy-β-D-glucopyranosyl)-3-O-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-2-acetamido-6-O-benzyl-2-deoxy-β-D-glucopyranoside oxidised biotin conjugate (42)

To a solution of **41** (0.019 g, 0.013 mmol) in anhydrous CH₂Cl₂ (0.5 mL), was added mCPBA (0.007 g, 0.039 mmol, 3 equiv) under argon. The mixture was stirred at room temperature overnight. The mixture was washed with a saturated NaHCO₃ solution. The organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (CH₂Cl₂/methanol: 9:1) to give 16 mg of **42** (84%) as a syrup. *R*_f: 0.26 (CH₂Cl₂/MeOH: 9:1). [α]_D²⁵ –50 (c 1, CHCl₃). ¹H NMR (400 MHz, CD₃OD) δ: 7.47–7.29 (m, 25H, H Ar), 5.43 (s, 1H, H benzylidene), 5.38 (d, 1H, *J*_{H1'-H2'} = 3.5 Hz, H_{1'}), 4.96 (d, 1H, *J*_{gem} = 11.2 Hz, CHPh), 4.88–4.81 (m, 3H, 3CHPh), 4.69–4.48 (m, 7H, 1H₁, 4CHPh, H₂₅, H₂₆), 4.43–4.38 (m, 2H, 1H₁, H_{5'}), 4.13 (dd, 1H, *J*_{gem} = 10.3 Hz, *J*_{H6-H5} = 4.9 Hz, 1H₆), 4.08–3.99 (m, 3H, 1H₂, 2H), 3.95–3.91 (m, 2H), 3.84–3.74 (m, 6H, 1H₂, 2H₆, 1H₇, 2H), 3.66 (m, 1H), 3.54 (t, 1H, *J*_{gem} = 10.2 Hz, 1H₆), 3.43 (m, 2H, 1H₇, 1H), 3.36–3.28 (m, 2H, 1H₂₇, 1H), 3.21–3.09 (m, 7H, H₁₃, H₁₈, 1H₂₇, H₂₄, 1H), 2.23–2.15 (m, 4H, H₁₁, H₂₀), 2.02 (s, 3H, CH₃ NHAc), 2.01 (s, 3H, CH₃ NHAc), 1.87 (m, 1H, 1H₂₃), 1.77–1.48 (m, 13H), 1.40 (m, 6H), 1.24 (d, 3H, *J*_{H6'-H5'} = 6.4 Hz, 1H_{6'}). ¹³C NMR (100 MHz, CD₃OD) δ: 175.0 (CO), 174.7 (CO), 172.7 (CO), 172.0 (CO), 163.6 (CO urea), 139.5 (Cq Ar), 139.2 (Cq Ar), 138.8 (Cq Ar), 138.7 (Cq Ar), 137.9 (Cq Ar), 128–126 (C Ar), 101.8 (C benzylidene), 101.5 (1C₁), 100.8 (1C₁), 96.1 (C_{1'}), 81.9, 78.8 (2C), 76.1, 75.6, 75.3 (CH₂Ph), 74.8, 73.6, 73.0 (CH₂Ph), 72.7 (CH₂Ph), 72.2 (CH₂Ph), 71.1, 69.4 (C₇), 69.1 (1C₆), 68.7 (1C₆), 66.9, 66.5, 60.8 (C₂₄), 57.1 (1C₅), 55.0 (1C₅), 54.6 (C₂₅ or C₂₆), 54.2 (C₂₇), 50.0 (C₂₅ or C₂₆), 39.2 (C₁₃ and C₁₈), 36.1 (C₁₁ or C₂₀), 35.6 (C₁₁ or C₂₀), 29.3–25.7 (C₈, C₉, C₁₀, C₁₄, C₁₅, C₁₆, C₁₇, C₂₁, C₂₂), 22.4 (CH₃ NHAc), 22.3 (CH₃ NHAc), 21.6 (C₂₃), 16.2 (C_{6'}). MS FAB+-HRMS *m/z* [M+Na]⁺ calcd for C₇₉H₁₀₄N₆O₂₀SNa 1511.6924, found 1511.6882.

4.2.24. 5-Carboxyethylpentyl 3,6-di-O-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-4-O-(2-acetamido-3-O-acetyl-4,6-O-benzylidene-2-deoxy-β-D-glucopyranosyl)-2-acetamido-2-deoxy-β-D-glucopyranoside (43)

Compounds **37** and **38** (1.030 g, 0.604 mmol) were dissolved in ethanol (15 mL), THF (5 mL) and hydrazine monohydrate (0.293 mL, 6.040 mmol, 10 equiv) was added. The solution was stirred at 90 °C overnight. The mixture was allowed to cool down to room temperature, filtered and concentrated. The residue was dissolved in anhydrous pyridine (10 mL) and acetic anhydride (1.2 mL) was added under argon. The mixture was stirred at room temperature overnight. Concentrated and the crude product was extracted with CH₂Cl₂, washed with an HCl solution (1 M) and neutralised with a saturated NaHCO₃ solution. The organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (EtOAc) and the diastereoisomers were separated by column chromatography on silica gel (CH₂Cl₂/EtOAc: 5:5) to give 540 mg of **43** (58%) as a syrup. *R*_f: 0.40 (EtOAc). [α]_D²⁵ –65 (c 1, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ: 7.44–7.33 (m, 35H, H Ar), 6.47 (br s, 1H, NHAc), 6.22 (br s, 1H, NHAc), 5.48 (s, 1H, H benzylidene), 5.35 (d, 1H, *J*_{H1-H2} = 2.4 Hz, 1H₁ fucose), 5.20 (t, 1H, *J*_{H3-H2} = *J*_{H3-H4} = 8.7 Hz, H₃), 5.03 (m, 2H, 2CHPh), 4.95–4.65 (m, 12H, 10CHPh, 2H₁), 4.43 (d, 1H, *J*_{H1-H2} = 5.6 Hz, 1H₁ fucose), 4.35 (dd, 1H, *J* = 4.5 Hz, *J* = 10.3 Hz), 4.29 (m, 1H), 4.19–4.12 (m, 5H, CH₂ OEt, 1H₂ fucose, 2H), 4.03–3.98 (m, 7H, 1H₅ fucose, 6H), 3.88 (m, 1H), 3.78–3.53 (m, 7H, 1H₇, 6H), 3.36 (m, 1H, 1H₇), 2.28 (t, 2H, *J*_{H11-H10} = 7.5 Hz, H₁₁), 2.08 (s, 3H, CH₃ OAc), 1.98 (CH₃ NHAc), 1.94 (CH₃ NHAc), 1.65–1.48 (m, 4H,

H₈, H₁₀), 1.36–1.26 (m, 8H, H₉, 1H₆ fucose, CH₃ OEt), 1.13 (d, 3H, *J*_{H6-H5} = 6.3 Hz, 1H₆ fucose). ¹³C NMR (100 MHz, CDCl₃) δ: 174.1 (CO COOEt), 171.6 (CO), 170.9 (CO), 170.5 (CO), 139.0–137.0 (Cq Ar), 129.0–126.0 (C Ar), 101.9 (C benzylidene), 101.3 (1C₁ fucose), 100.6 (1C₁), 98.7 (1C₁), 97.4 (1C₁ fucose), 80.2, 79.9, 79.1, 78.2, 77.8, 77.2, 76.0, 75.8, 75.4 (CH₂Ph), 75.3 (CH₂Ph), 74.7, 74.4, 74.1 (CH₂Ph), 73.7 (CH₂Ph), 73.4 (CH₂Ph), 73.2 (CH₂Ph), 72.0, 69.2 (C₇), 69.1 (1C₆), 67.4 (1C₆), 67.3, 67.0, 66.6, 60.6 (CH₂ OEt), 55.7 (1C₂), 54.2 (1C₂), 34.6 (C₁₁), 29.4 (C₈ or C₁₀), 25.9 (C₉), 25.0 (C₈ or C₁₀), 23.8 (CH₃ NHAc), 23.7 (CH₃ NHAc), 21.3 (CH₃ OAc), 17.4 (1C₆ fucose), 17.6 (1C₆ fucose), 14.7 (CH₃ OEt). MS FAB+-HRMS *m/z* [M+Na]⁺ calcd for C₈₇H₁₀₄N₂O₂₂Na 1551.6978, found 1551.6990.

4.2.25. 5-Carboxypentyl 3,6-di-O-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-4-O-(2-acetamido-4,6-O-benzylidene-2-deoxy-β-D-glucopyranosyl)-2-acetamido-2-deoxy-β-D-glucopyranoside biotin conjugate (44)

Compound **43** (0.466 g, 0.304 mmol) was dissolved in THF (3 mL) and NaOH (10 M, 300 μL, 3.040 mmol, 10 equiv) was added. The solution was stirred at 75 °C overnight. The mixture was allowed to cool down to room temperature, neutralised (IR 120 H⁺), filtered and concentrated. The crude product was dissolved in anhydrous DMF (6 mL) under argon with **10** (0.205 g, 0.608 mmol, 2 equiv), DMAP (0.043 g, 0.360 mmol, 1.2 equiv) and EDC (0.086 g, 0.450 mmol, 1.5 equiv). The mixture was stirred for 1 h at 70 °C. EDC (0.028 g, 0.150 mmol, 0.5 equiv) was added to complete the reaction and after 3 h, concentrated. The residue was extracted with CH₂Cl₂ and washed with water. The organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (CH₂Cl₂/methanol: 9:1) to give 0.273 g of **44** (51%) as a syrup. *R*_f: 0.24 (CH₂Cl₂/methanol: 9:1). [α]_D²⁵ –53 (c 7, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ: 7.43–7.23 (m, 35H, H Ar), 6.64 (s, 1H, NHCO), 6.52 (s, 1H, NHCO), 6.32 (s, 1H, NH urea), 5.80 (s, 1H, NH urea), 5.44 (s, 1H, H benzylidene), 5.36 (s, 1H, 1H₁ fucose), 5.01–4.57 (m, 14H, 1H₁, 1H₁ fucose, 12H CHPh), 4.43 (d, 1H, *J*_{H1-H2} = 5.4 Hz, 1H₁), 4.30–3.35 (m, 24H), 3.17 (m, 4H, H₁₃, H₁₈), 3.00 (m, 1H, H₂₄), 2.68 (m, 1H, 1H₂₇), 2.56 (d, 1H, *J*_{gem} = 12.4 Hz, 1H₂₇), 2.15 (m, 4H, H₁₁, H₂₀), 1.98 (s, 3H, CH₃ NHAc), 1.94 (s, 3H, CH₃ NHAc), 1.75–1.09 (m, 26H, *J*_{H6-H5} = 5.8 Hz, *J*_{H6-H5} = 6.1 Hz, 2H₆ fucose, H₈, H₉, H₁₀, H₁₄, H₁₅, H₁₆, H₁₇, H₂₁, H₂₂, H₂₃). MS FAB+-HRMS *m/z* [M+Na]⁺ calcd for C₉₉H₁₂₆N₆O₂₂SNa 1805.8544, found 1805.8570.

4.2.26. 5-Carboxypentyl 3,6-di-O-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-4-O-(2-acetamido-4,6-O-benzylidene-2-deoxy-β-D-glucopyranosyl)-2-acetamido-2-deoxy-β-D-glucopyranoside oxidised biotin conjugate (45)

To a solution of **44** (0.230 g, 0.128 mmol) in anhydrous CH₂Cl₂ (5 mL), was added mCPBA (0.066 g, 0.386 mmol, 3 equiv) under argon. The mixture was stirred at room temperature overnight. The mixture was washed with a saturated NaHCO₃ solution. The organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by column chromatography on silica gel (CH₂Cl₂/methanol: 8:2) to give 195 mg of **45** (84%) as a white foam. *R*_f: 0.07 (CH₂Cl₂/methanol: 9:1). [α]_D²⁵ –54 (c 1, CHCl₃). ¹H NMR (400 MHz, CD₃OD) δ: 7.42–7.18 (m, 35H, H Ar), 5.45 (d, 1H, *J*_{H1-H2} = 2.9 Hz, 1H₁ fucose), 5.39 (s, 1H, H benzylidene), 5.01 (m, 2H, 1H₁, 1CHPh), 4.96 (d, 1H, *J*_{H1-H2} = 3.0 Hz, 1H₁ fucose), 4.93–4.65 (m, 10H, 1H₅ fucose, 9CHPh), 4.63–4.59 (m, 2H, 2CHPh), 4.48 (m, 2H, H₂₅, H₂₆), 4.36 (d, 1H, *J* = 7.5 Hz), 4.19–3.86 (m, 12H, 3H₆, 1H₅ fucose, 8H), 3.82–3.72 (m, 6H, 1H₆, 1H₇, 4H), 3.50–3.38 (m, 3H, 1H₇, 2H), 3.28 (dd, 1H, *J*_{H27-H26} = 5.8 Hz, *J*_{gem} = 14.2 Hz, 1H₂₇), 3.18–3.13 (m, 5H, H₂₄, H₁₃, H₁₈), 3.09 (d, 1H, 1H₂₇), 2.23–2.15 (m, 4H, H₁₁, H₂₀), 2.02 (s, CH₃ NHAc), 2.00 (s, CH₃ NHAc), 1.86 (m, 1H, 1H₂₃), 1.76–1.49 (m, 13H), 1.35–1.22 (m, 10H, 1H₆ fucose, 7H), 1.11 (d,

^3H , $J_{\text{H6-H5}} = 6.3 \text{ Hz}$, 1H_6 fucose). ^{13}C NMR (100 MHz, CD_3OD) δ : 174.9 (CO), 174.6 (CO), 172.6 (CO), 172.1 (CO), 163.6 (CO urea), 139.6–138.0 (Cq Ar), 129.0–126.5 (C Ar), 101.9 (C benzylidene), 101.6 (1C_1), 100.7 (1C_1), 97.4 (1C_1 fucose), 96.3 (1C_1 fucose), 82.4, 79.4, 79.0, 78.8 (2C), 76.6, 75.8, 75.4 (CH_2Ph), 75.2 (CH_2Ph), 74.6, 74.2, 73.5, 73.0 ($2\text{CH}_2\text{Ph}$), 72.8 (CH_2Ph), 72.3 (CH_2Ph), 71.4, 69.1 (C_7), 69.0 (1C_6), 67.0, 66.8, 66.4, 65.3 (1C_6), 60.8 (C_{24}), 57.0, 56.1, 54.6 (C_{25} or C_{26}), 54.2 (C_{27}), 50.0 (C_{25} or C_{26}), 39.2 (C_{13} , C_{18}), 36.1 (C_{11} or C_{20}), 35.6 (C_{11} or C_{20}), 29.0–25.0 (C_8 , C_9 , C_{10} , C_{14} , C_{15} , C_{16} , C_{17} , C_{21} , C_{22}), 22.6 ($\text{CH}_3 \text{NHAc}$), 22.1 ($\text{CH}_3 \text{NHAc}$), 21.6 (C_{23}), 16.4 (1C_6 fucose), 16.0 (1C_6 fucose). MS FAB+–HRMS m/z [$\text{M}+\text{Na}$] $^+$ calcd for $\text{C}_{99}\text{H}_{126}\text{N}_6\text{O}_{24}\text{SNa}$ 1837.8441, found 1837.8444.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.bmc.2010.12.001.

References and notes

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Synthesis of cross-reacting carbohydrate determinants' fragments as tools for in vitro allergy diagnosis

Supporting Information: NMR Spectra: ^1H and ^{13}C , and mass spectra

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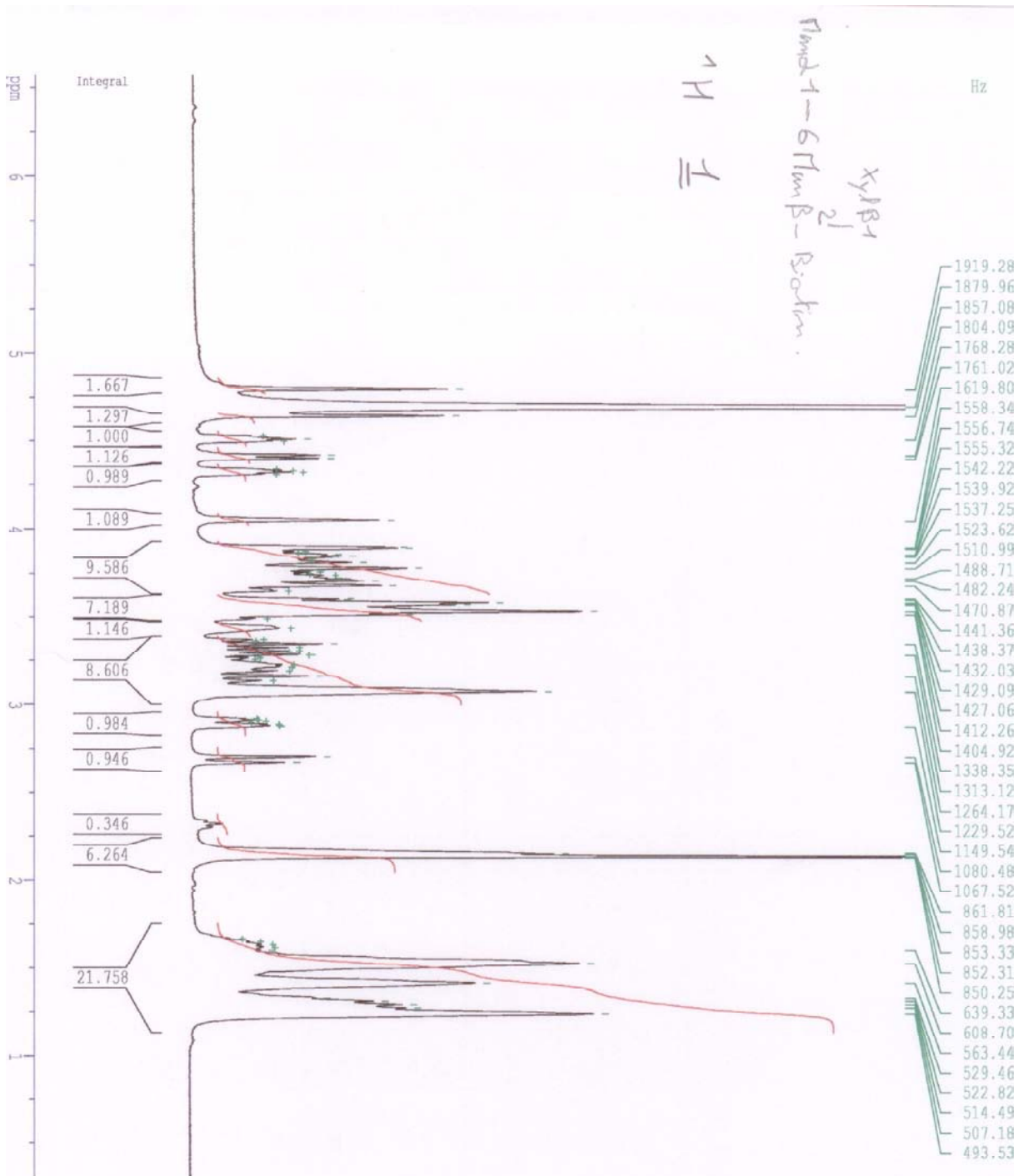
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Current Data Parameters

NAME	mayalic
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

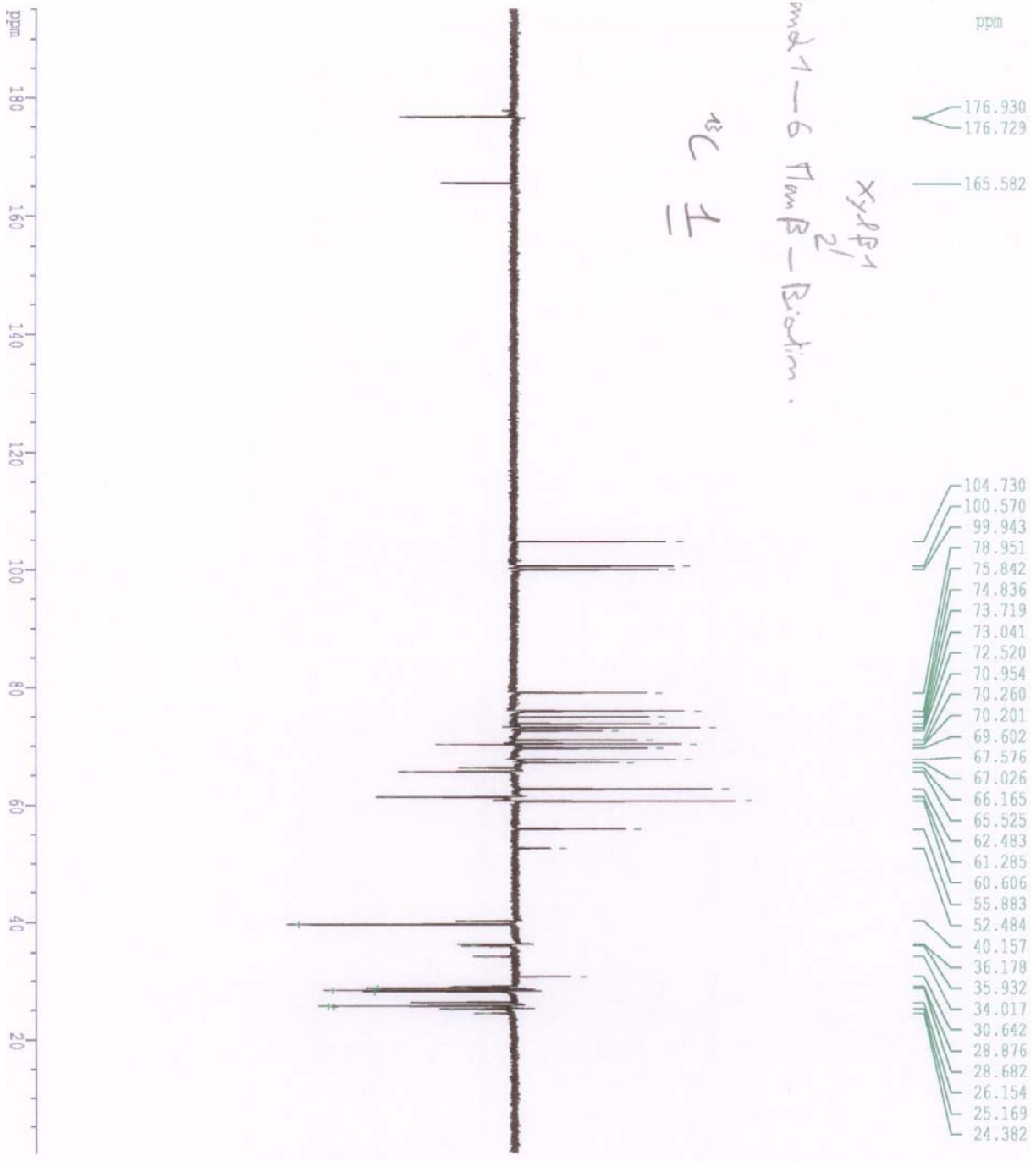
Date_	500000
Time	18.53
INSTRUM	spect
PROBHD	5 mm 1H/13C
PULPROG	zg30
TD	16384
SOLVENT	CDCl3
NS	16
DS	2
SWH	4006.410 Hz
FIDRES	0.244532 Hz
AQ	2.0447731 sec
RG	57
DM	124.800 usec
DE	4.50 usec
TE	300.0 K
D1	0.10000000 sec
P1	9.50 usec
DE	4.50 usec
SFO1	400.1319206 MHz
NUC1	1H
PL1	-3.00 dB

F2 - Processing parameters

SI	16384
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.00 Hz
GB	0
PC	0.10

1D NMR plot parameters

CX	22.00 cm
F1P	6.578 ppm
F1	2632.00 Hz
F2P	0.301 ppm
F2	120.49 Hz
PPMCM	0.28531 ppm/cm
HZCM	114.15952 Hz/cm



Current Data Parameters

NAME	mayalic
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	500000
Time	19.46
INSTRUM	spect
PROBHD	5 mm 1H/13C
PULPROG	jmod2.php
TD	65536
SOLVENT	CDCl3
NS	4096
DS	4
SWH	24154.590 Hz
FIDRES	0.368770 Hz
AQ	1.3566452 sec
RG	6502
DW	20.700 usec
DE	4.50 usec
TE	300.0 K
P1	17.00 usec
P2	34.0 usec
DELTA	0.0000108 sec
D20	0.00714000 sec
PL12	17.50 dB
D1	1.2999995 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1317000 MHz
NUC2	1H
PL2	120.00 dB
D13	0.00000300 sec
SFO1	100.6237964 MHz
NUC1	13C
PL1	0.00 dB
DE	4.50 usec

F2 - Processing parameters

SI	65536
SF	100.612790 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	0.30

1D NMR plot parameters

CX	22.00 cm
FLP	195.049 ppm
F1	19624.40 Hz
F2P	0.459 ppm
F2	46.18 Hz
PCNOM	8.84499 ppm/cm
HCKM	891.91895 Hz/cm

[Mass Spectrum]

Data : COLLOT-MC539-FRB+-NBR-NR002 Date : 28-Jun-2007 10:07

Sample : -

Note : -

Ion Mode : FRB+

Inlet : Direct

Spectrum Type : Normal Ion [MF-Linear]

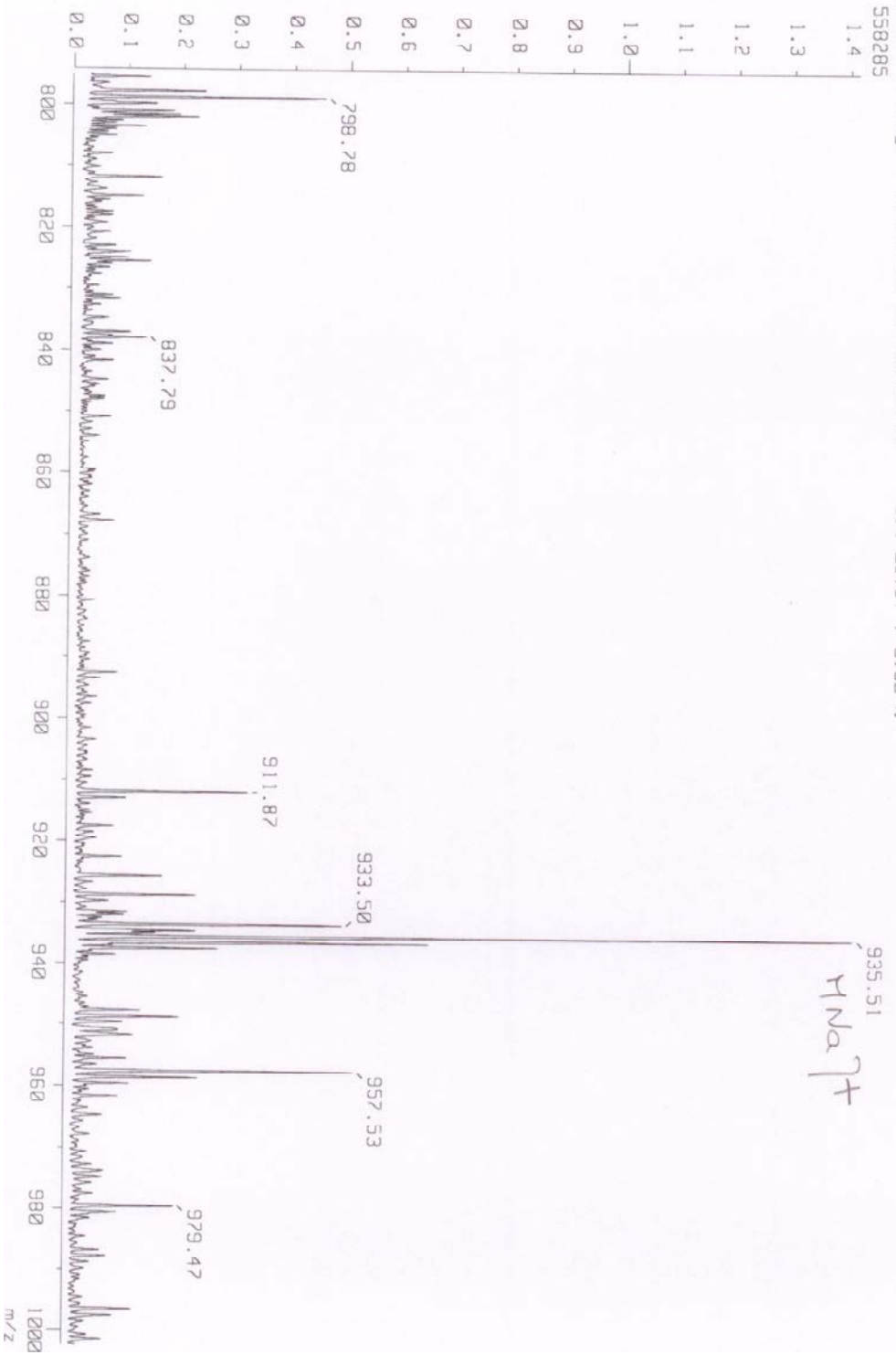
RT : 2.43 min Scan# : (3,31)

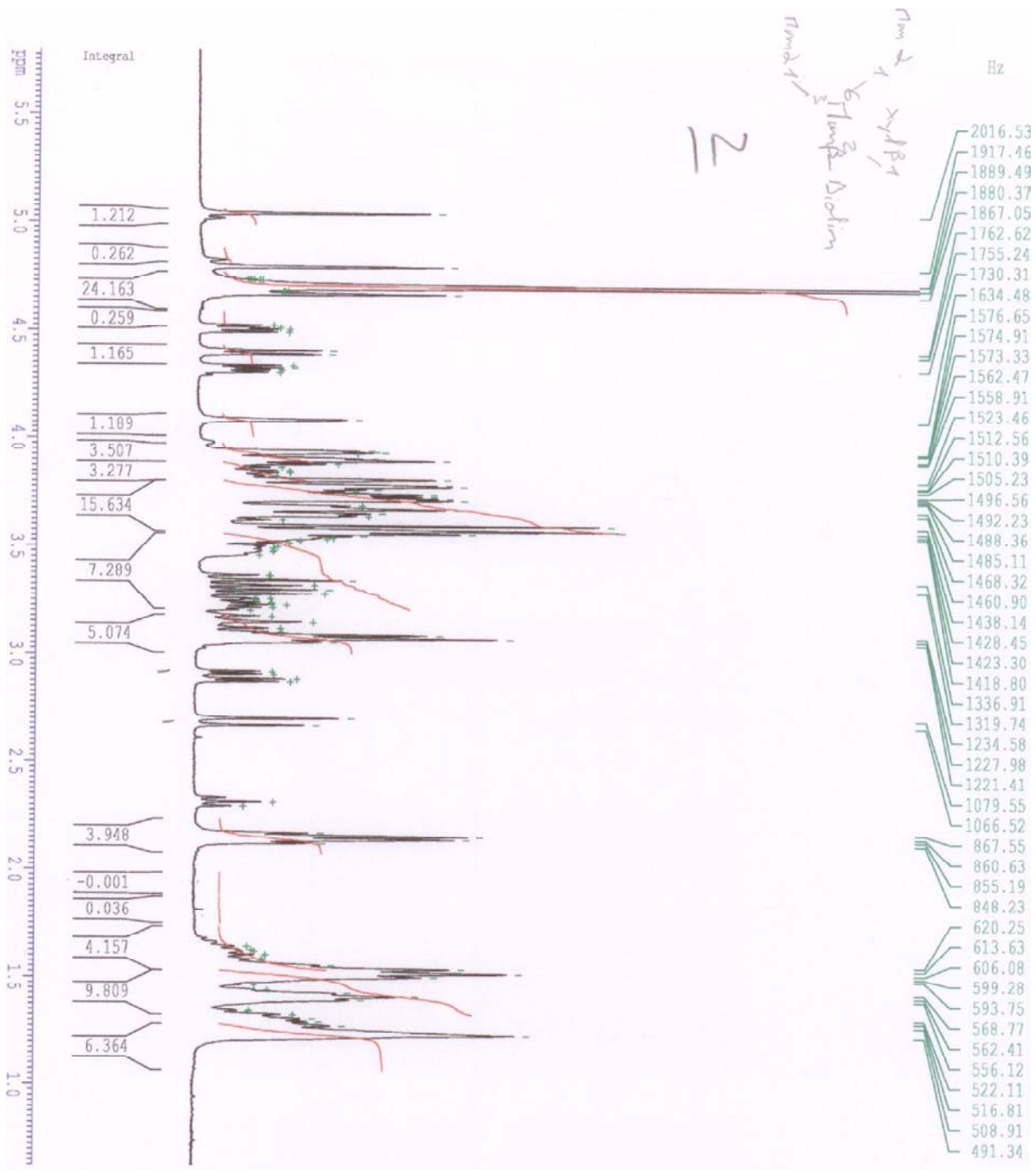
BP : m/z 176.1154 Int. : 129.73

Output m/z range : 795.1780 to 1002.3735

Cut Level : 0.00 %

558285





ppm 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0

Integral

1.212
0.262
24.163
0.259
1.165
1.189
3.507
3.277
15.634
7.289
5.074
3.948
-0.001
0.036
4.157
9.809
6.364

Hz

2016.53
1917.46
1889.49
1880.37
1867.05
1762.62
1755.24
1730.31
1634.48
1576.65
1574.91
1573.33
1562.47
1558.91
1523.46
1512.56
1510.39
1505.23
1496.56
1492.23
1488.36
1485.11
1468.32
1460.90
1438.14
1428.45
1423.30
1418.80
1336.91
1319.74
1234.58
1227.98
1221.41
1079.55
1066.52
867.55
860.63
855.19
848.23
620.25
613.63
606.08
599.28
593.75
568.77
562.41
556.12
522.11
516.81
508.91
491.34

Current Data Parameters

NAME mayalic
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

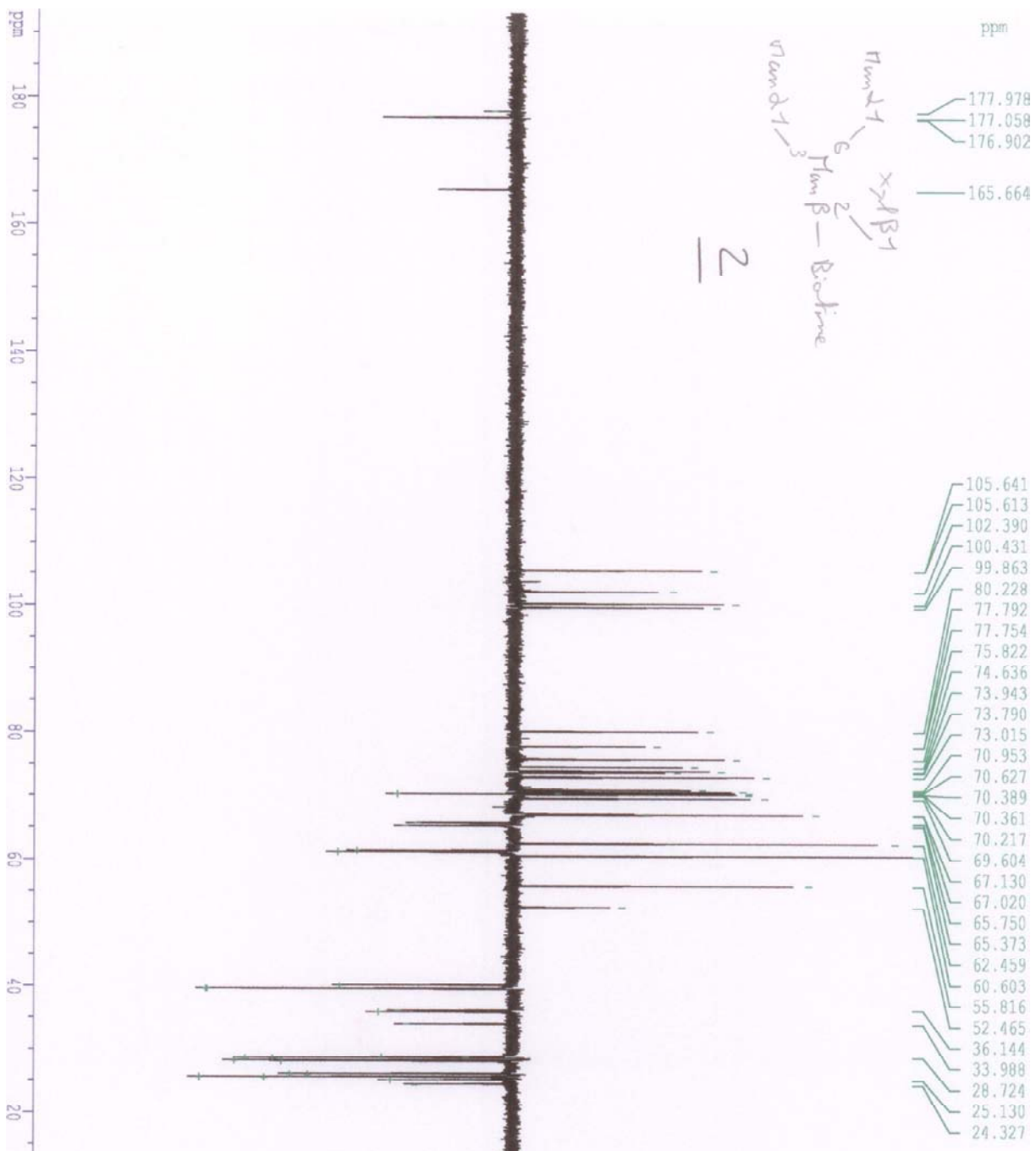
Date_ 500000
Time_ 19.22
INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 32
DS 2
SWH 4006.410 Hz
FIDRES 0.24532 Hz
AQ 2.0447731 sec
RG 181
DM 124.800 usec
DE 4.50 usec
TE 300.0 K
D1 0.1000000 sec
P1 9.50 usec
DE 4.50 usec
SFO1 400.1318206 MHz
NUC1 1H
P11 -3.00 dB

F2 - Processing parameters

SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 0.10

1D NMR plot parameters

CX 22.00 cm
F1P 5.795 ppm
F1 2318.61 Hz
F2P 0.622 ppm
F2 249.07 Hz
PERCM 0.23510 ppm/cm
HZCM 94.06984 Hz/cm



ppm

177.978
177.058
176.902
165.664

105.641
105.613
102.390
100.431
99.863
80.228
77.792
77.754
75.822
74.636
73.943
73.790
73.015
70.953
70.627
70.389
70.361
70.217
69.604
67.130
67.020
65.750
65.373
62.459
60.603
55.816
52.465
36.144
33.988
28.724
25.130
24.327

Current Data Parameters

NAME mayalic
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

Date_ 500000
Time 19.42

INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG jmod2.php
TD 65536
SOLVENT CEC13
NS 16384
DS 4
SHE 24154.590 Hz
FIDRES 0.365570 Hz
AQ 1.3566452 sec
RG 4096
DW 20.700 usec
DE 4.50 usec
TE 300.0 K
P1 17.00 usec
P2 34.0 usec
DELTA 0.0000108 sec
D20 0.00714000 sec
PL12 17.50 dB
D1 1.29999995 sec
waitz16

PCPD2 100.00 usec
SFO2 400.1317000 MHz
NUC2 1H
PI2 120.00 dB
D13 0.00000300 sec
SFO1 100.6237964 MHz
NUC1 13C
PL1 0.00 dB
DE 4.50 usec

F2 - Processing parameters

SI 65536
SF 100.6127290 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.30

1D NMR plot parameters

CX 22.00 cm
F1 193.418 ppm
F1 19460.30 Hz
F2 12.796 ppm
F2 1287.41 Hz
PRNCK 8.21010 ppm/cm
HZCM 825.04065 Hz/cm

1D NMR plot parameters

CX 22.00 cm
F1 193.418 ppm
F1 19460.30 Hz
F2 12.796 ppm
F2 1287.41 Hz
PRNCK 8.21010 ppm/cm
HZCM 825.04065 Hz/cm

1D NMR plot parameters

CX 22.00 cm
F1 193.418 ppm
F1 19460.30 Hz
F2 12.796 ppm
F2 1287.41 Hz
PRNCK 8.21010 ppm/cm
HZCM 825.04065 Hz/cm

1D NMR plot parameters

CX 22.00 cm
F1 193.418 ppm
F1 19460.30 Hz
F2 12.796 ppm
F2 1287.41 Hz
PRNCK 8.21010 ppm/cm
HZCM 825.04065 Hz/cm

[Mass Spectrum]

Data : COLLOT-MC520-FRB+-NBR-NR-HR0 Date : 28-Jun-2007 15:03

Sample: -

Note: -

Inlet: Direct Ion Mode: FRB+

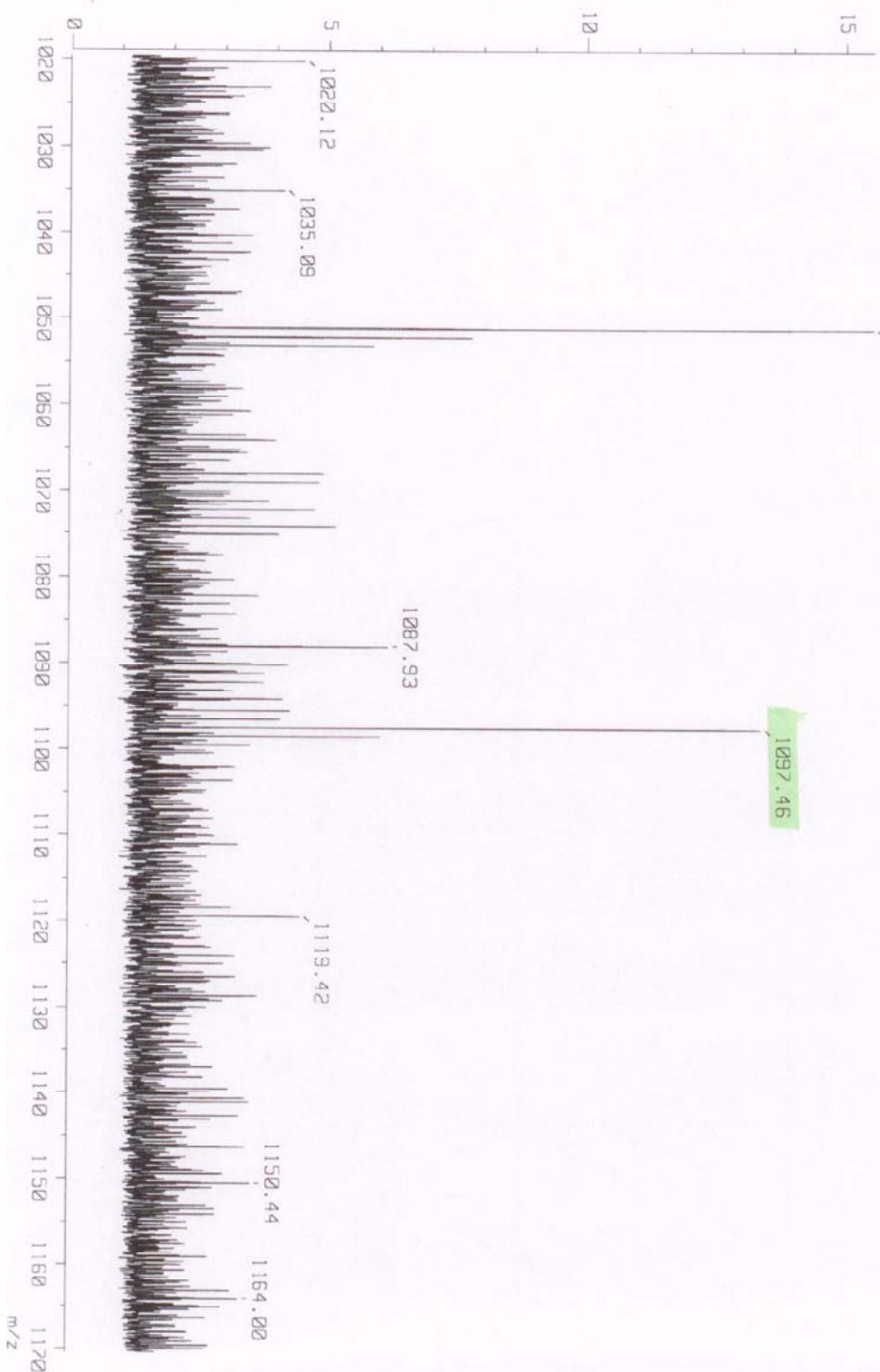
Spectrum Type: Normal Ion [EF-Linear]

RT: 18.22 min Scan#: (165, 169)

BP: m/z 1002.7848 Int.: 14.00

Output m/z range: 1019.5846 to 1170.3264 Cut Level: 0.00 %

114228 1051.08



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13 MARS 2007

Current Data Parameters
NAME mayalic
EXPNO 1
PROCNO 1

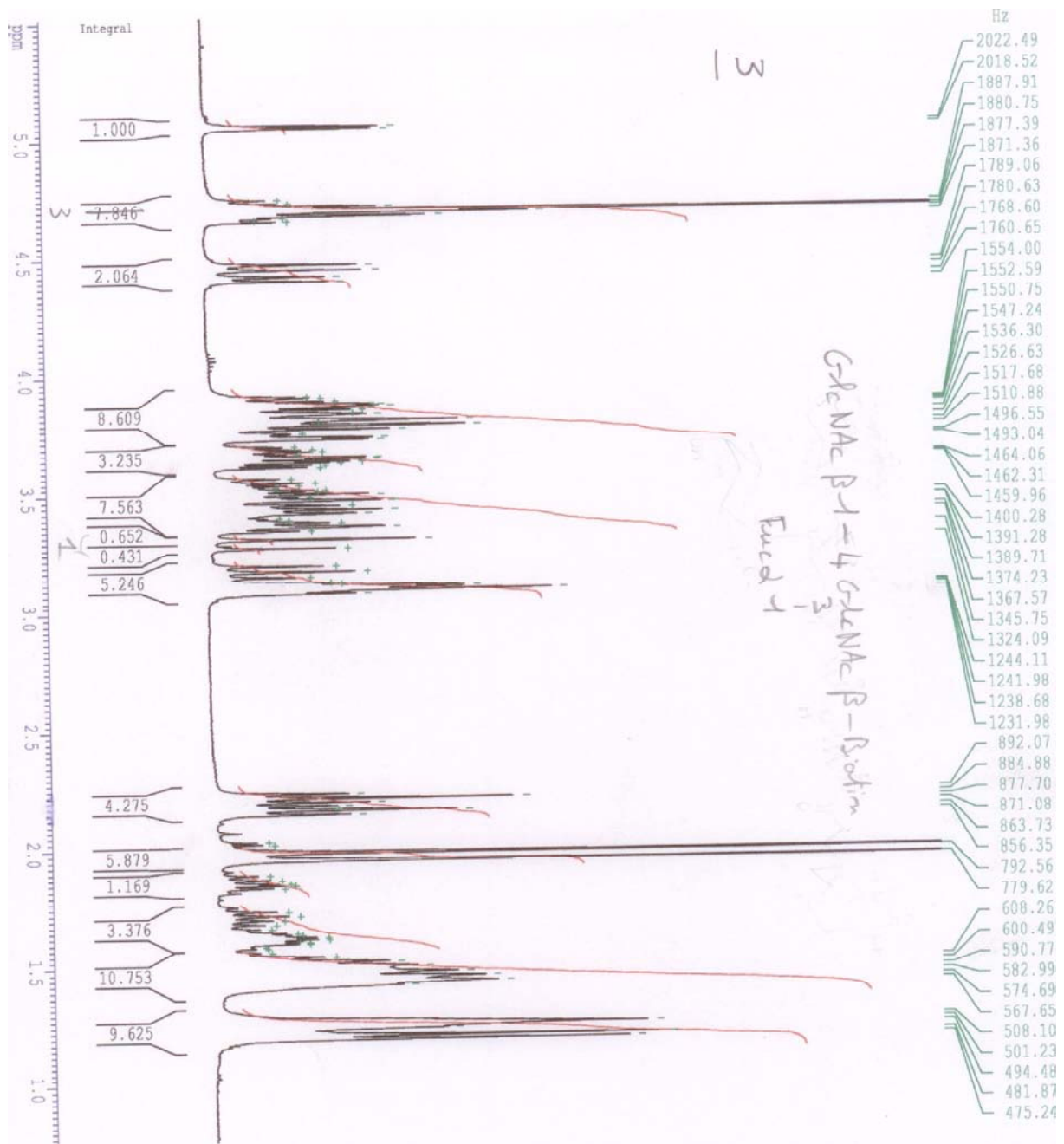
F2 - Acquisition Parameters

Date 500000
Time 21.45
INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 32
DS 2
SWH 4006.410 Hz
FIRRES 0.244332 Hz
AQ 2.044731 sec
RG 181
DW 124.800 usec
DE 4.50 usec
TE 300.0 K
D1 0.10000000 sec
P1 9.50 usec
DE 4.50 usec
SF01 400.1319206 MHz
NUC1 1H
P11 -3.00 dB

F2 - Processing parameters

SI 16384
SF 400.1300000 MHz
WDM EX
SSB 0
LB 0.00 Hz
GB 0
PC 0.10

1D NMR plot parameters
CX 22.00 cm
C1P 5.515 ppm
F1 2206.83 Hz
F2 0.754 ppm
F2 301.62 Hz
PRN 0.21643 ppm/cm
HR 86.68041 Hz/cm



ppm
177.010
176.701
174.979
174.505
164.484

GlcNAc β -1-4 GlcNAc β -Erdim
Fuc α -1-3

101.305
100.774
98.896
76.357
75.741
75.302
74.004
73.985
72.456
71.108
70.748
69.584
68.081
67.051
61.998
60.736
60.315
56.200
56.023
54.580
54.130
50.116
39.631
39.583
36.145
35.815
28.685
28.564
25.026
22.660
22.488
15.884

ppm
160
140
120
100
80
60
40
20

Current Data Parameters
NAME mayalic
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 500000
Time 22.07
INSTRUM spect
PROBHD 3 mm 1H/13C
PULPROG jmod2.pip
TD 65536
SOLVENT CDCl3
NS 4036
DS 4
SHE 2415.580 Hz
FIDRES 0.368570 Hz
AQ 1.356432 sec
RG 4597.6
DM 20.760 usec
DE 4.50 usec
TE 300.0 K
P1 17.00 usec
P2 34.0 usec
DELTA 0.0000108 sec
D20 0.00714000 sec
P112 17.50 dB
D1 1.2939995 sec
CPDPRG2 waltz16
PCPD2 100.00 usec
SFO2 400.1317000 MHz
NUC2 1H
P12 120.00 dB
D13 0.00000300 sec
SFO1 100.6237964 MHz
NUC1 13C
P11 0.00 dB
DE 4.50 usec

F2 - Processing parameters
SI 65536
SF 100.6127290 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.30

1D NMR plot parameters
CX 22.00 cm
F1P 187.844 ppm
F1 18899.50 Hz
F2P 91.70 Hz
F2 91.70 Hz
PPHCK 8.4694 ppm/cm
HZCM 854.9009 Hz/cm

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[Mass Spectrum]

Date : COLLOT MC487-FRB+-NB+-Na+HR0 Date : 20-Fpr-2007 16:52

Sample: -

Note: -

Inlet: Direct Ion Mode: FRB+

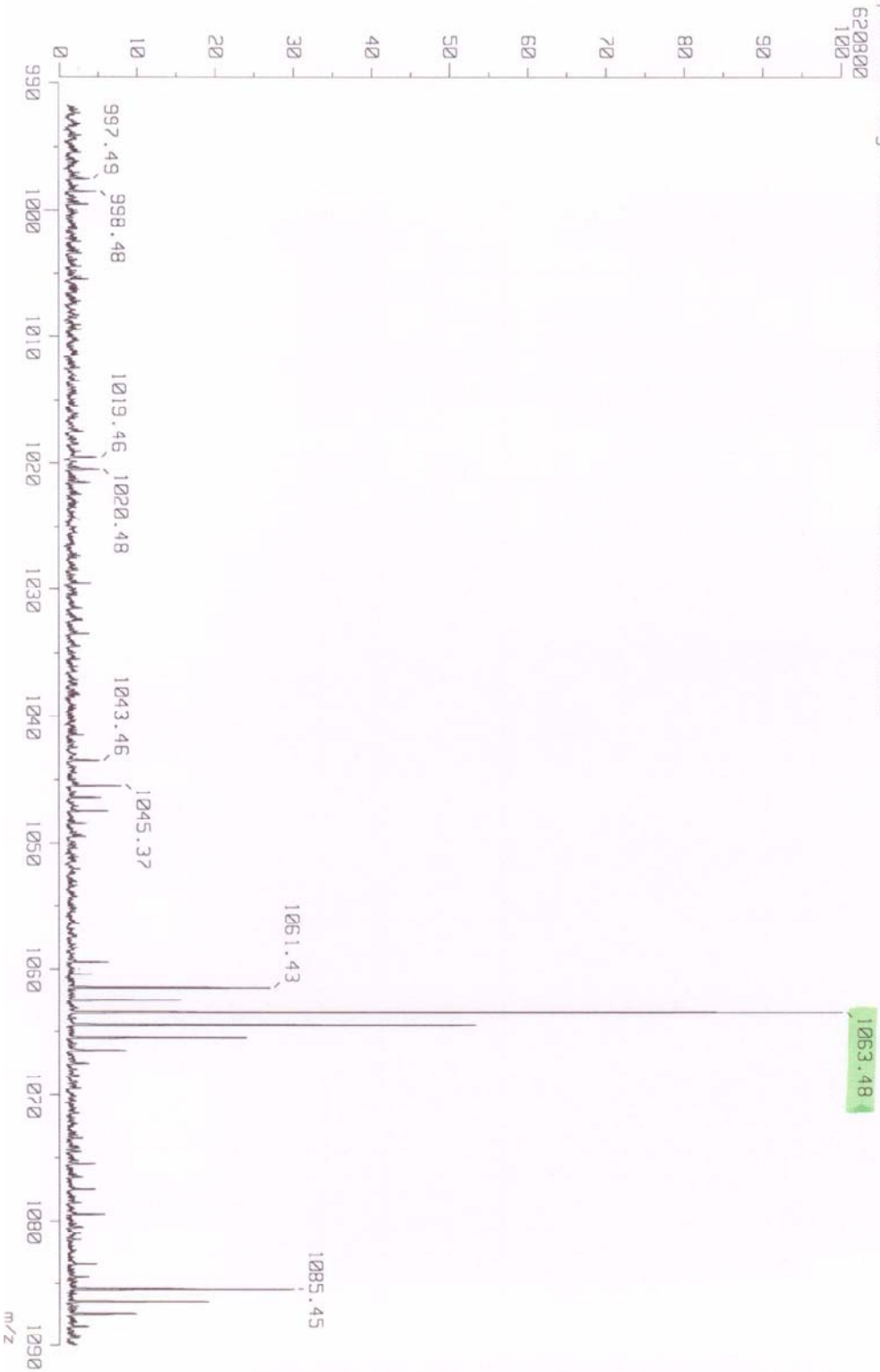
Spectrum Type: Normal Ion [EF-Linear]

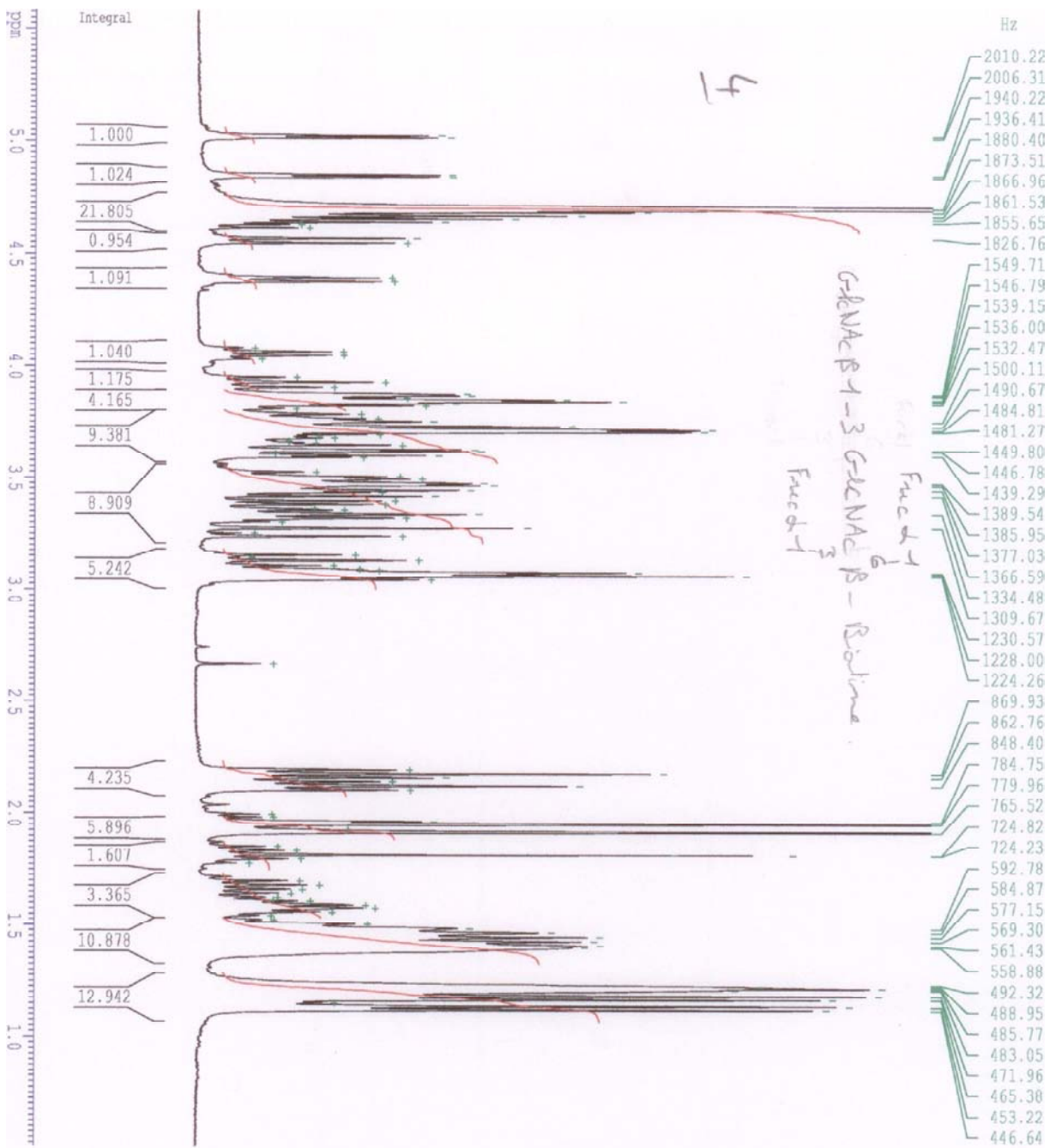
RT: 1.47 min Scan#: (19,23)

BP: m/z 1063.4768 Int.: 11.84

Output m/z range: 990.0000 to 1090.0000 Cut Level: 0.00 %

3





Current Data Parameters

NAME mayalic
EXNO 1
PROCNO 1

F2 - Acquisition Parameters

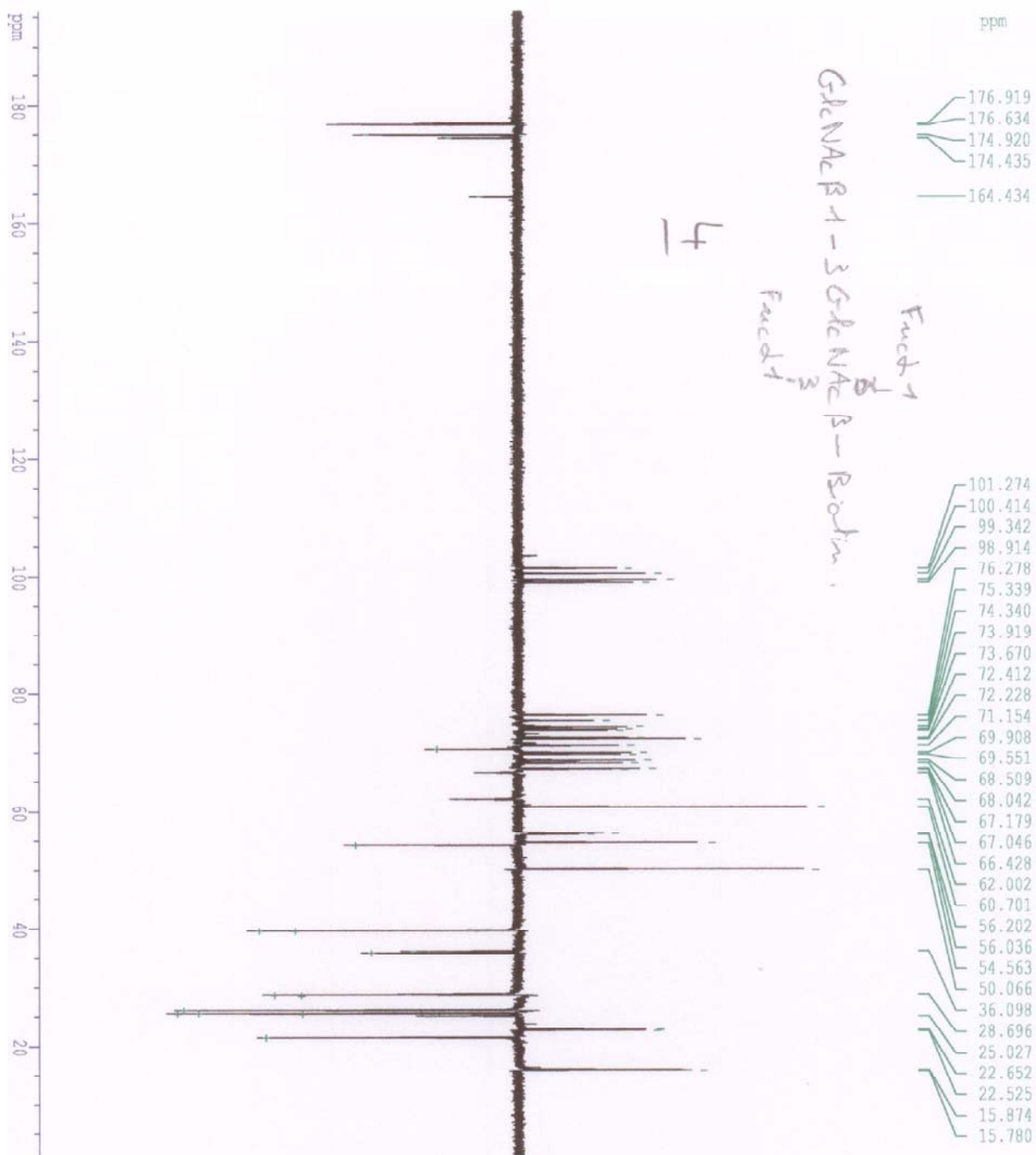
Date 5/08/00
Time 11 41
INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 16
DS 2
SWH 4006.410 Hz
FIDRES 0.24432 Hz
AQ 2.044731 sec
RG 90.5
DM 124.800 usec
DE 4.50 usec
TE 300.0 K
D1 0.1000000 sec
P1 9.50 usec
DE 4.50 usec
SFO1 400.139206 MHz
NUC1 1H
P11 -3.00 dB

F2 - Processing Parameters

SI 16384
SF 400.130000 MHz
WDW EM
SSB 0
TB 0.00 Hz
GB 0
PC 0.10

1D NMR plot parameters

CX 22.00 cm
F1P 5.578 ppm
F1 2231.87 Hz
F2P 0.506 ppm
F2 202.51 Hz
PRCM 0.23053 ppm/cm
HZCM 92.2451 Hz/cm



Current Data Parameters	
NAME	maybolic
EXPNO	2
PROCNO	1
F2 - Acquisition Parameters	
Date_	500000
Time	12.10
INSTRUM	spect
PROBHD	5 mm 1H/13C
PULPROG	jmod2.pulpr
TD	65536
NS	CDC13
DS	8192
SM	4
F2FIDRES	24154.590 Hz
RG	0.366570 Hz
AQ	1.3566452 sec
RG	9195.2
DM	20.700 usec
DE	4.50 usec
TE	300.0 K
P1	17.00 usec
P2	34.0 usec
DELTA	0.000108 sec
D2	0.00714000 sec
PL12	17.50 dB
D1	1.23993995 sec
CEPRG2	waltz16
PCPD2	100.00 usec
SF02	400.1317000 MHz
NUC2	1H
PL2	120.00 dB
D13	0.0000300 sec
SF01	100.6231964 MHz
NUC1	13C
PL1	0.00 dB
DE	4.50 usec
F2 - Processing Parameters	
S1	65536
SF	100.6127290 MHz
MM	EM
SSB	0
LB	0.50 Hz
GB	0
PC	0.30
1D NMR plot parameters	
CX	22.00 cm
RF	105.955 ppm
F1	19705.46 Hz
RF2	0.827 ppm
PRCM	83.19 ppm
PRCM	8.86490 ppm/cm
HCM	851.92145 Hz/cm

[Mass Spectrum]

Data : COLLOT-MC509-FRBNeg-MB001

Date : 08-Jun-2007 16:24

Sample: -

Note: -

Inlet: Direct

Ion Mode: FRB-

Spectrum Type: Normal Ion [MF-Linear]

RT: 0.57 min Scan#: (2,4)

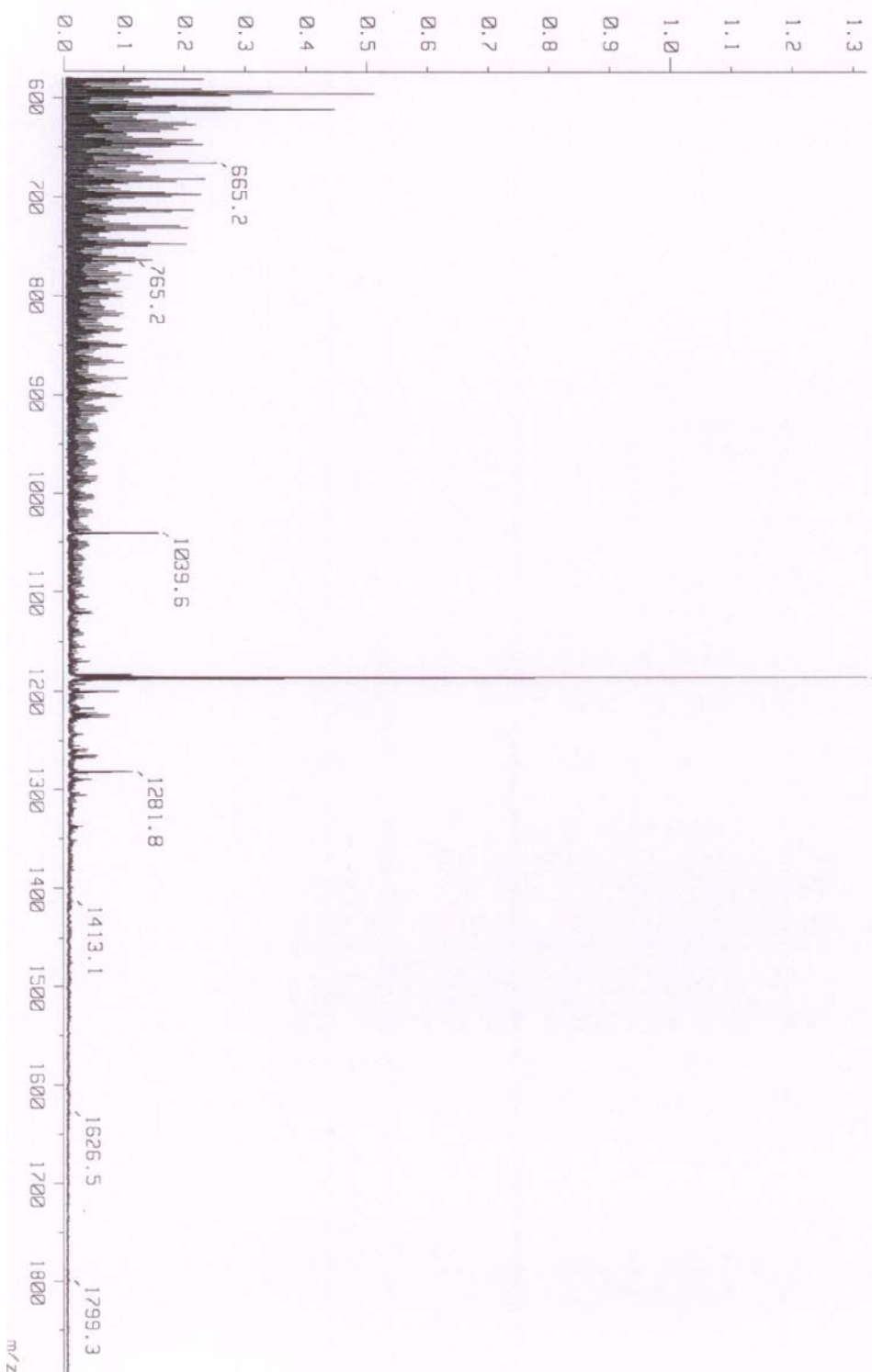
BP: m/z 153.0280 Int.: 216.72

Output m/z range: 579.7033 to 1895.3264

Cut Level: 0.00 %

90082

1185.7



m/z

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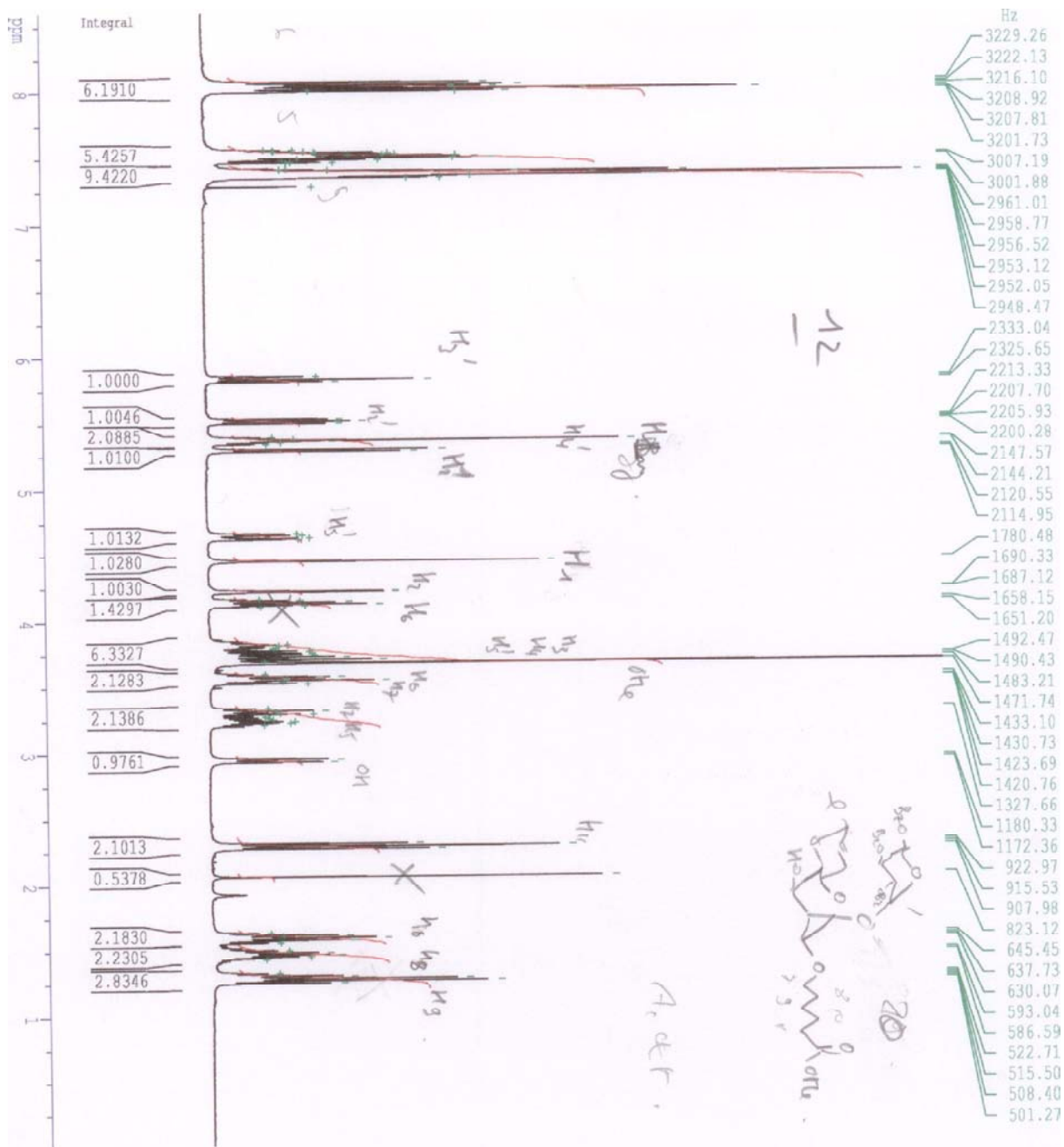
Current Data Parameters
NAME mayalic
EXNO 1
PROCNO 1

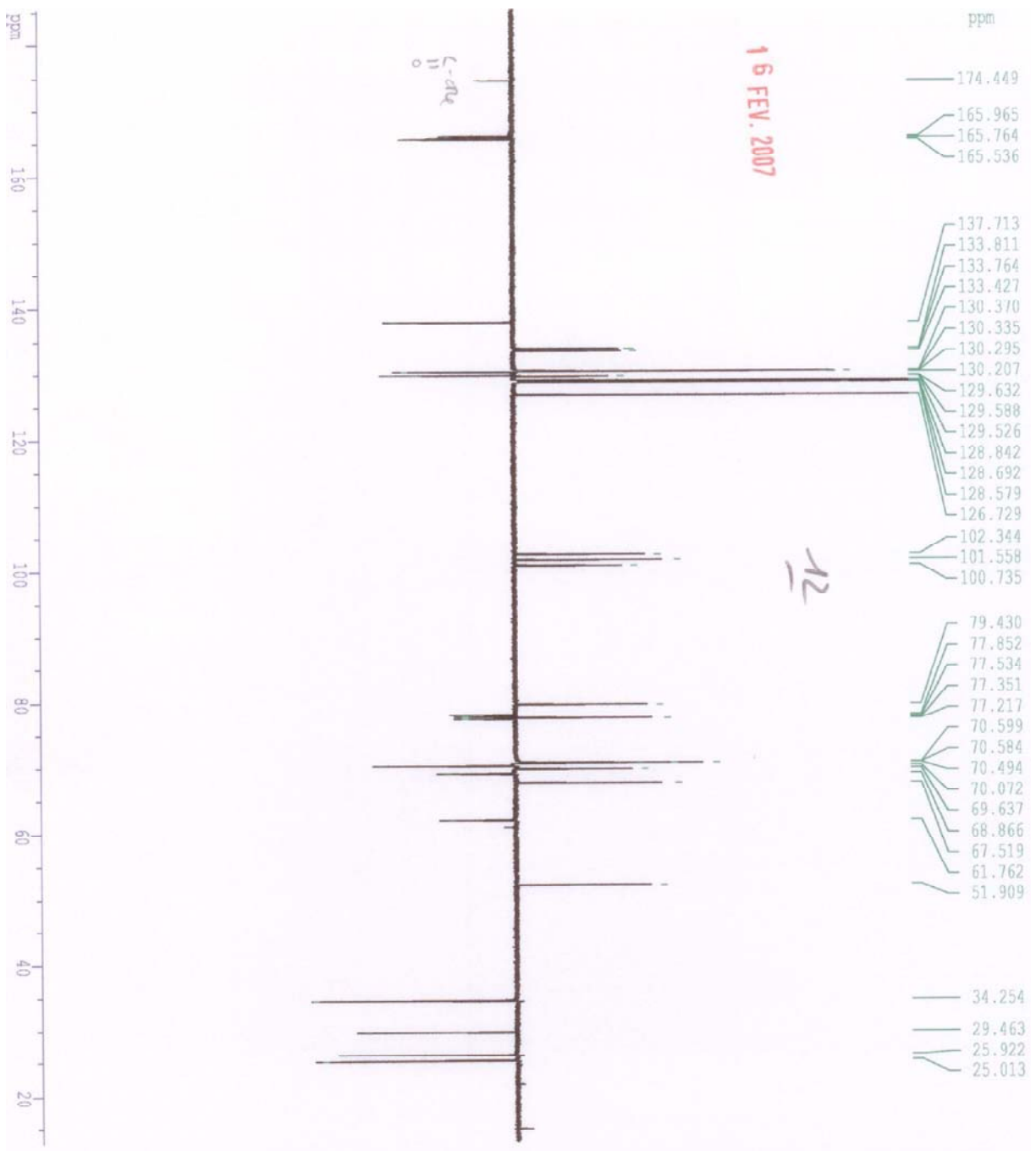
F2 - Acquisition Parameters
Date 500000
Time 11.26

INSTRUM spect
PROBHD 5 mm 1H/13C
TD 2530
SOLVENT CDCl3
NS 16
DS 2
SWE 4006.410 Hz
FIDRES 0.24532 Hz
AQ 2.044731 sec
RG 71.8
DW 124.300 usec
DE 4.50 usec
TE 300.0 K
DI 0.10000000 sec
P1 9.50 usec
DE 4.50 usec
SED1 400.1319205 MHz
NUC1 1H
PL1 -3.00 dB

F2 - Processing Parameters
SI 16384
SE 400.1300000 MHz
WDM EM
SSB 0
LB 0.00 Hz
GB 0
PC 0.10

10 NMR plot parameters
CX 21.00 cm
ETP 8.802 ppm
F1 3441.82 Hz
F2P 0.015 ppm
F2 5.86 Hz
PPMCM 0.39032 ppm/cm
HSCM 156.18003 Hz/cm





Current Data Parameters
NAME mayelic
EXNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 508000
Time_ 11.35
INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG jmod2.prg
TD 65536
SOLVENT DMSO
NS 819
DS 4
SHE 2415.590 Hz
FIDRES 0.369370 Hz
AQ 1.356452 sec
RG 7298.2
TM 20.700 usec
DE 4.50 usec
TE 300.0 K
P1 17.00 usec
P2 34.0 usec
DELTA 0.000108 sec
D20 0.00714000 sec
P112 17.50 dB
D11 1.2999995 sec
CDEPRG2 Waltz16
PCPD2 100.00 usec
SFO2 400.131700 MHz
NUC2 1H
P12 120.00 dB
D13 0.0000306 sec
SFO1 100.6237964 MHz
NUC1 13C
P11 0.00 dB
DE 4.50 usec

F2 - Processing parameters
SI 65536
SF 100.6127290 MHz
WDM EX
SSB 0
LB 0.30 Hz
GB 0
PC 0.30

1D NMR plot parameters
CX 22.00 cm
E1P 185.262 ppm
F1 18639.66 Hz
F2P 12.774 ppm
F2 1285.21 Hz
PPMCK 7.84035 ppm/cm
HCM 788.83923 Hz/cm

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[Mass Spectrum]

Date : COLLOT-MC468-FRB+-NBR-Na-HR0 Date : 28-Feb-2007 11:11

Sample: -

Note: -

Inlet: Direct Ion Mode: FRB+

Spectrum Type: Normal Ion [FF-Linear]

RT: 0.70 min Scan#: (1,12)

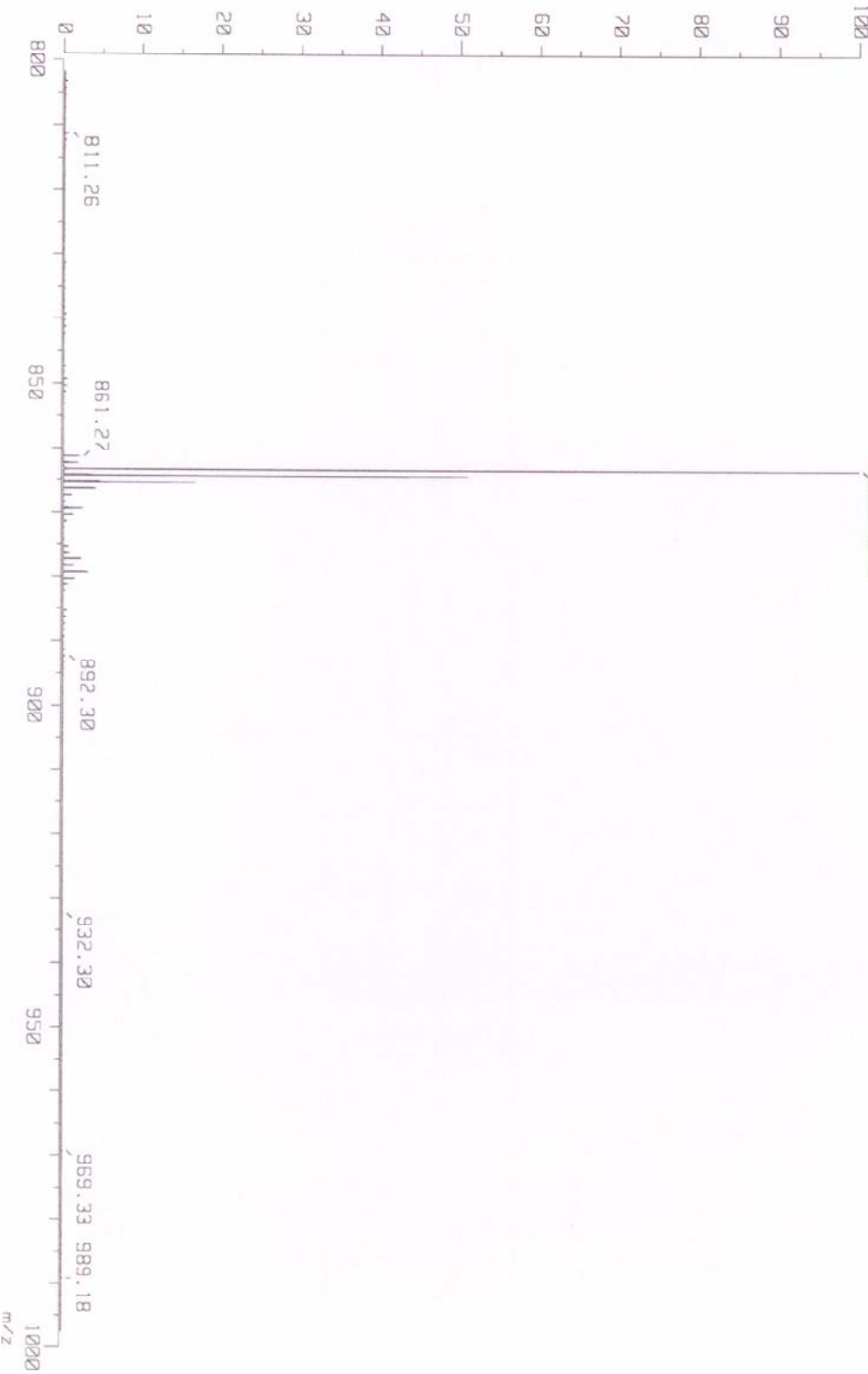
BP: m/z 863.2871 Int.: 107.55

Output m/z range: 800.0000 to 1000.0000

Cut Level: 0.00 %

13532328

863.29



12

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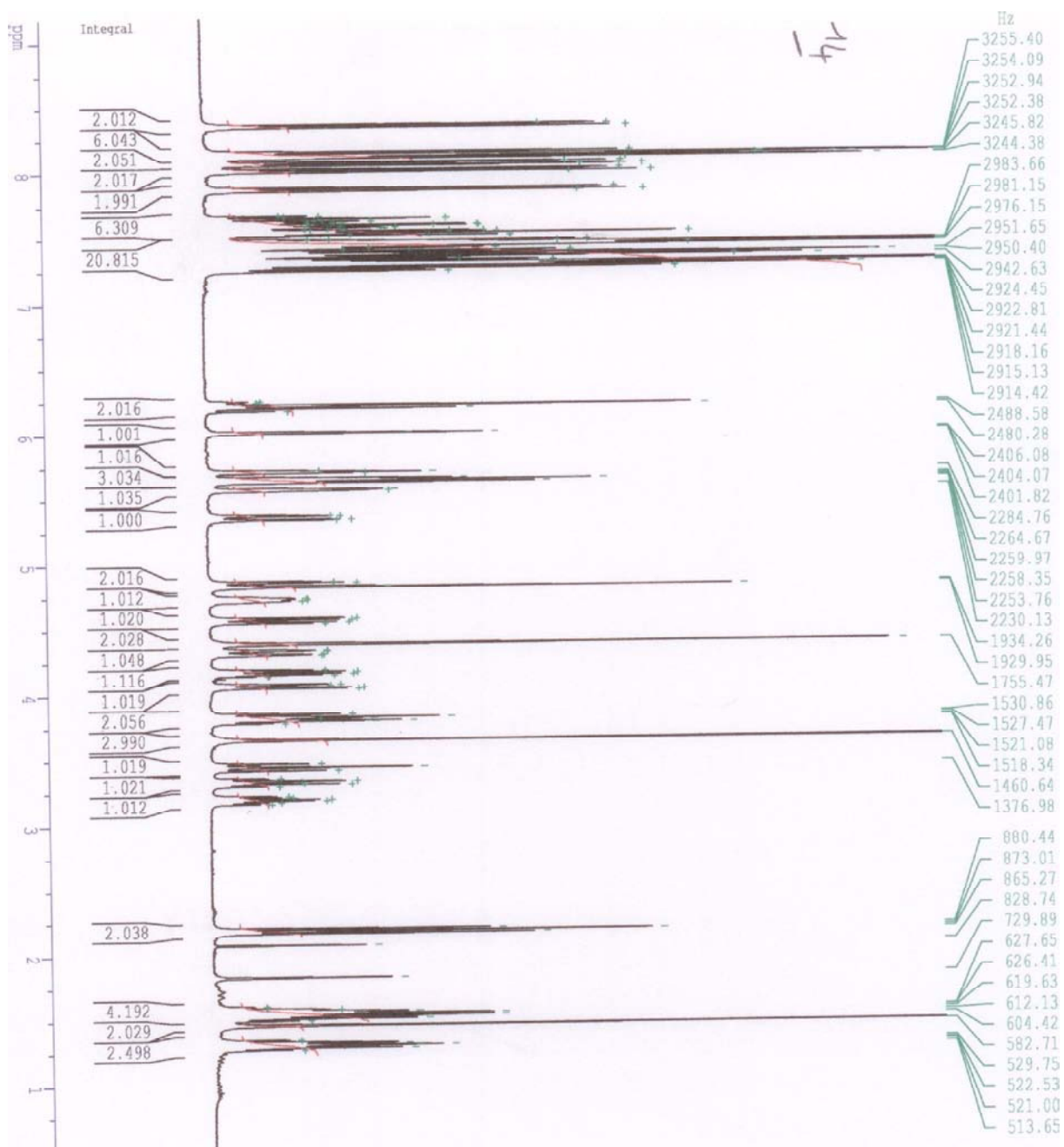
Current Data Parameters
NAME Mayelic
EXNO 1
PROCNO 1

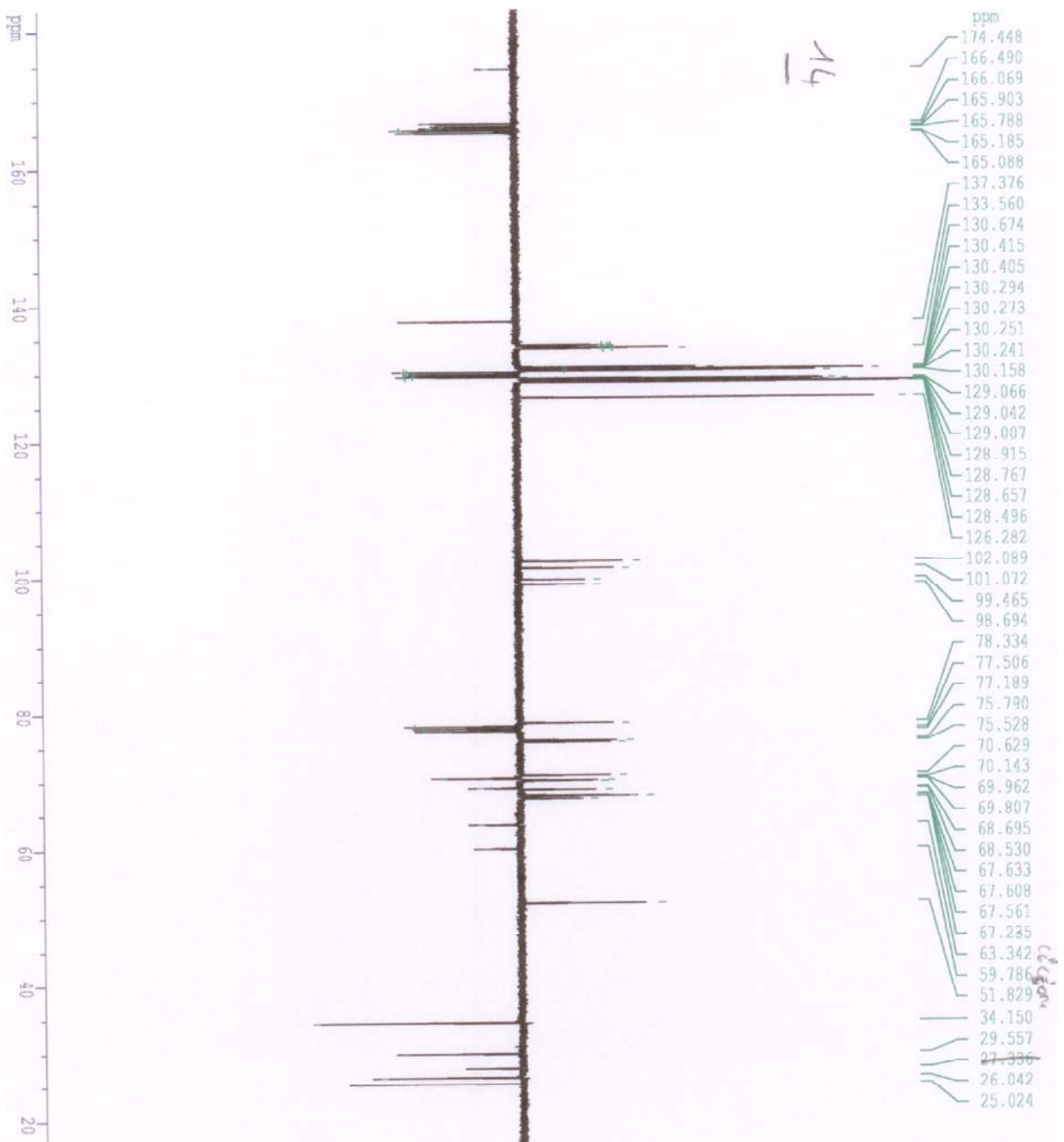
F2 - Acquisition Parameters
Date 500000
Time 19.21

INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 16
DS 2
SWE 4006.410 Hz
FIDRES 0.244332 Hz
AQ 2.044731 sec
RG 71.8
DE 124.800 usec
TE 300.0 K
P1 9.50 usec
DE 4.50 usec
SFO1 400.1319206 MHz
NUC1 1H
FL1 -3.00 dB

F2 - Processing Parameters
SI 16384
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 0.10

1D NMR plot parameters
CX 22.00 cm
F1P 9.184 ppm
F1 3674.75 Hz
F2P 0.505 ppm
F2 201.98 Hz
PPMCM 0.39451 ppm/cm
HICM 157.85332 Hz/cm





Current Data Parameters
NAME mayalic
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 500000
Time 19.39
INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG jmod2 bdp
TD 65536
SOLVENT CDCl3
NS 745
DS 4
SWH 2415.590 Hz
FIDRES 0.368570 Hz
AQ 1.356452 sec
RG 4096
DM 20.700 usec
DE 4.50 usec
TE 300.0 K
P1 17.00 usec
P2 34.0 usec
DELTA 0.0000108 sec
D20 0.00714000 sec
P112 17.50 dB
D1 1.2993995 sec
CPDPRG2 waltz16
PCPD2 100.00 usec
SFO2 400.1317000 MHz
NUC2 1H
P12 120.00 dB
D13 0.0000300 sec
SFO1 100.6237964 MHz
NUC1 13C
P11 0.00 dB
DE 4.50 usec

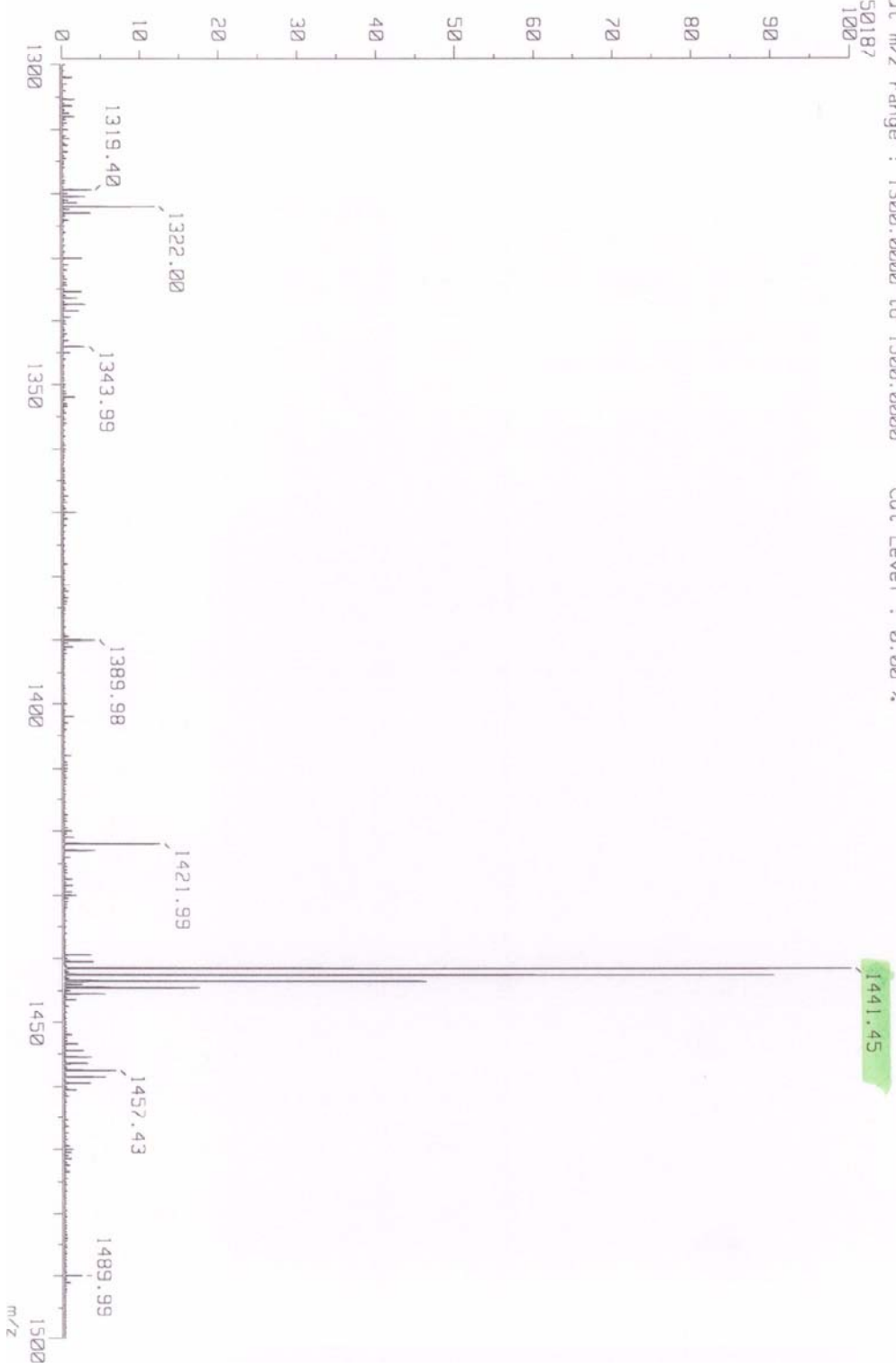
F2 - Processing parameters
SI 65536
SF 100.6127296 MHz
WDW EN
SSB 0
LB 0.30 Hz
GB 0
PC 0.30

1D NMR plot parameters
CX 22.00 cm
FIP 183.135 ppm
F1 18425.75 Hz
F2P 15.666 ppm
F2 1376.19 Hz
PRCKN 7.61225 ppm/cm
HZCK 765.88904 Hz/cm

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14

[Mass Spectrum]
Data : COLLOT-MC472-FRB+-NBA-NA-HR0 Date : 27-Feb-2007 18:38
Sample: -
Note : -
Inlet : Direct Ion Mode : FRB+
Spectrum Type : Normal Ion [EF-Linear]
RT : 6.92 min Scan# : (16,33)
BP : m/z 141.4496 Int. : 73.91
Output m/z range : 1300.0000 to 1500.0000 Cut Level : 0.00 %
13950187



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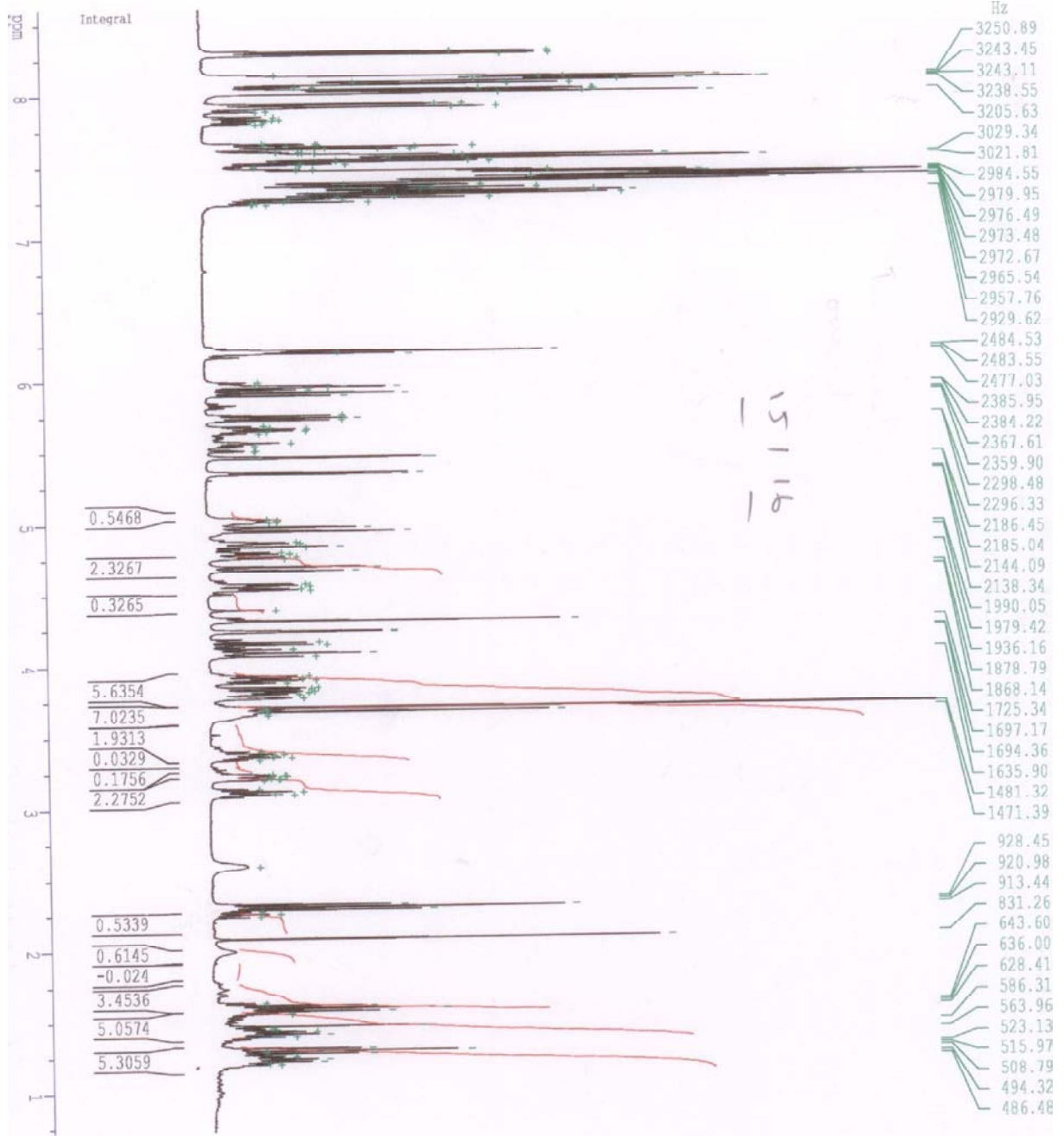
Current Data Parameters
NAME mayalic
EXPNO 1
PROCNO 1

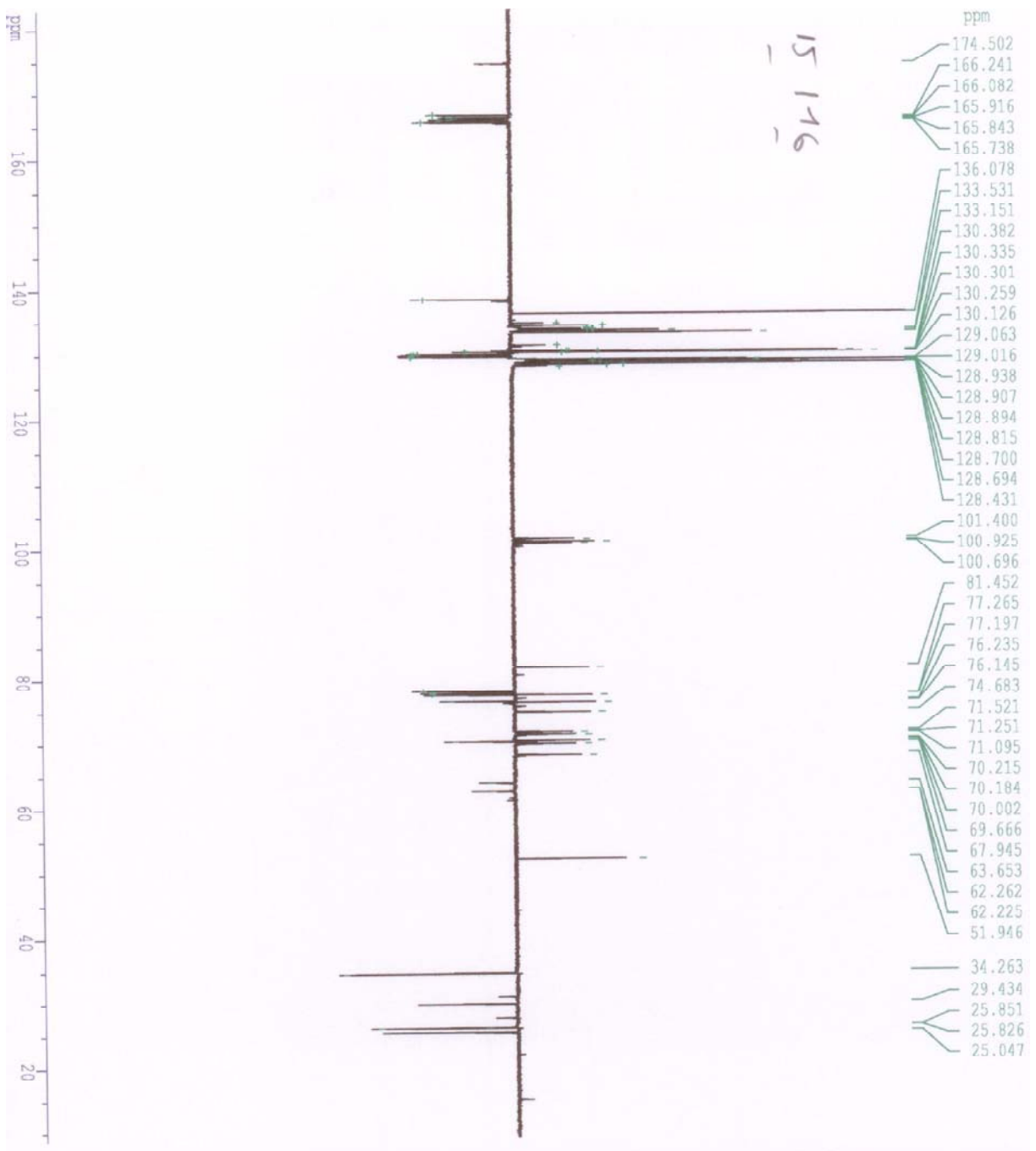
F2 - Acquisition Parameters

Date 500000
Time 21.00
INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 16
DS 2
SWE 4006.410 Hz
FIDRES 0.24432 Hz
AQ 2.044731 sec
RG 71.8
DE 124.800 usec
TE 300.0 K
DE 4.50 usec
DI 0.1000000 sec
P1 9.50 usec
DE 4.50 usec
SFO1 400.1319206 MHz
NUC1 1H
P11 -3.00 dB

F2 - Processing parameters
SI 16384
SF 400.130000 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 0.10

10 NMR plot parameters
CX 22.00 cm
FIP 8.613 ppm
F1 3446.24 Hz
F2 0.722 ppm
F2 288.87 Hz
PPMCM 0.3586 ppm/cm
HZCM 143.51680 Hz/cm





Current Data Parameters
NAME maleic
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 500000
Time_ 21.16

INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG jmod2.php
TD 65536
SOLVENT DMSO
NS 4096
DS 4

SF 24154.590 Hz
FIDRES 0.368370 Hz
AQ 1.3568452 sec
RG 4096

DM 20.700 usec
DE 4.50 usec
TE 300.0 K
P1 17.00 usec
P2 34.0 usec

DELTA 0.0000108 sec
D20 0.0014000 sec
PL12 17.50 dB
D1 1.2999995 sec

CEDEPRG2 waltz16
PCPD2 100.00 usec
SF02 400.131000 MHz
NUC2 1H

PL2 121.00 dB
D13 0.0000300 sec
SF01 100.6231964 MHz
NUC1 13C

PL1 0.00 dB
DE 4.50 usec

F2 - Processing parameters
SI 65536
SF 100.6121290 MHz
WDM EN
SSB 0
LB 0.30 Hz
GB 0
PC 0.30

I0 NMR plot parameters
CX 22.00 cm
FIP 182.907 ppm
F1 18402.79 Hz
F2P 8.787 ppm

F2 884.07 Hz
PRMCN 7.91456 ppm/cm
HSCN 796.30579 Hz/cm

26 MARS 2007

[Mass Spectrum]

Date : COLLOT-MC489B-FRB+-NBR-Na+-H Date : 17-Feb-2007 14:25

Sample: -

Note: -

Inlet: Direct Ion Mode: FRB+

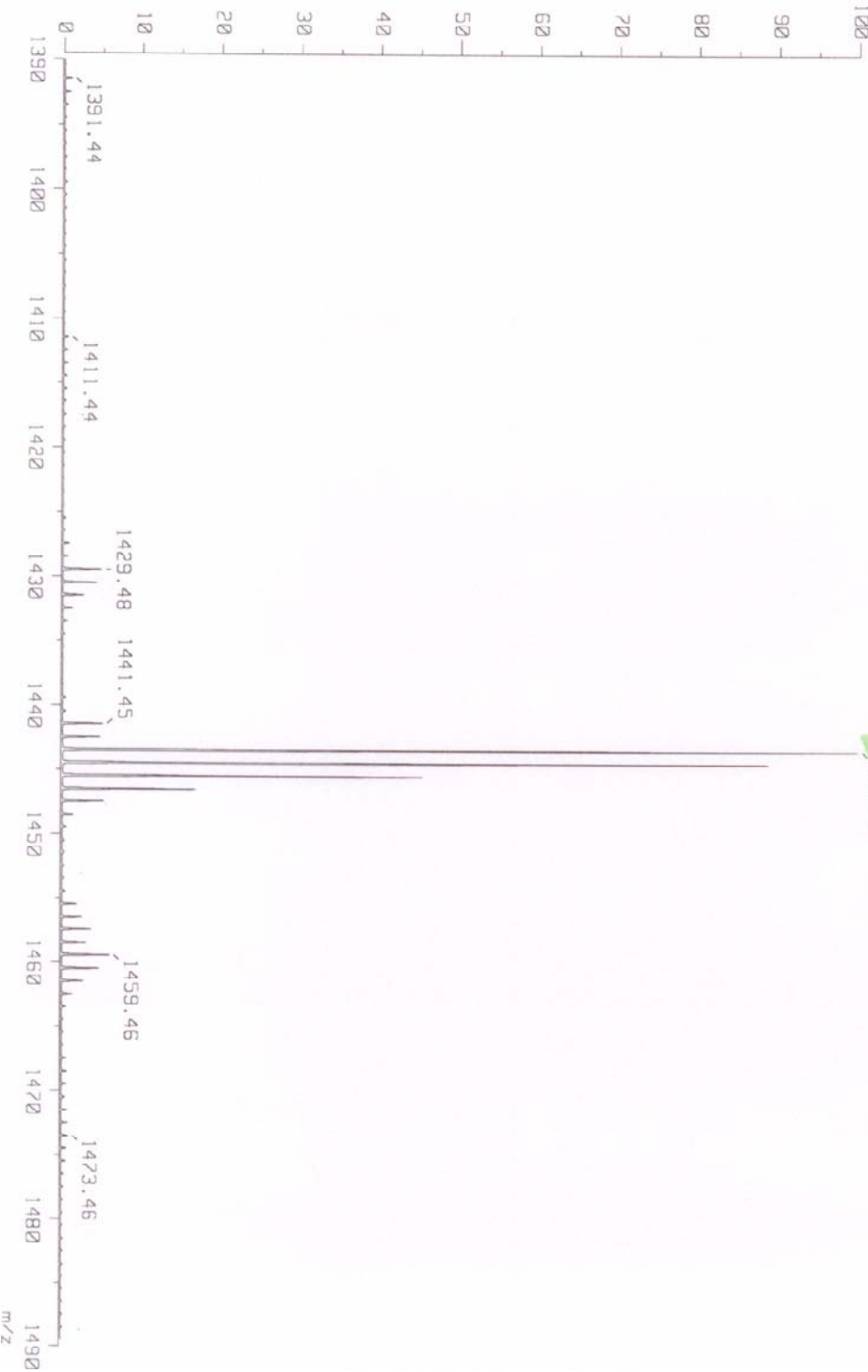
Spectrum Type: Normal Ion [EF-Linear]

RT: 1.06 min Scan#: (3,12)

BP: m/z 1443.4628 Int.: 415.62

Output m/z range: 1390.0000 to 1490.0000 Cut Level: 0.00 %

43581264



1514

02 AVR 2007

Current Data Parameters

NAME mayalic
EXNO 1
PROCNO 1

F2 - Acquisition Parameters

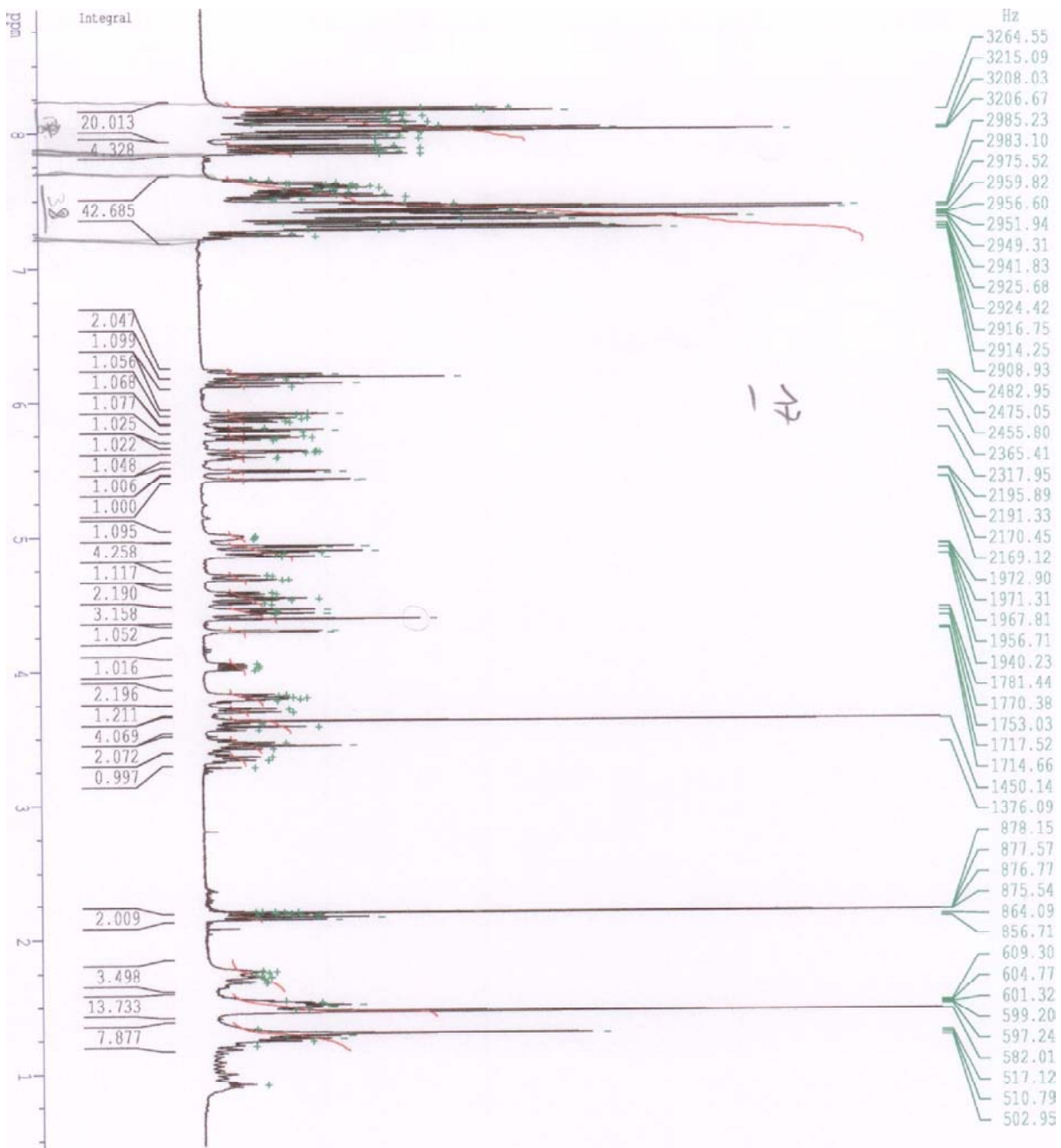
Date_ 500000
Time_ 20.30
INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 16
DS 2
SWH 4006.410 Hz
FIDRES 0.24552 Hz
AQ 2.041731 sec
RG 114
RW 124.800 usec
TE 4.50 usec
DE 340.0 K
D1 0.10000000 sec
P1 9.50 usec
DE 4.50 usec
SFO1 400.131206 MHz
NOC1 1H
PL1 -3.00 dB

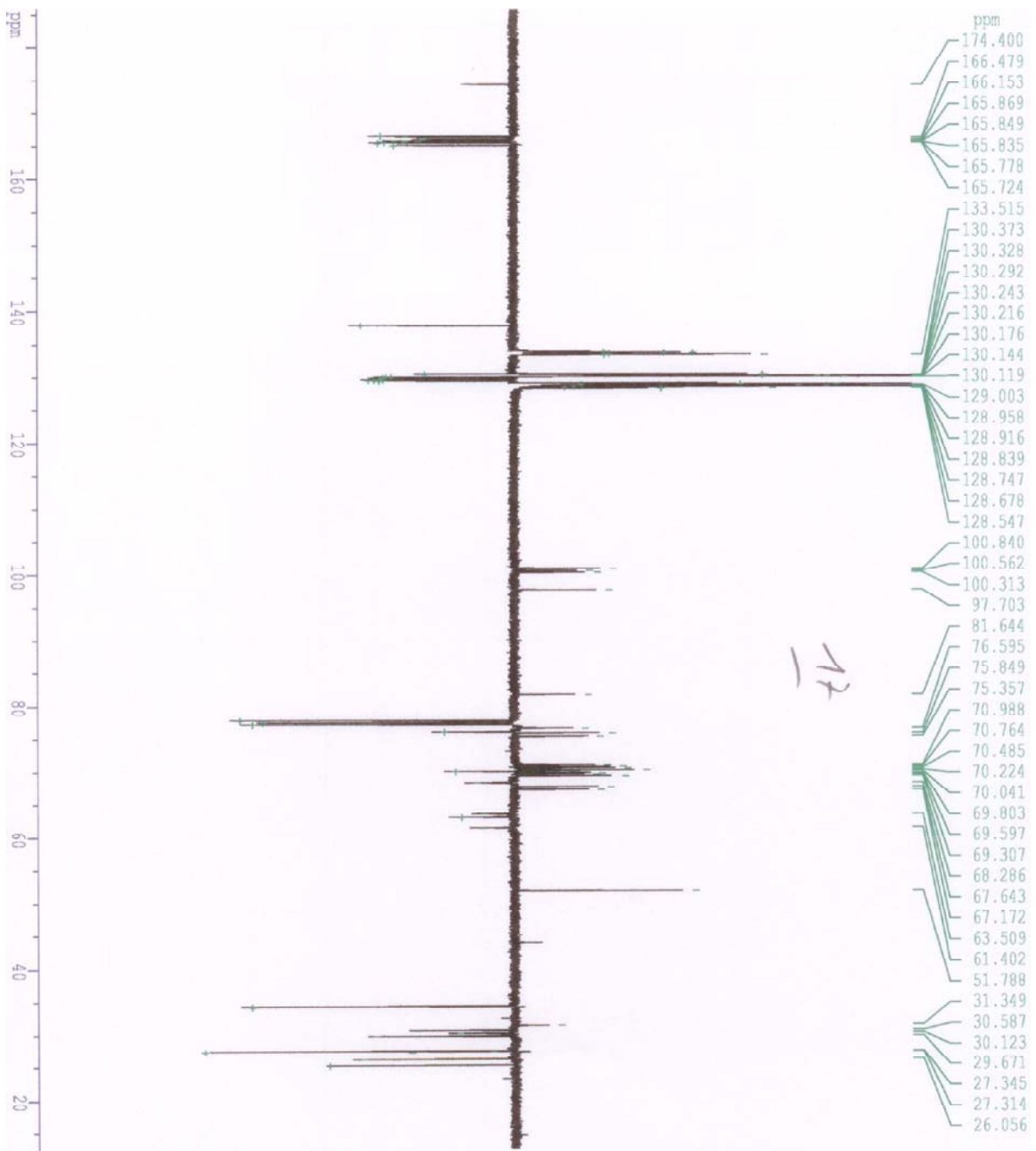
F2 - Processing Parameters

SI 16384
SF 400.130000 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 0.10

1D NMR plot parameters

CX 22.00 cm
F1P 8.917 ppm
F1 3567.85 Hz
F2P 0.451 ppm
F2 180.53 Hz
PPMCM 0.39480 ppm/cm
HZCM 153.95901 Hz/cm





ppm

174.400
166.479
166.153
165.869
165.849
165.835
165.778
165.724
133.515
130.373
130.328
130.292
130.243
130.216
130.176
130.144
130.119
129.003
128.958
128.916
128.839
128.747
128.678
128.547
100.840
100.562
100.313
97.703
81.644
76.595
75.849
75.357
70.988
70.764
70.485
70.224
70.041
69.803
69.597
69.307
68.286
67.643
67.172
63.509
61.402
51.788
31.349
30.587
30.123
29.671
27.345
27.314
26.056

Current Data Parameters

NAME mayenc
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

Date_ 5/00/00
Time 23.40

INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG jmod2.php
TD 65536
SOLVENT CDCl3
NS 4096
DS 4

SWH 24154.590 Hz
FIDRES 0.368510 Hz
AQ 1.3566452 sec
RG 5792.6
DW 20.700 usec
DE 4.50 usec
TE 300.0 K
F1 17.00 usec
P2 34.0 usec
DELTA 0.0000108 sec
D20 0.00714000 sec
F112 17.50 dB
D1 1.2993995 sec
COPPRG2 waltz16
F2P2 100.00 usec
F2P2 400.1317000 MHz
NUC2 1H
F12 120.00 dB
D13 0.0000300 sec
SFO1 100.6237964 MHz
NUC1 13C
P11 0.00 dB
DE 4.50 usec

F2 - Processing parameters

SI 65536
SF 100.6127290 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.30

1D NMR plot parameters

CX 22.00 cm
F1P 185.785 ppm
F1 13892.36 Hz
F2P 12.485 ppm
F2 1156.26 Hz
PPMCM 7.87723 ppm/cm
HZCM 792.54980 Hz/cm

03 AVR. 2007

[Mass Spectrum]

Data : COLLOT-MCS00-FRB+-NBR-Na-HR0 Date : 20-Apr-2007 16:15

Sample: -

Note: -

Inlet : Direct

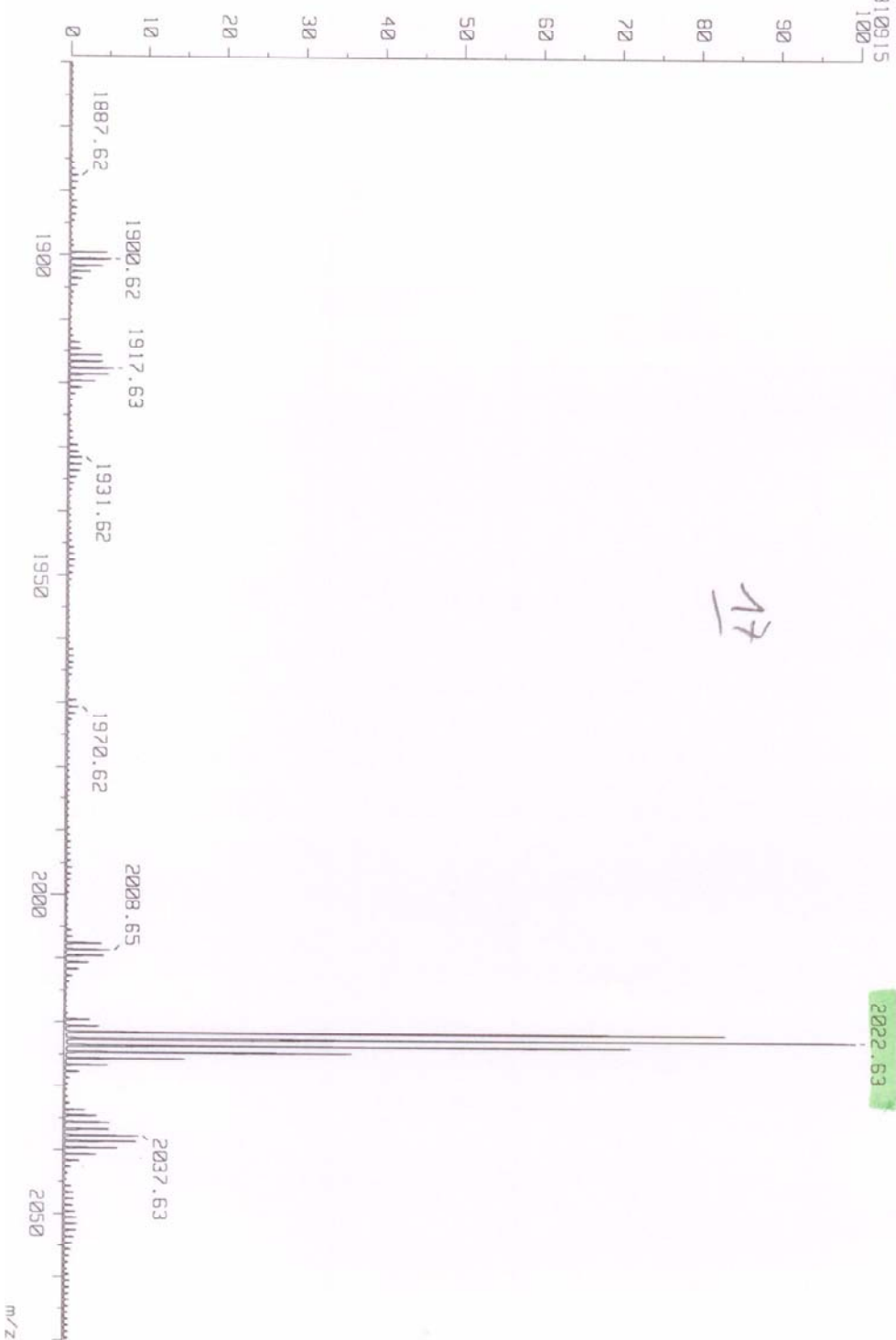
Ion Mode : FRB+

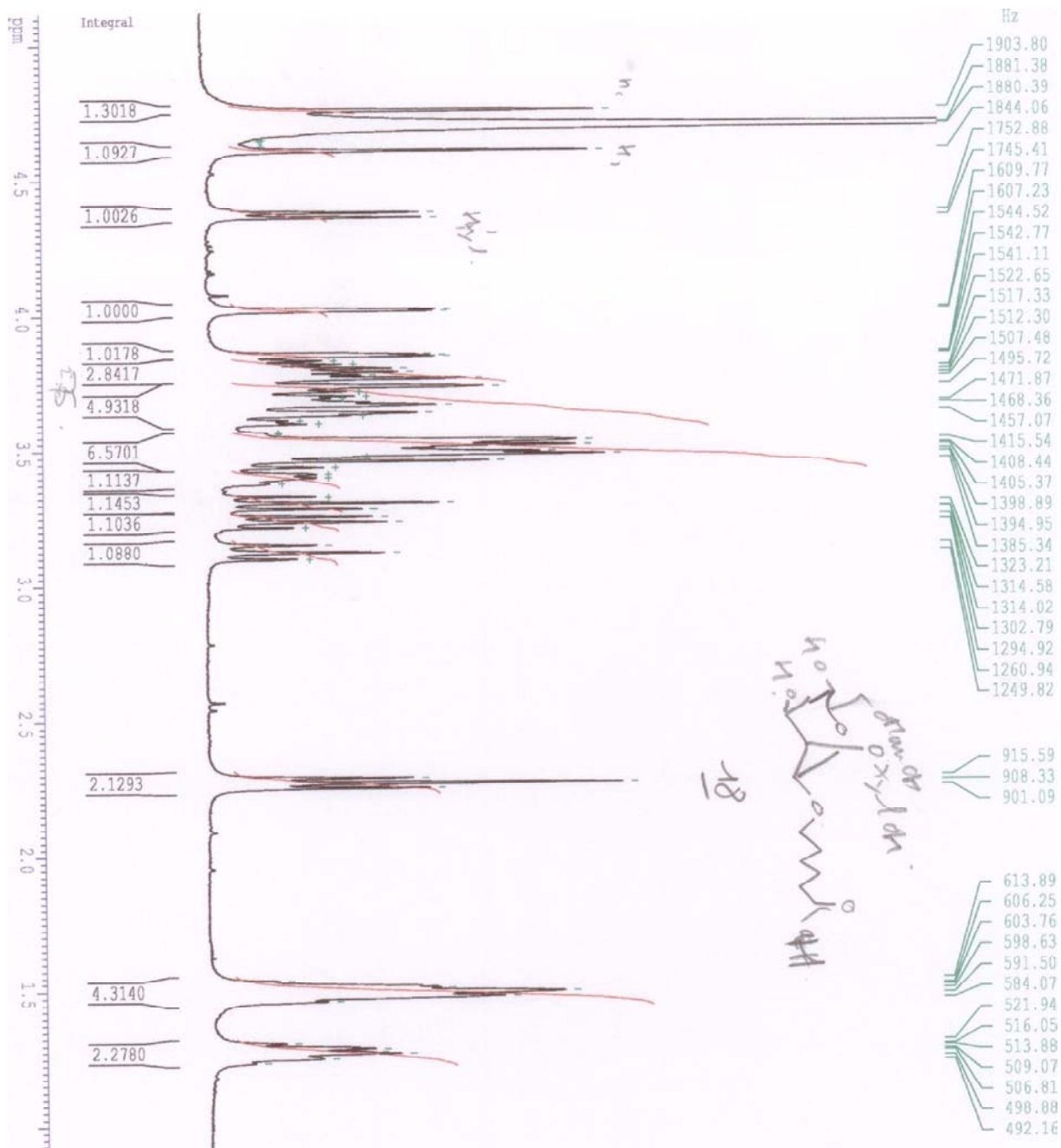
Spectrum Type : Normal Ion [EF-Linear]

RT : 5.41 min Scan# : (28, 32)

BP : m/z 2022.6267 Int. : 282.50

Output m/z range : 1870.0000 to 2070.0000 Cut Level : 0.00 %



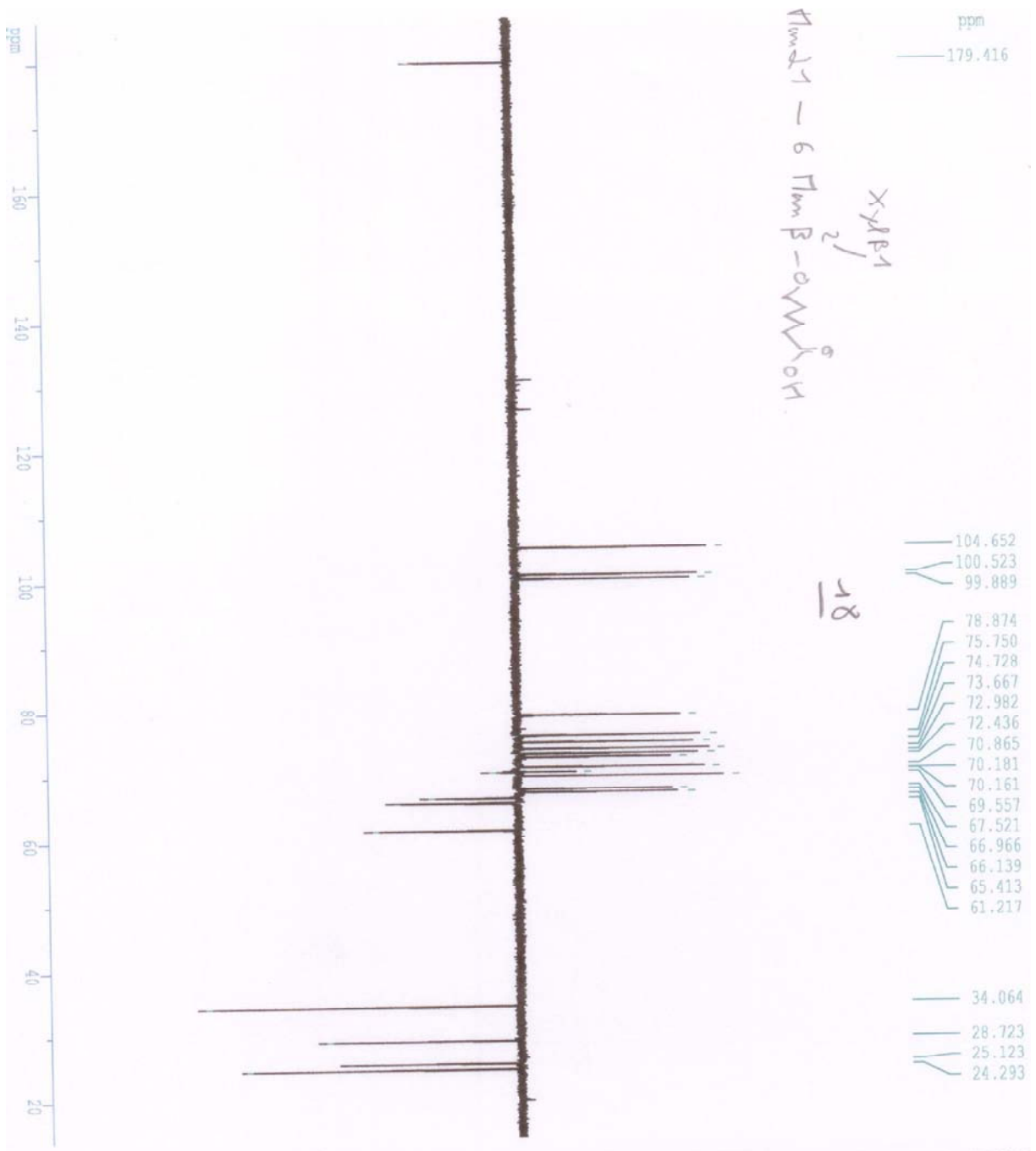


Current Data Parameters
NAME mayalic
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 50000
Time 21.40
INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 16
DS 2
SWH 4006.410 Hz
FIDRES 0.24532 Hz
AQ 2.044731 sec
RG 161.3
DE 124.800 usec
DWE 4.50 usec
TE 300.0 K
D1 0.10000000 sec
P1 9.50 usec
DE 4.50 usec
SFO1 400.131206 MHz
NUC1 1H
P11 -3.00 dB

F2 - Processing parameters
SI 16384
SF 400.130000 MHz
WDW EN
SSB 0
LB 0.00 Hz
GB 0
PC 0.10

1D NMR plot parameters
CX 22.00 cm
FIP 5.120 ppm
F1 2048.86 Hz
F2 0.921 ppm
F2 368.47 Hz
PFGMCH 0.13089 ppm/cm
HZCM 76.38148 Hz/cm



Current Data Parameters

NAME	mayalic
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	500000
Time	22.00
INSTRUM	spect
PROBHD	5 mm 1H/13C
PULPROG	jmod2.php
TD	65536
SOLVENT	CDCl3
NS	8192
DS	4
SWH	24154.590 Hz
FIDRES	0.368570 Hz
AQ	1.356452 sec
RG	7298.2
DM	20.700 usec
DE	4.50 usec
TE	300.0 K
P1	26.50 usec
DELTA	0.000169 sec
D2	0.0071400 sec
P2	17.50 dB
D1	1.2999995 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SEF02	400.131700 MHz
NUC02	1H
P12	120.00 dB
D13	0.0000360 sec
SEF01	100.6231964 MHz
NUC01	13C
P11	0.00 dB
P2	53.00 usec
DE	4.50 usec

F2 - Processing parameters

SF	65536
SE	100.6127290 MHz
WDM	EN
SSB	0
LB	0.30 Hz
GB	0
PC	0.30

1D NMR plot parameters

CH	22.06 cm
F1P	186.389 ppm
F1	18753.04 Hz
F2P	13.771 ppm
F2	1385.51 Hz
PPMCK	7.84628 ppm/cm
HZCM	789.43583 Hz/cm

[Mass Spectrum]

Data : COLLECT-MC455-CI-NH3-HR003

Date : 06-Feb-2007 12:05

Sample: -

Note: -

Inlet : Direct

Ion Mode : DCI+

Spectrum Type : Normal Ion [EF-Linear]

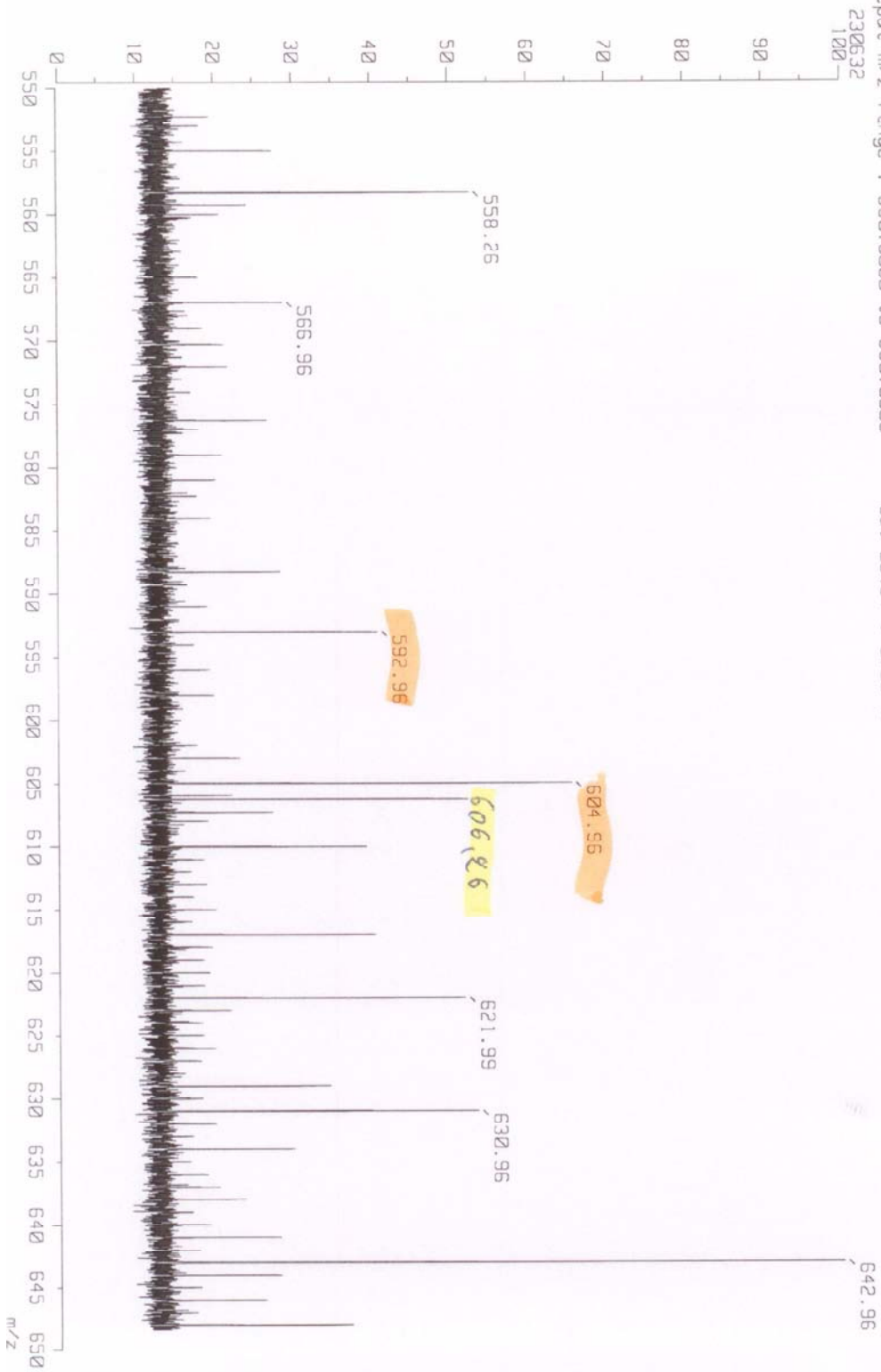
RT : 1.47 min Scan# : (2,29)

BP : m/z 642.9554 Int. : 0.79

Output m/z range : 550.0000 to 650.0000

Cut Level : 0.00 %

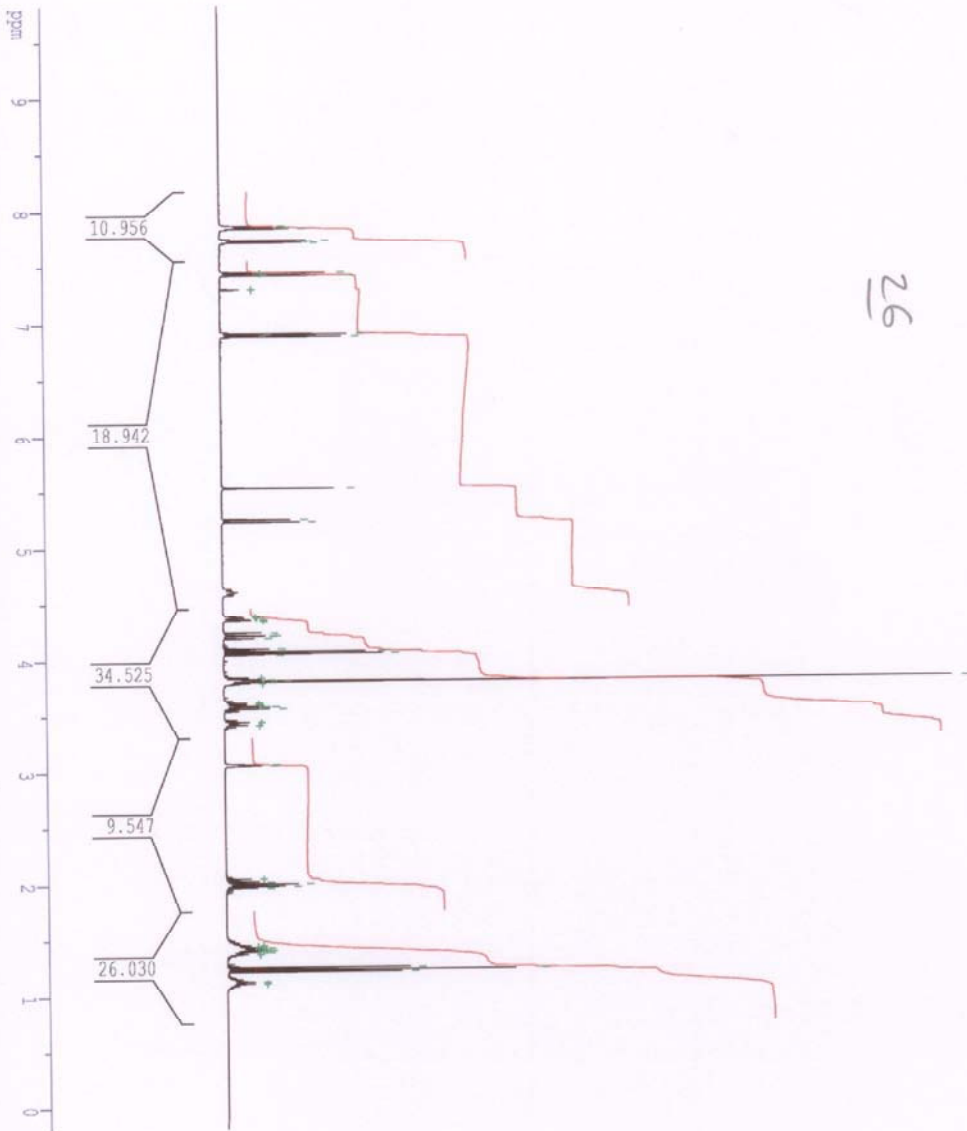
18



Hz

3146.23
3143.12
3140.65
3137.69
3094.80
3091.71
3089.29
3086.27
2978.52
2971.76
2969.75
2762.57
2760.56
2755.81
2753.78
2212.08
2098.97
2090.52
1737.88
1695.49
1687.03
1685.02
1676.46
1638.21
1631.18
1623.97
1616.86
1529.55
1526.01
1524.65
1519.79
1433.81
1432.16
1425.24
1223.92
1220.12
806.28
798.92
791.07
784.08
572.01
563.18
556.64
554.83
499.10
491.94
484.87
449.25

26



- 4 MAY 2006

Current Data Parameters
NAME mayu1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

Date_ 5/01/00
Time 13:02
INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG zgpg30
TD 16384
SOLVENT CDCl3
NS 64
DS 0
SWH 4006.410 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 57
IN 124.800 usec
DE 4.50 usec
TE 300.0 K
D1 0.10000000 sec
P1 9.50 usec
DE 4.50 usec
SFO1 400.131206 MHz
WFO1 1H
P11 -1.00 dB

F2 - Processing parameters

SI 4192
SF 400.1291930 MHz
WDW GN
SSB 0
LB -0.30 Hz
GB 0.3
PC 1.10

1D NMR plot parameters

CX 22.00 cm
F1p 10.500 ppm
F1 4201.37 Hz
F2p -0.500 ppm
F2 -200.07 Hz
FPCX 0.50000 ppm/cm
HZCN 200.06500 Hz/cm

Integral

ppm

180 160 140 120 100 80 60 40 20 0



Current Data Parameters
NAME mayenlic
EXPNO 2
PROCNO 4
F400 2006

F2 - Acquisition Parameters

Date 500000

Time 13.08

INSTRUM spect

PROBHD 5 mm 1H/13C

PULPROG 1mod

TD 65536

SOLVENT CDCl3

NS 320

DS 0

SMH 24154.590 Hz

FIDRES 0.368370 Hz

AQ 1.3564452 sec

RG 9195.2

DM 20.700 usec

DE 4.50 usec

TE 300.0 K

PI 16.00 usec

DELTA 0.0000204 sec

D20 0.00714000 sec

PL12 17.50 dB

D1 1.2999995 sec

CPDPRG2 waltz16

PCPD2 100.00 usec

SFO2 400.1317000 MHz

NUC2 1H

PL2 120.00 dB

D13 0.0000300 sec

P2 32.00 usec

SFO1 100.6237964 MHz

NUC1 13C

PL1 0.00 dB

DE 4.50 usec

F2 - Processing parameters

SI 32768

SF 100.6127822 MHz

WVM BK

SSB 0

LB 1.00 Hz

GB 0

PC 0.50

1D NMR plot parameters

CX 22.00 cm

F1P 210.000 ppm

F1 21128.49 Hz

F2P -10.000 ppm

F2 -1006.13 Hz

PPMCK 10.00000 ppm/cm

HZCM 1006.12787 Hz/cm

[Mass Spectrum]

Data : COLLOT-MC325-CI+-NH3-HR

Date : 09-May-2006 16:49

Sample : -

Note : -

Inlet : Direct

Ion Mode : DCI+

Spectrum Type : Normal Ion [EF-Linear]

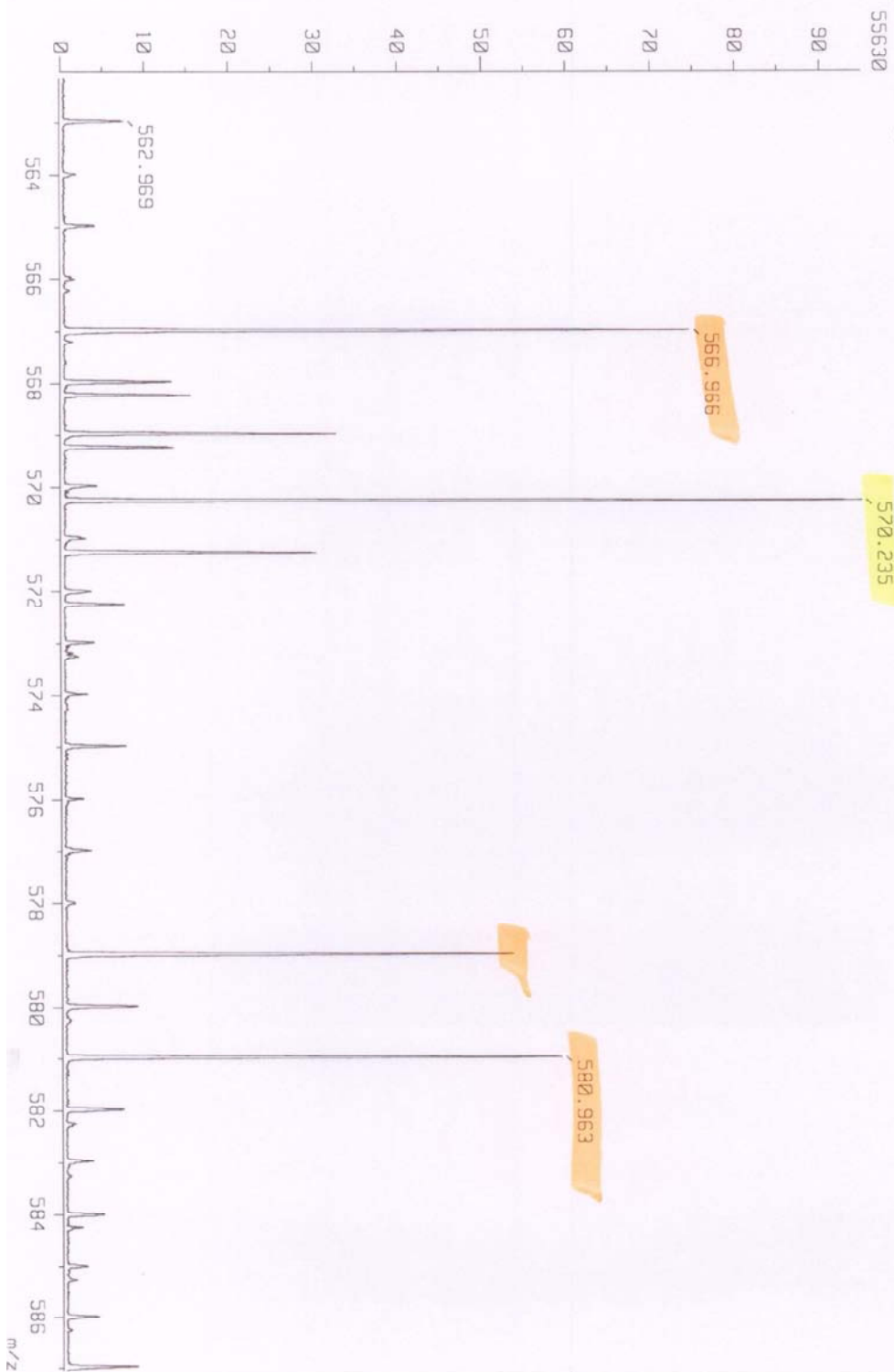
RT : 1.77 min Scan# : (17, 19)

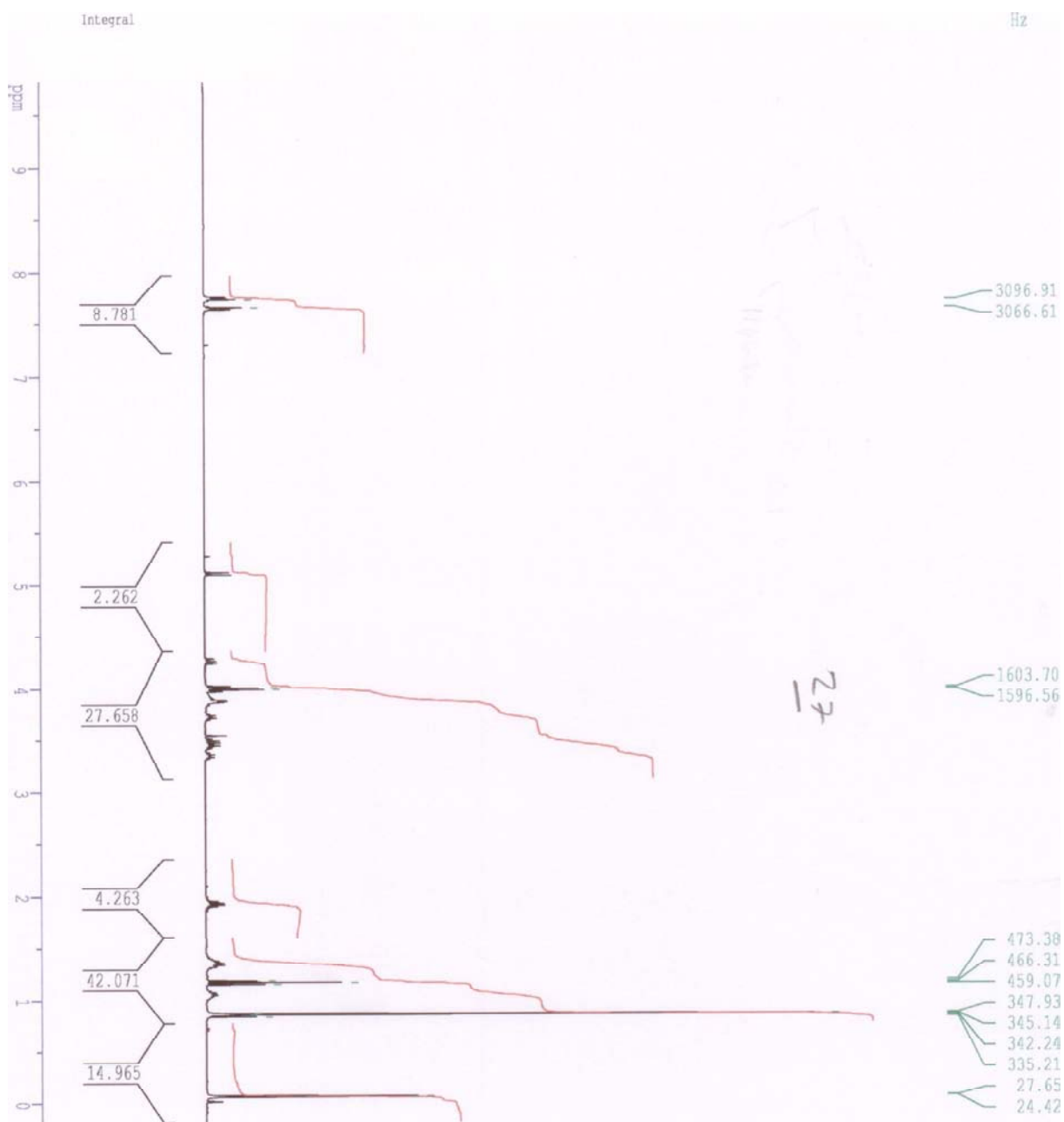
BP : m/z 530.9665 Int. : 1.86

Output m/z range : 552.1355 to 587.0623

Cut Level : 0.00 %

26





- 9 FEB. 2006

Current Data Parameters

NAME mayul

EXNO 2

PROCNO 1

F2 - Acquisition Parameters

Date_ 500000

Time_ 10.25

INSTRUM spect

PROBHD 5 mm 1H/13C

PULPROG zg30

TD 16384

SOLVENT CDCl3

NS 64

DS 0

SWH 4006.410 Hz

FIDRES 0.244532 Hz

AQ 2.0447731 sec

RG 16

TM 124.800 usec

DE 4.50 usec

TE 300.0 K

D1 0.10000000 sec

P1 9.50 usec

DE 4.50 usec

SFO1 400.1319206 MHz

NUC1 1H

PC 3.00 dB

F2 - Processing parameters

SI 8192

SR 400.129925 MHz

WWM CW

SSB 0

IS -0.30 Hz

GB 0.3

PC 0.10

1D NMR plot parameters

CK 22.00 cm

FLP 10.500 ppm

E1 4201.37 Hz

F2P -0.500 ppm

F2 -200.07 Hz

PRMCM 0.50000 ppm/cm

HCN 200.06500 Hz/cm



Current Data Parameters

NAME	VALUE	UNIT
NAME	mayalic	
EXPNO	2	
PROCNO	1	

F2 - Acquisition Parameters

Parameter	Value	Unit
Date_	500000	
Time	10.31	
INSTRUM	spect	
PROBHD	5 mm 1H/13C	
PULPROG	zgpg30	
TD	65536	
SOLVENT	CDCl3	
NS	168	
DS	0	
SF	24154.590	Hz
FIDRES	0.36870	Hz
AQ	1.356452	sec
RG	919.12	
DM	20.700	usec
DE	4.50	usec
TE	300.0	K
P1	16.00	usec
DELTA	0.0000204	sec
D20	0.00714000	sec
P112	17.50	dB
D1	1.2399995	sec
CEPREP2	wait16	
PCPD2	100.00	usec
SF02	400.131000	MHz
NUC2	1H	
P12	120.00	dB
D13	0.0000300	sec
P2	32.00	usec
SF01	100.6237864	MHz
NUC1	13C	
P11	0.00	dB
D8	4.50	usec

F2 - Processing Parameters

Parameter	Value	Unit
SI	32768	
SF	100.6237864	MHz
WDM	EX	
SSB	0	
IB	1.00	Hz
GB	0	
PC	0.50	

1D NMR plot parameters

Parameter	Value	Unit
CX	22.00	cm
F1P	210.000	ppm
F1	21128.69	Hz
F2P	-13.000	ppm
F2	-1006.13	Hz
PPM04	10.00000	ppm/cm
HZCM	1006.12787	Hz/cm

ppm

173.418
168.137

133.818
131.435
123.117

97.851

27

77.322
77.003
76.684
74.694
73.587
71.379
68.885
64.053
59.946
56.243
51.205

33.792
33.511
28.724
25.655
25.443
25.115
24.191
18.044
13.984

-5.542
-5.565

[Mass Spectrum]

Date : MARYEL-MC256A-CI-NH3-HR002 Date : 09-Feb-2006 10:51

Sample : -

Note : -

Inlet : Direct Ion Mode : DCI+

Spectrum Type : Normal Ion [FF-Linear]

RT : 8.03 min Scan# : (58, 88)

BP : m/z 583.3058 Int. : 6.28

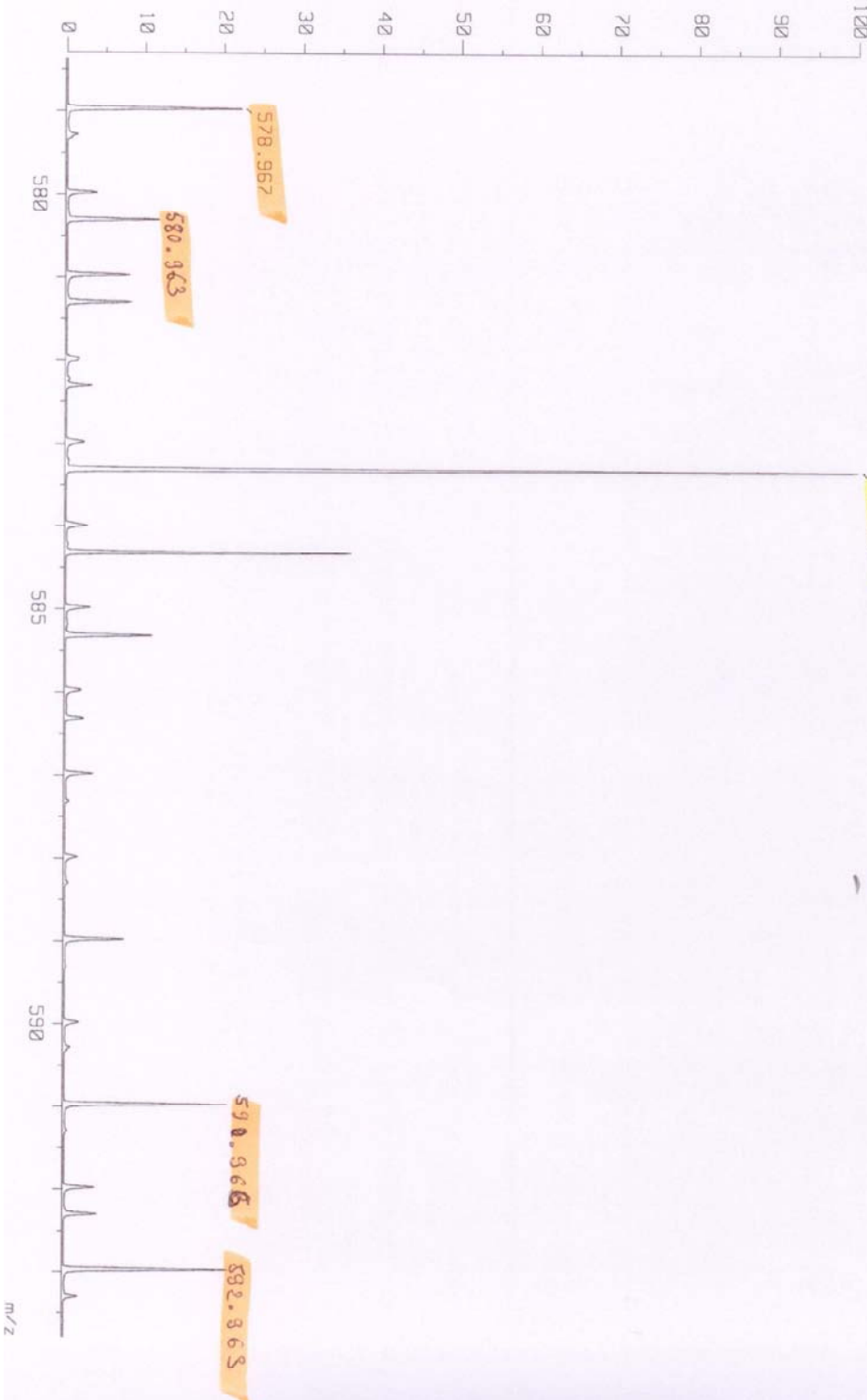
Output m/z range : 578.3680 to 593.7982

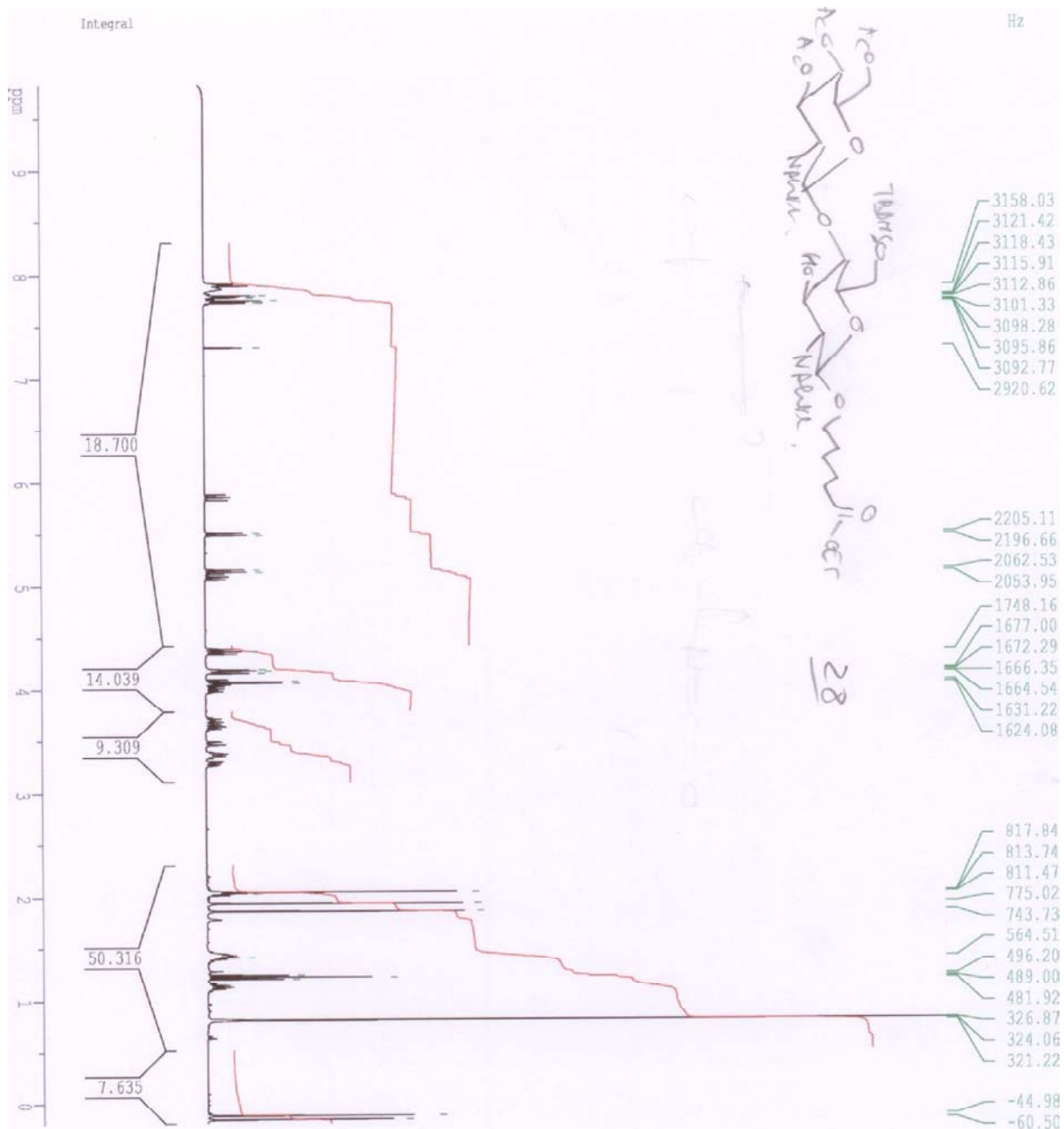
1383537

Cut Level : 0.00 %

583.306

27





17 FEB. 2006

Current Data Parameters
NAME maye1
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters

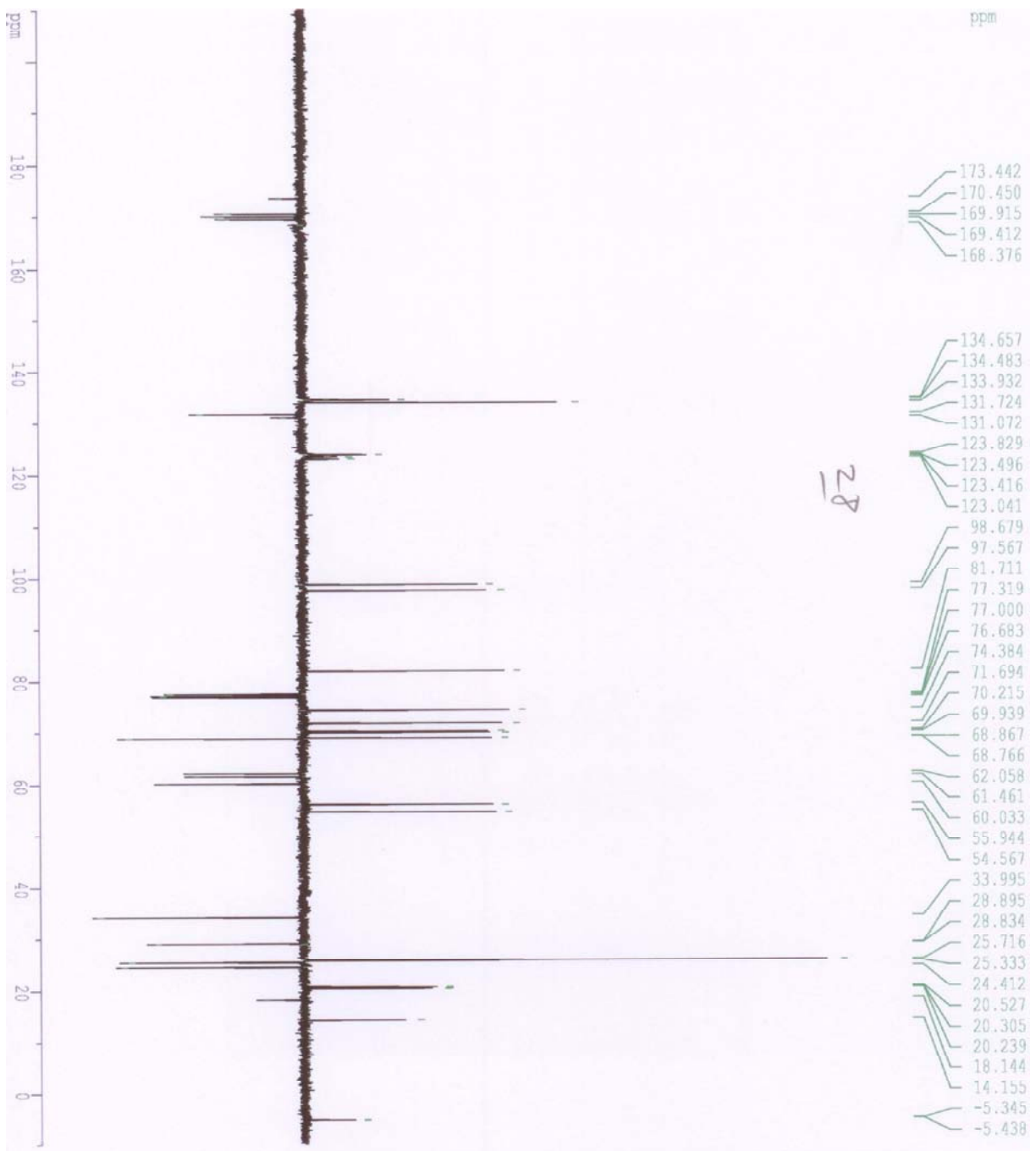
Date_ 5/0/00
Time_ 11.01
INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 80
DS 0
SWH 4005.410 Hz
FIDRES 0.244532 Hz
AQ 2.041731 sec
RG 90.5
DM 124.800 usec
DE 4.50 usec
TE 300.0 K
D1 0.10000000 sec
P1 9.50 usec
DE 4.50 usec
SFO1 400.1319206 MHz
NUC1 1H
P11 -3.00 dB

F2 - Processing parameters

SI 8192
SF 400.129935 MHz
WDW GM
SSB 0
LB -0.30 Hz
GB 0.3
PC 0.10

1D NMR plot parameters

CX 22.00 cm
FLP 10.500 ppm
F1 4201.37 Hz
F2P -0.500 ppm
F2 -200.07 Hz
FREQC 0.50000 ppm/cm
H2CM 200.06500 Hz/cm



173.442
170.450
169.915
169.412
168.376

134.657
134.483
133.932
131.724
131.072
123.829
123.496
123.416
123.041
98.679
97.567
81.711
77.319
77.000
76.683
74.384
71.694
70.215
69.939
68.867
68.766
62.058
61.461
60.033
55.944
54.567
33.995
28.895
28.834
25.716
25.333
24.412
20.527
20.305
20.239
18.144
14.155
-5.345
-5.438

Current Data Parameters
NAME Mayalic
EXPNO 2
PROCNO 17
17 FEB, 2016

F2 - Acquisition Parameters
Date_ 500000
Time 11.07

INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 448
DS 0

SMH 24154.596 Hz
FIDRES 0.368376 Hz
AQ 1.356452 sec
RG 9195.2

DM 20.700 usec
DE 4.50 usec
TE 300.0 K
PI 16.00 usec

DELTA 0.0010204 sec
D20 0.00714000 sec
P1.2 17.50 dB
D1 1.2995995 sec

CPDPRG2 waltz16
PCPD2 100.00 usec
SFO2 400.1317003 MHz
NUC2 13

P1.2 120.00 dB
D1.3 0.0000300 sec
P2 32.00 usec
SFO1 100.6271964 MHz

NUC1 13C
P1.1 0.00 dB
DE 4.50 usec

F2 - Processing parameters
SI 32768
SF 100.6127749 MHz
WDW EM
SSB 0

LB 1.00 Hz
GB 0
PC 0.50

1D NMR plot parameters
CX 22.00 cm
EIP 210.000 ppm
F1 21128.48 Hz
F2 -1006.13 Hz

PERCK 10.00000 ppm/cm
HCCM 1006.12761 Hz/cm

[Mass Spectrum]

Data : MRYELL-MC260R-FRB+-NBP+NaI-H Date : 03-Mar-2006 15:00

Sample: -

Note: -

Inlet: Direct Ion Mode: FRB+

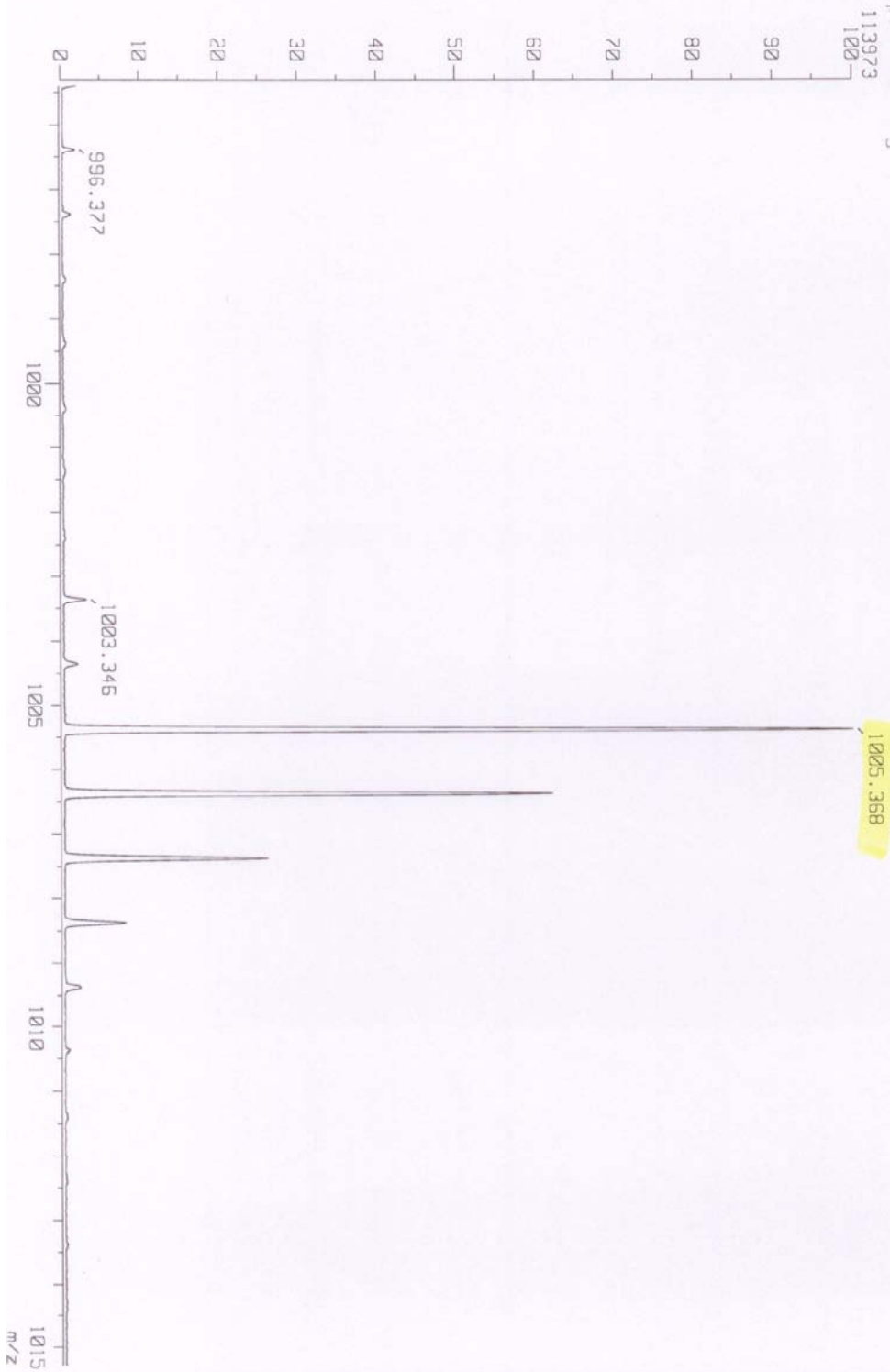
Spectrum Type: Normal Ion [FF-Linear]

RT: 19.20 min Scan#: (156,171)

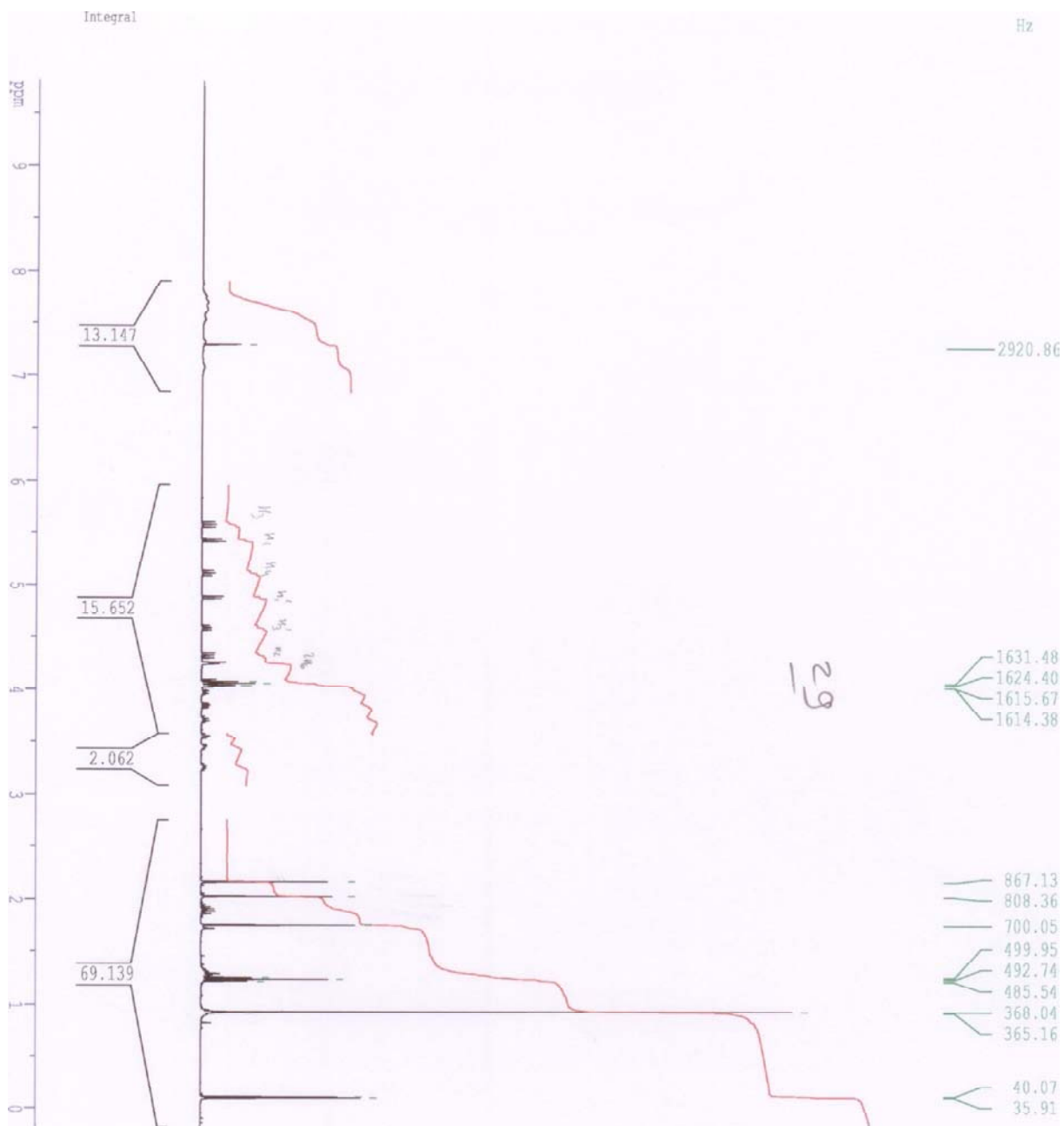
BP: m/z 1005.3679 Int.: 0.68

Output m/z range: 995.4006 to 1015.2819

Cut Level: 0.00 %



28



18 FEB. 2006

Current Data Parameters
NAME mayell
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters

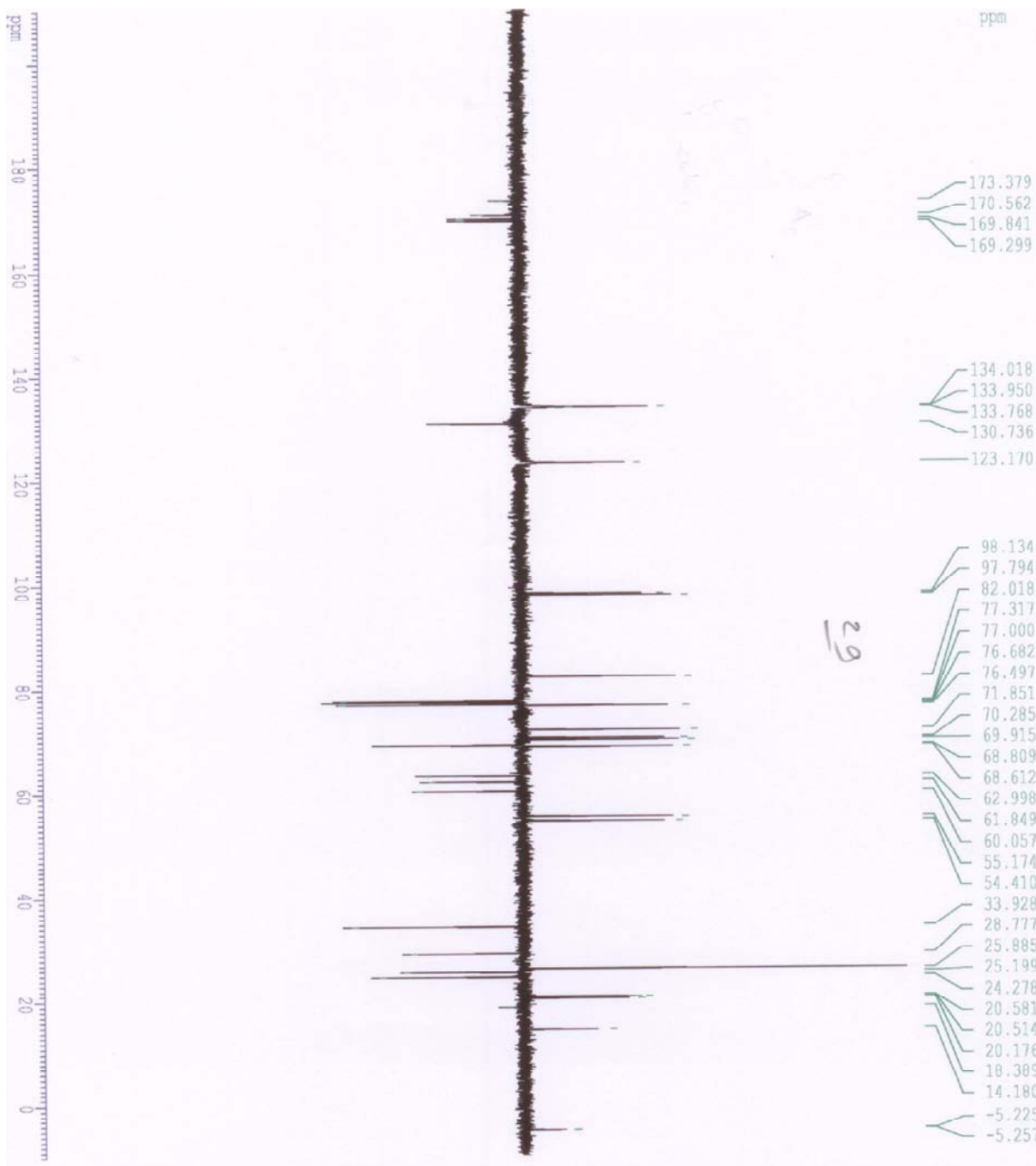
Date_ 500000
Time 12.33
INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 64
DS 0
SWH 4006.410 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 161.3
CW 124.800 usec
DE 4.50 usec
TE 300.0 K
D1 0.10000000 sec
P1 9.50 usec
DE 4.50 usec
SFO1 400.1319206 MHz
NUC1 1H
PL1 -3.00 dB

F2 - Processing parameters

SI 8192
SF 400.1299935 MHz
WDW GM
SSB 0
LB -0.30 Hz
GB 0.3
PC 0.01

1D NMR plot parameters

CX 22.00 cm
F1P 10.500 ppm
F1 4201.37 Hz
F2P -0.560 ppm
F2 -200.07 Hz
PPMCM 0.50000 ppm/cm
HZCM 200.06500 Hz/cm



173.379
170.562
169.841
169.299

134.018
133.950
133.768
130.736
123.170

98.134
97.794
82.018
77.317
77.000
76.682
76.497
71.851
70.285
69.915
68.809
68.612
62.998
61.849
60.057
55.174
54.410
33.928
28.777
25.885
25.199
24.278
20.581
20.514
20.176
18.389
14.180
-5.225
-5.257

29

Current Data Parameters
NAME mayalic
EXPNO 3
PROCNO 8
8 FEB. 2008

F2 - Acquisition Parameters
Date_ 500000
Time_ 11.38

INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG tmod
TD 6536
SOLVENT CDCl3
NS 368
DS 0

SWH 2415.590 Hz
FIDRES 0.36570 Hz
AQ 1.356452 sec
RG 9135.2
IM 20.700 usec
DE 4.50 usec
TE 300.0 K

PI 16.00 usec
DELTA 0.000024 sec
D20 0.00714000 sec
P112 17.50 dB
D1 1.2999995 sec

CPDPRG2 waltz16
PCPD2 109.00 usec
SFO2 400.1317000 MHz
NUC2 1H
P12 129.00 dB

D13 0.0000300 sec
P2 32.00 usec
SFO1 100.6237964 MHz
NUC1 13C
P11 0.00 dB

DE 4.50 usec
F2 - Processing parameters
SI 32768
SF 100.6127734 MHz
WIM EN
SSB 0
LB 1.00 Hz
GB 0
PC 0.10

1D NMR plot parameters
CX 22.00 cm
FIP 216.000 ppm
F1 2118.83 Hz
F2P -16.000 ppm
F2 -1006.13 Hz
PMCK 10.00003 ppm/cm
HZCM 1006.12769 Hz/cm

[Mass Spectrum]

Data : MRYEUL-MC260B-FRB+-NBr+NaI-H Date : 03-Mar-2006 16:13

Sample : -

Note : -

Inlet : Direct

Ion Mode : FRB+

Spectrum Type : Normal Ion [E⁻-Linear]

RT : 1.24 min Scan# : (7,16)

BP : m/z 1005.3672 Int. : 2.19

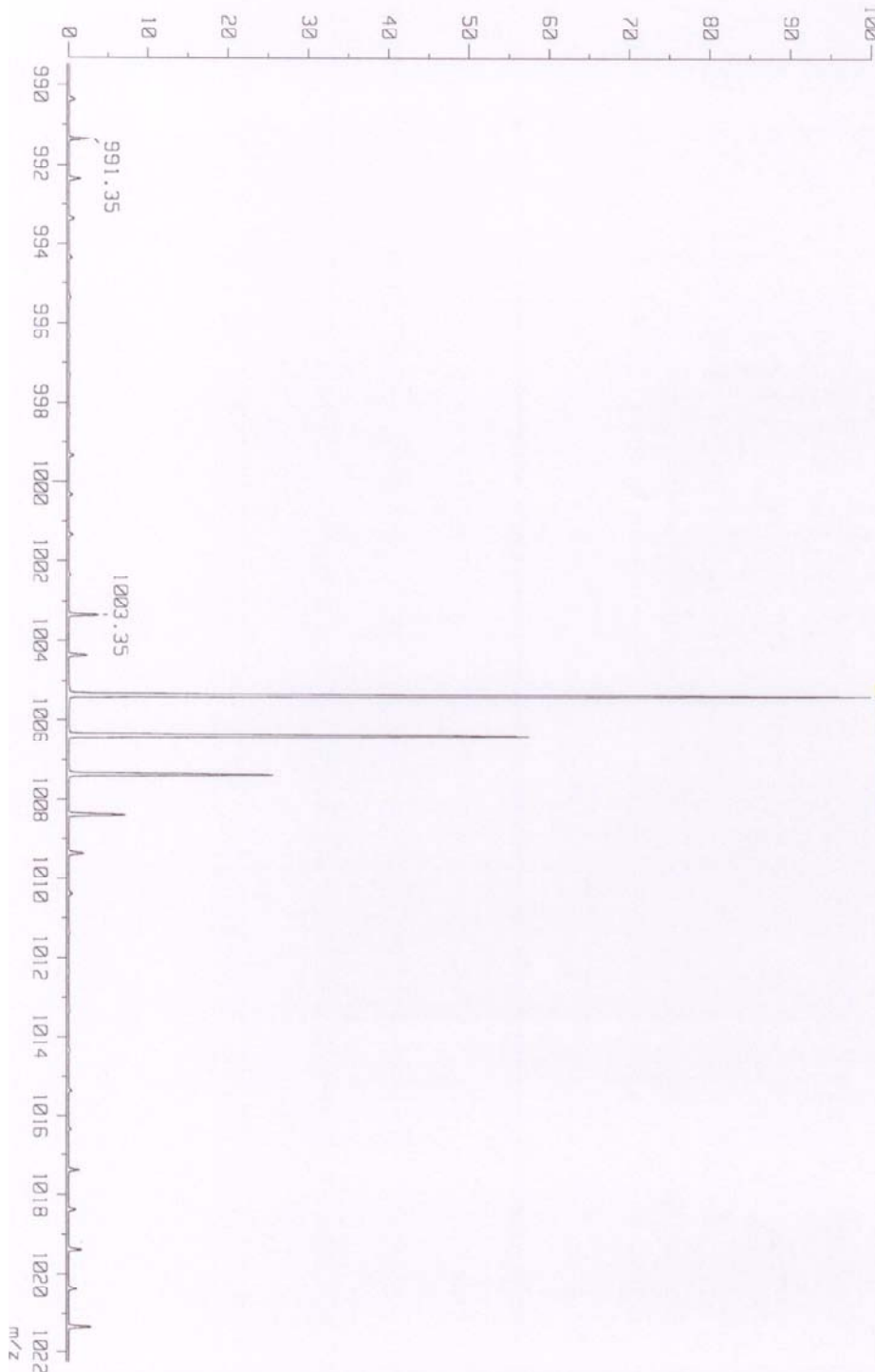
Output m/z range : 989.4659 to 1022.2552

Cut Level : 0.00 %

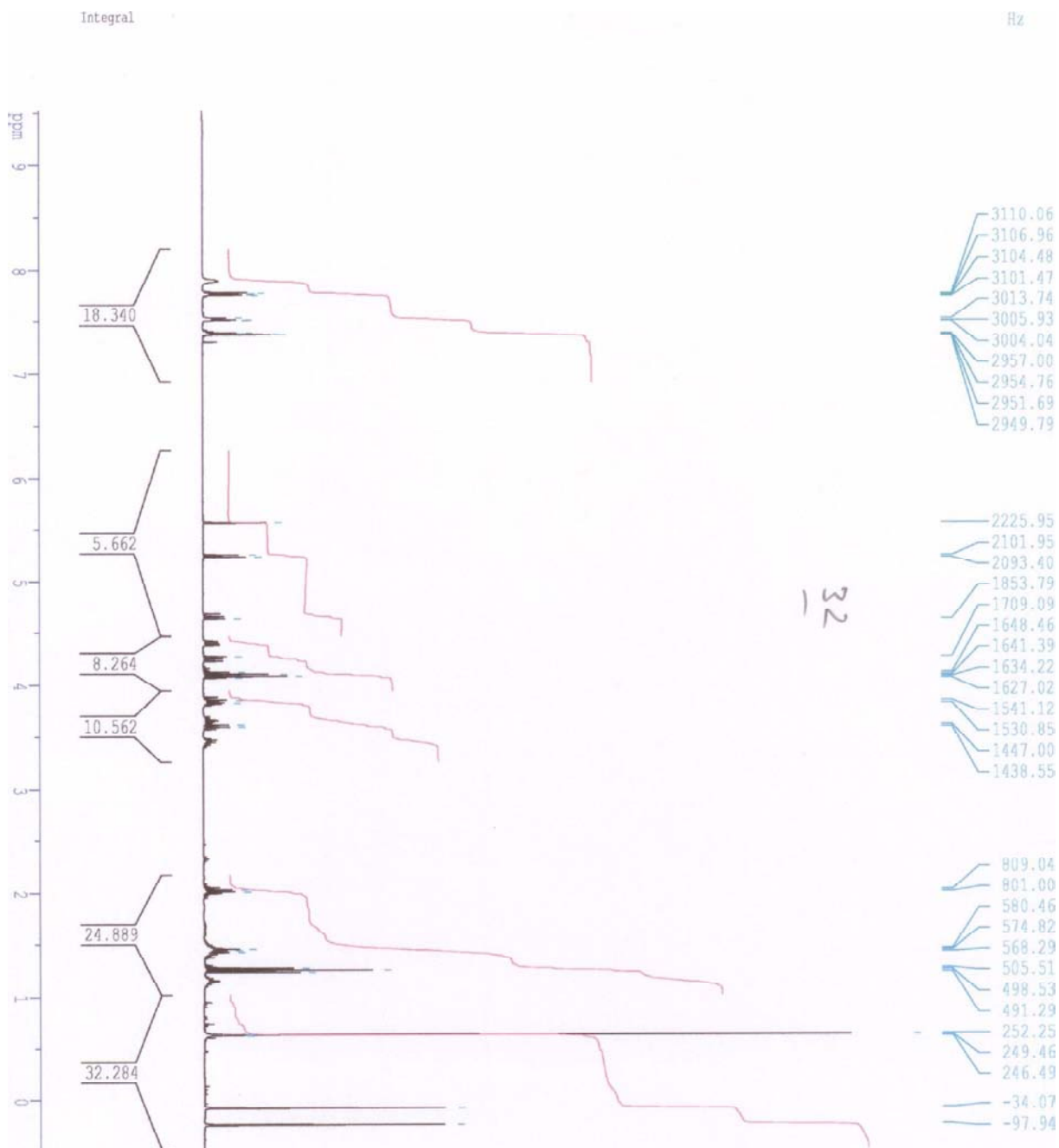
229597

100

1005.37



29



20 JUL. 2006

Current Data Parameters

NAME	EXPNO	PROCNO
mayeul	3	1

F2 - Acquisition Parameters

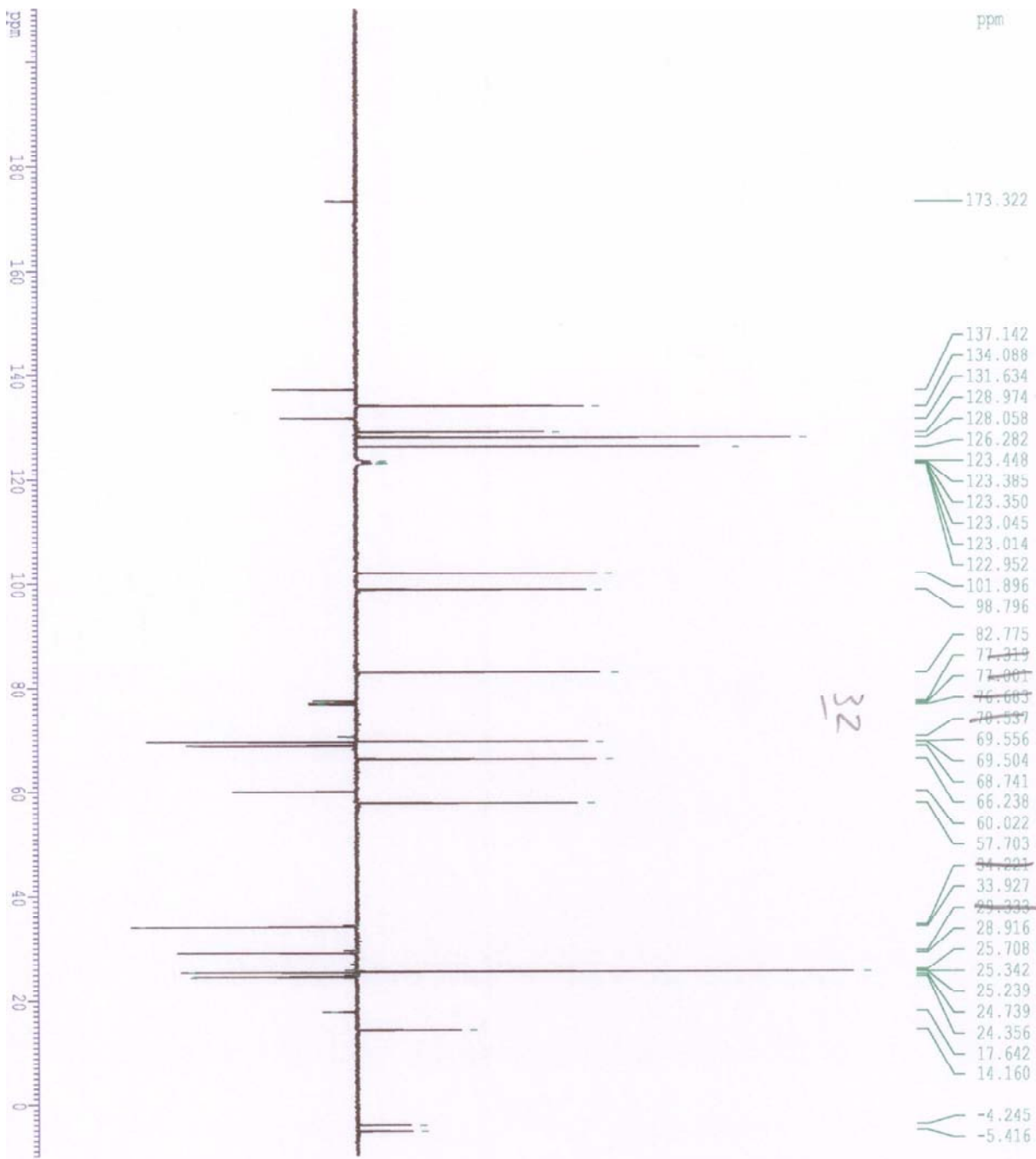
Date_	Time	INSTRUM	PROBHD	PULPROG	TD	SOLVENT	NS	DS	SWH	FIDRES	AQ	RG	DW	DE	TE	D1	P1	DE	SEF01	MDC1	PL1
500000	11.43	spec	5 mm 1H/13C	zg30	16384	CDCl3	80	0	4006.410 Hz	0.24532 Hz	2.0447731 sec	57	124.800 usec	4.50 usec	300.0 K	0.10000000 sec	9.50 usec	4.50 usec	400.1318006 MHz	1H	-3.00 dB

F2 - Processing parameters

SI	SF	WDW	SSB	LB	GB	PC
8152	400.129932 MHz	GM	0	-0.30 Hz	0.3	0.01

1D NMR plot parameters

CX	F1P	F1	F2P	F2	P2KCM	HZCN
22.00 cm	10.500 ppm	4201.37 Hz	-0.500 ppm	-200.07 Hz	0.50000 ppm/cm	200.06500 Hz/cm



Current Data Parameters
 NAME mayalic
 EXNO 3
 PROCMO 20 JUL 2006

F2 - Acquisition Parameters
 Date_ 5/0/00
 Time 11.48

INSTRUM spect
 PROBED 5 mm 1H/13C
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 704
 DS 0
 SWH 24154.590 Hz
 FIDRES 0.38870 Hz
 AQ 1.356452 sec
 RG 9195.2
 DW 20.700 usec
 DE 4.50 usec
 TE 300.0 K

DELTA 16.00 usec
 D20 0.0014000 sec
 D12 17.50 dB
 D1 1.2999995 sec
 CPDPRG2 waltz16
 PCPD2 100.00 usec
 SEQ2 400.1317000 MHz
 NUC2 1H
 PL2 120.00 dB
 D13 0.00000300 sec
 F2 32.00 usec
 SFO1 100.6237964 MHz
 NUC1 13C
 F1 13C
 FILL 0.00 dB
 IE 4.50 usec

F2 - Processing Parameters
 SI 32768
 SE 100.6127763 MHz
 WCN EX
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 0.30

1D NMR plot parameters
 CX 22.00 cm
 F1P 210.000 ppm
 F1 21128.68 Hz
 F2P -10.000 ppm
 F2 -1006.13 Hz
 PPMCM 10.00000 ppm/cm
 HZCM 1006.12781 Hz/cm

[Mass Spectrum]

Data : MRYELL-MC384-CI+-NH3-HR201 Date : 20-Jul-2006 11:29

Sample: -

Note: -

Inlet : Direct Ion Mode : DCI+

Spectrum Type : Normal Ion [EF-Linear]

RT : 5.37 min Scan# : (57,60)

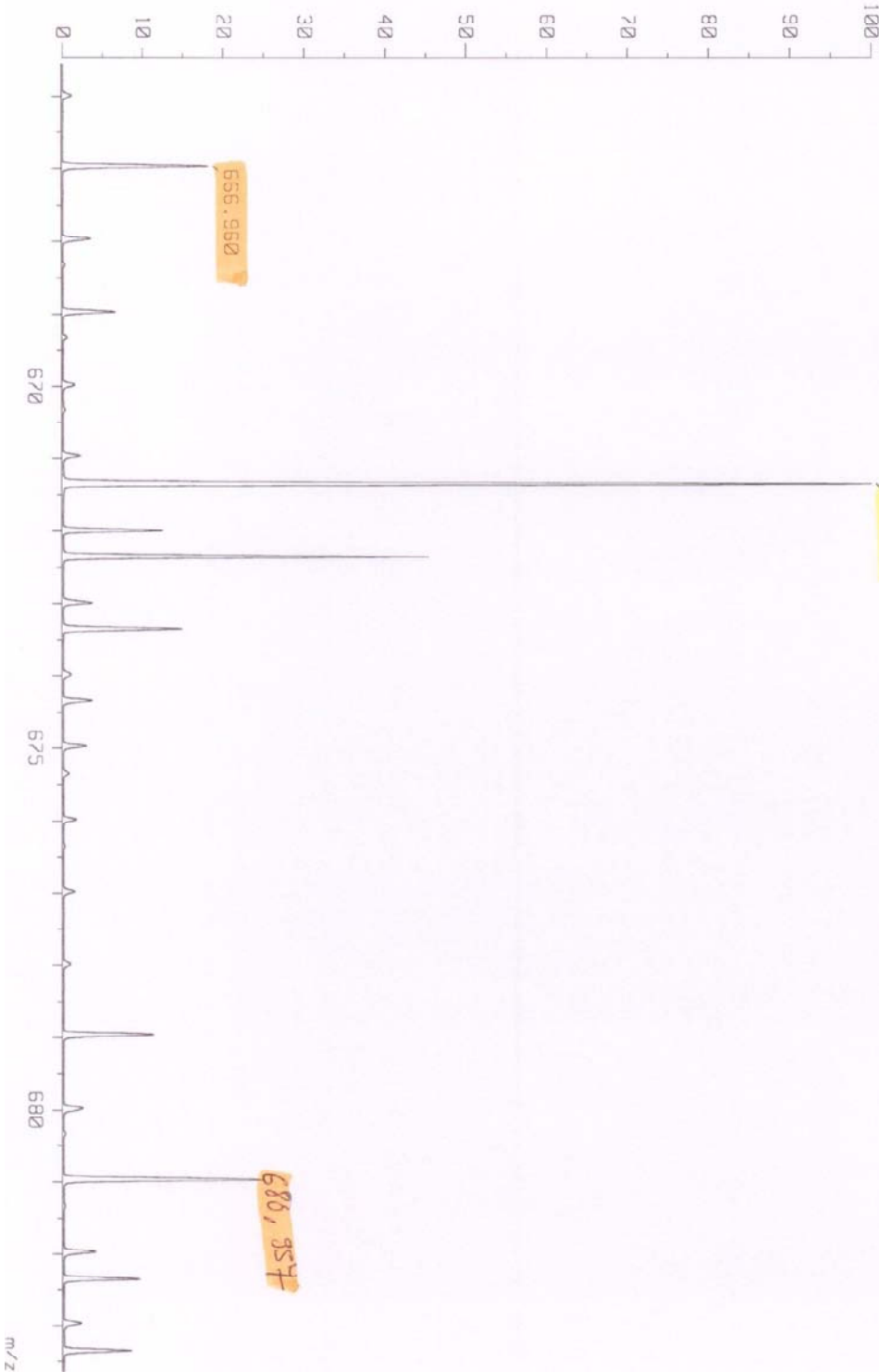
BP : m/z 671.3356 Int. : 30.59

Output m/z range : 665.5490 to 683.6499

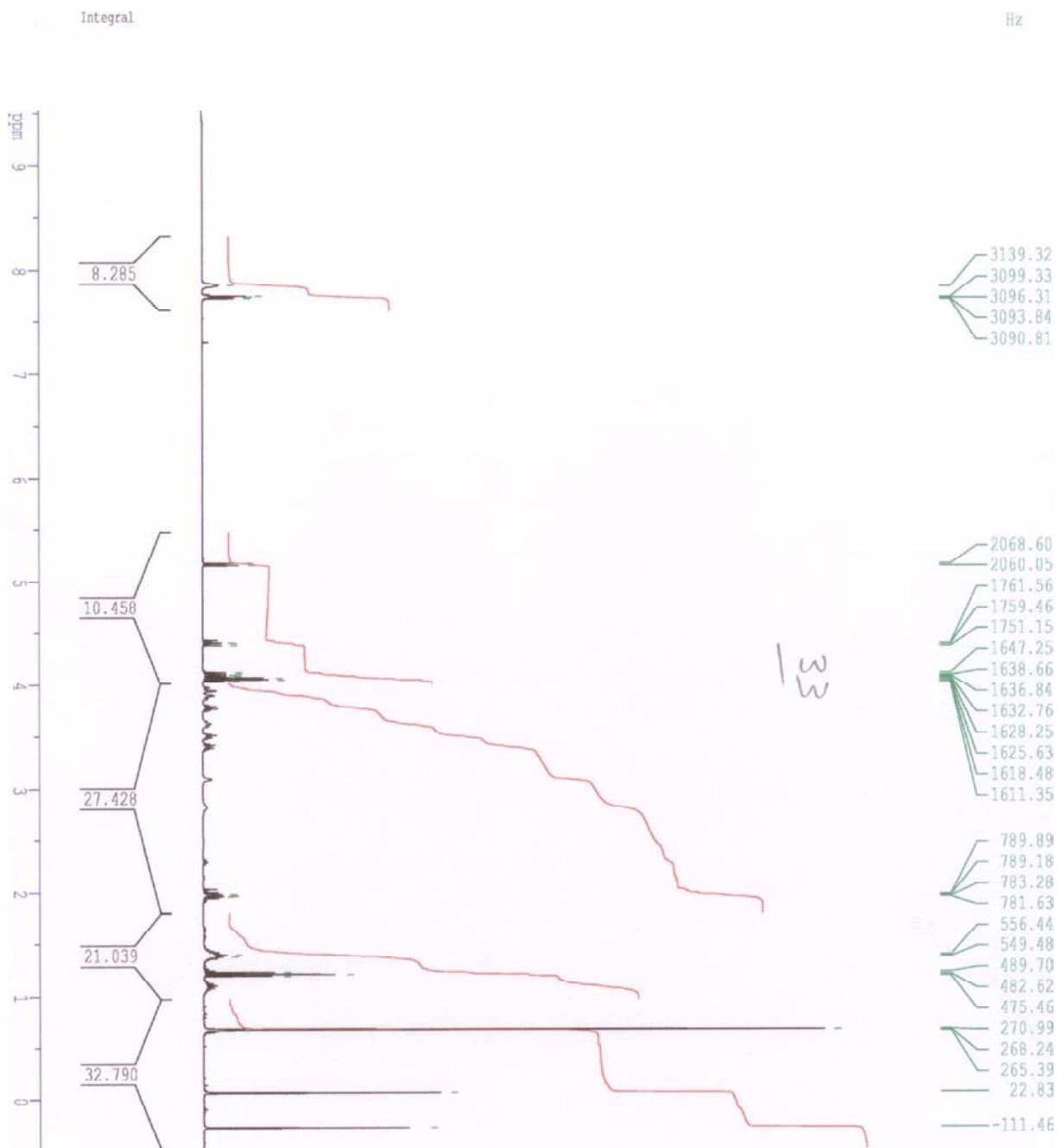
1283235

Cut Level : 0.00 %

671.335



32



21 JUL. 2006

Current Data Parameters
NAME mayeul
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 500000
Time 15.25

INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 64
DS 0

SWH 4006.410 Hz
FIDRES 0.244532 Hz
AQ 2.0447731 sec
RG 35.9

DM 124.800 usec
DE 4.50 usec
TE 300.0 K
D1 0.10000000 sec
P1 9.50 usec

DE 4.50 usec
SFO1 400.1318006 MHz
MPC1 1H
P11 -3.00 dB

F2 - Processing parameters
SI 8192
SF 400.129932 MHz
MCM GM
SSB 0

LB -0.30 Hz
GB 0.3
PC 0.01

ID NMR plot parameters
CX 22.00 cm
F1P 10.560 ppm
F1 4201.37 Hz
F2P -0.500 ppm
F2 -200.07 Hz
ZPCMCM 0.50000 ppm/cm
HZCM 200.06500 Hz/cm

ppm

173.491
168.655
168.624
167.627
167.579

134.054
131.619
123.523
123.375
122.915

98.131
77.318
77.000
76.681
75.212
72.606
72.495
72.404
70.470
69.202
62.362
62.289
60.060
57.102
34.171
33.879
29.233
28.820
25.926
25.595
25.424
25.323
25.264
25.173
24.967
24.243
17.677
14.080
-4.151
-5.204

33

180
160
140
120
100
80
60
40
20
0

Current Data Parameters
NAME mayalic
EXPNO 1 JUL 2006
PROCNO 1

F2 - Acquisition Parameters
Date_ 508000
Time_ 15.32
INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG imod
TD 6536
SOLVENT CDCl3
NS 104
DS 0
SHE 2415.590 Hz
FIDRES 0.38370 Hz
AQ 1.356452 sec
RG 9135.2
TM 20.700 usec
DE 4.50 usec
TE 300.0 K
PI 16.00 usec
DELTA 0.0000204 sec
D20 0.00714000 sec
P112 17.50 dB
D1 1.2999995 sec
CDEPRG2 waltz16
PCPD2 100.00 usec
SFO2 400.1317000 MHz
NUC2 1H
P12 120.00 dB
D13 0.0000300 sec
P2 32.00 usec
SFO1 100.623964 MHz
NUC1 13C
P11 0.00 dB
DE 4.50 usec

F2 - Processing parameters
SI 12768
SF 100.617785 MHz
K1W EX
SSB 0
LB 1.00 Hz
GB 0
PC 0.30

1D NMR plot parameters
CX 22.00 cm
ETP 210.000 ppm
F1 21128.48 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
FREQH 10.00000 ppm/cm
HZCM 1006.12789 Hz/cm

[Mass Spectrum]

Data : MRYELL-MC385-CI+-NH3-HR201 Date : 26-Jul-2006 09:06

Sample: -

Note: -

Inlet : Direct Ion Mode : DCI+

Spectrum Type : Normal Ion [EF-Linear]

RT : 3.32 min Scan# : (26,40)

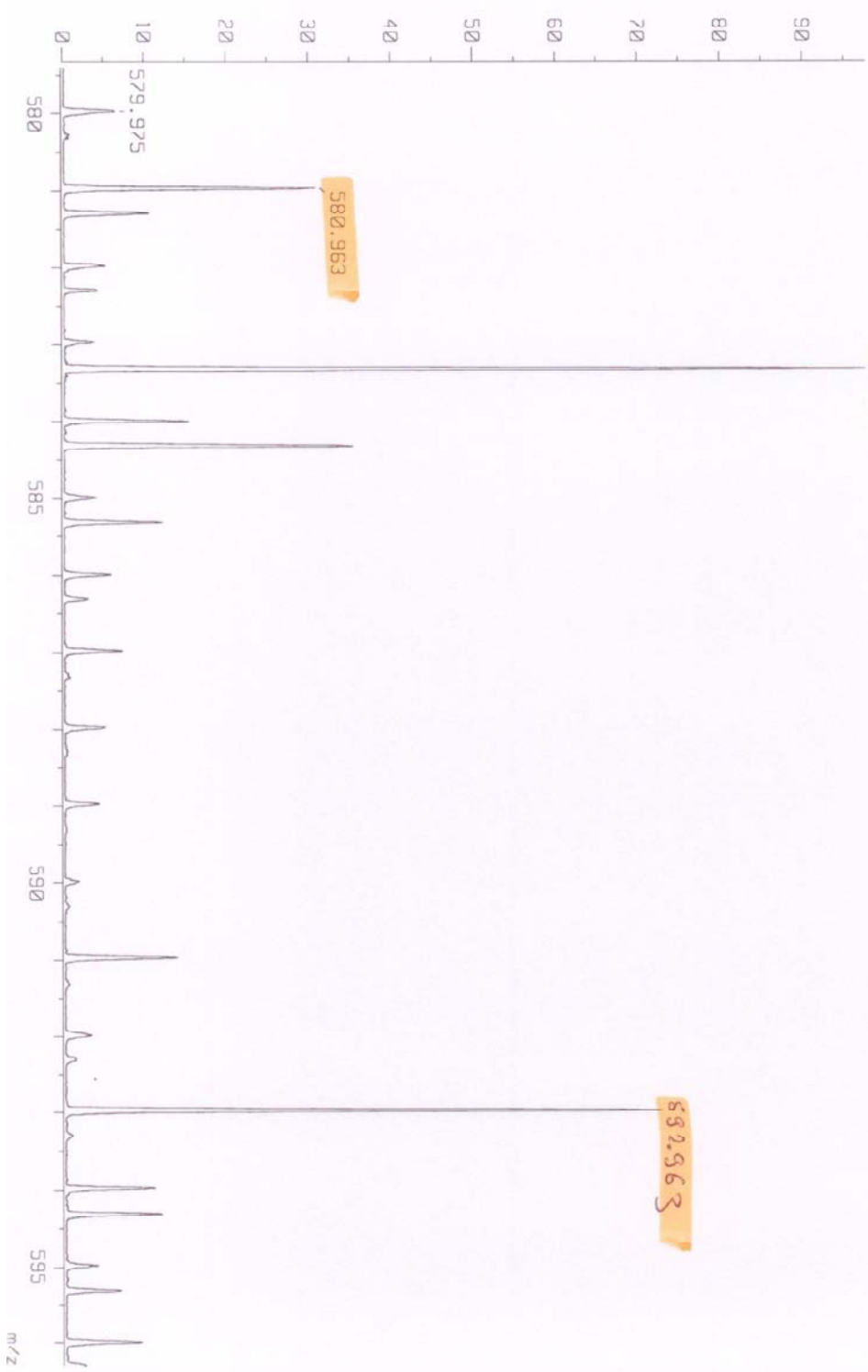
BP : m/z 604.9633 Int. : 71.04

Output m/z range : 579.4055 to 596.3205 Cut Level : 0.00 %

12915493

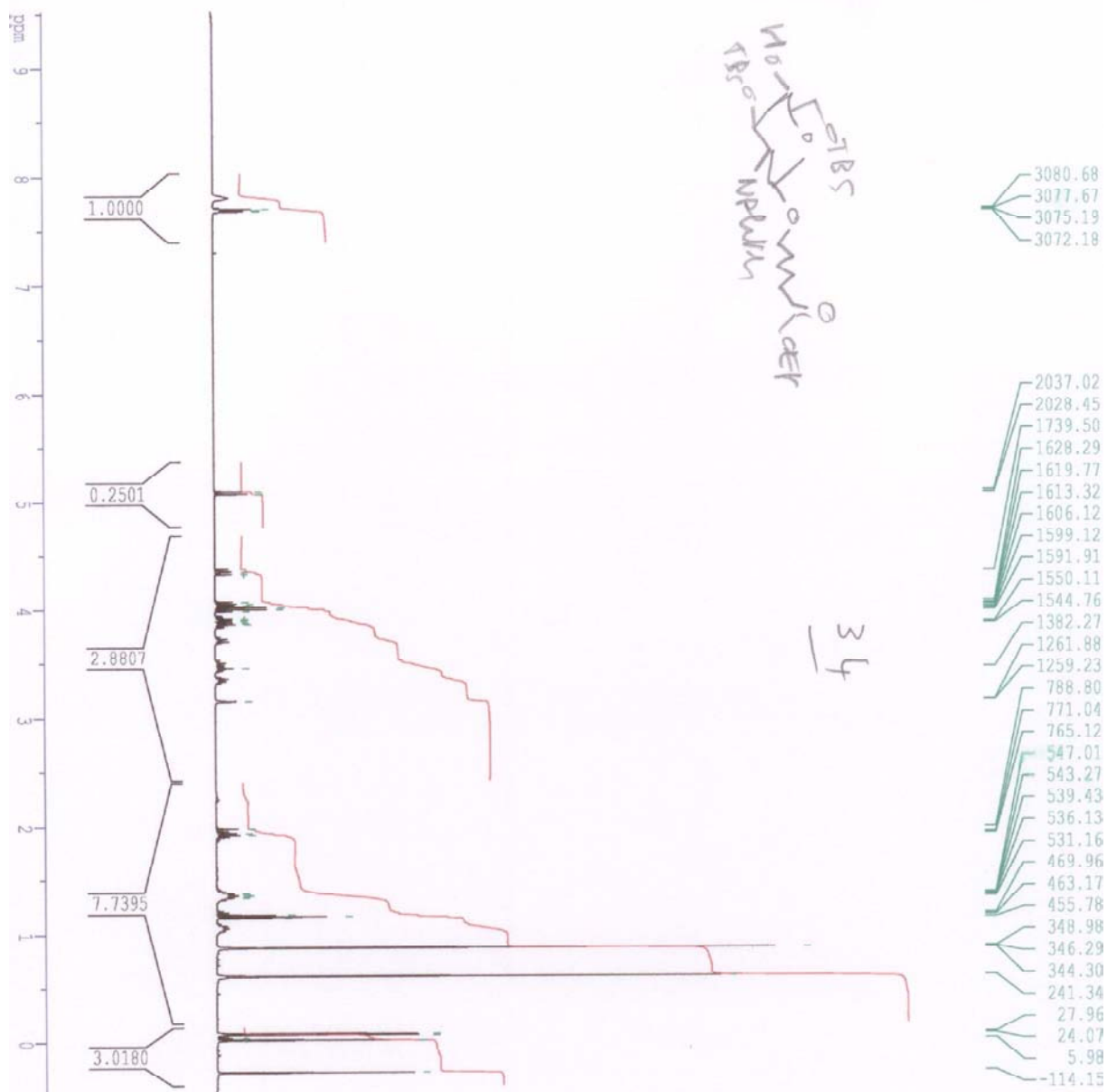
583.304

33



m/z

Integral



24 JUL. 2006

EXPMO	PROCMO
2	1

—

Date_ 50000

PROBHD 5 mm 1H/13C

SOLVENT CDCl₃

4006.410
SWE

16

300.0

100

PI 1
2001
-3 00

0107
17 - processing parameters

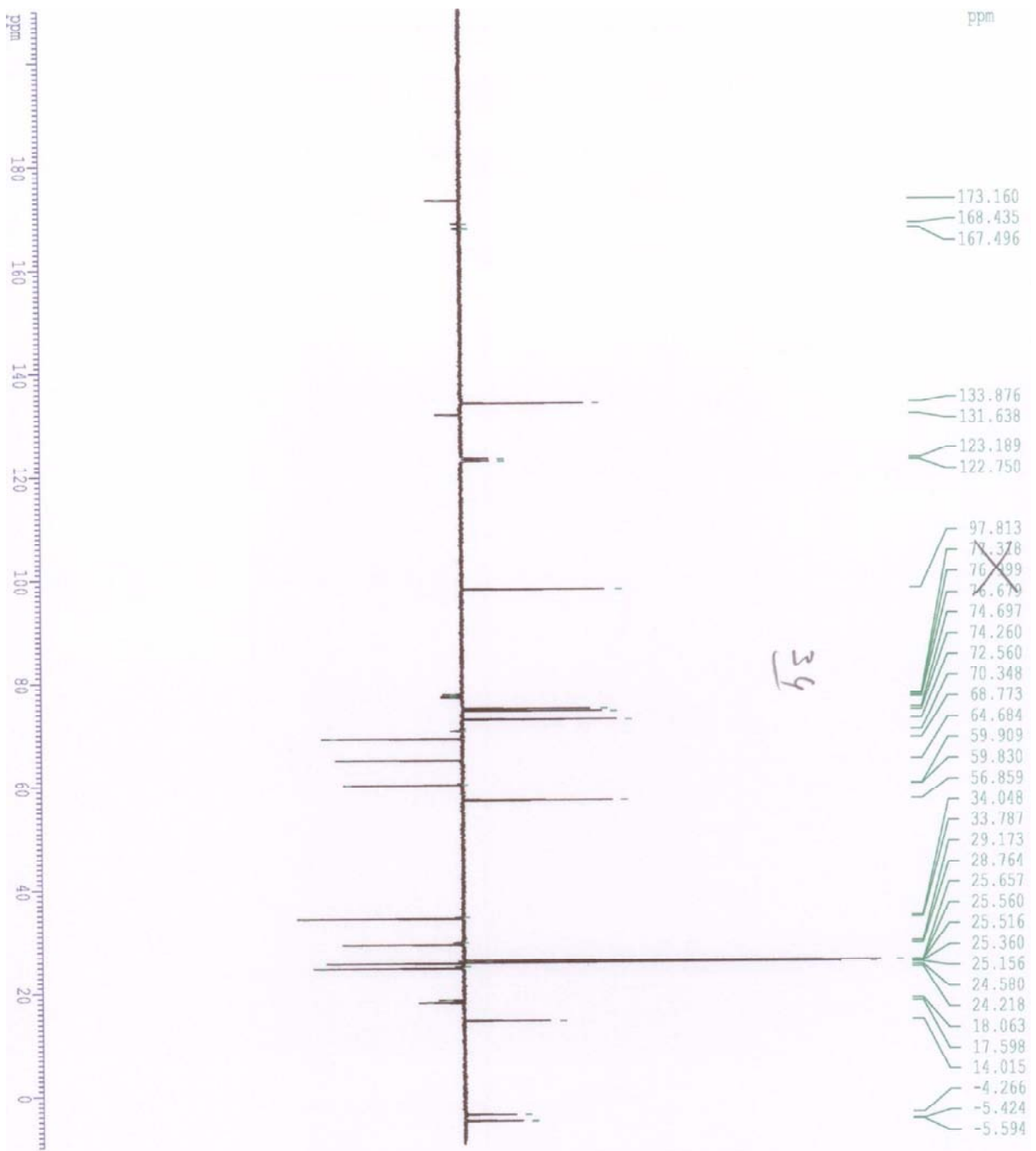
WDM

33

1D NMR plot parameters

4201.37

00005 0
00005 0
00005 0



Current Data Parameters
NAME maynuc
EXPNO 4
PROCNO 4
DATE_ 4 JUL 2006

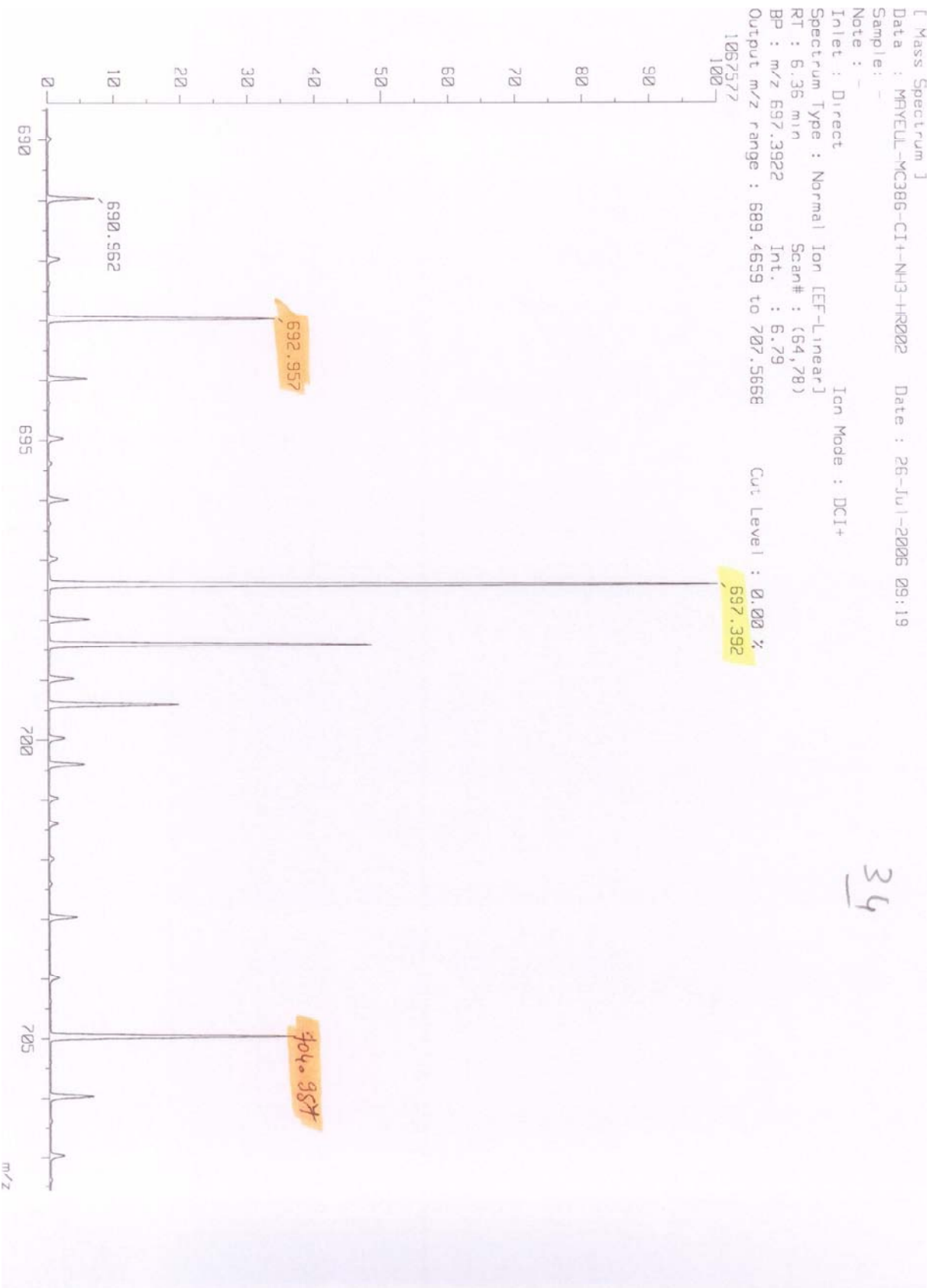
F2 - Acquisition Parameters
Date_ 5/00/00
Time_ 16.21
INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 80
DS 0

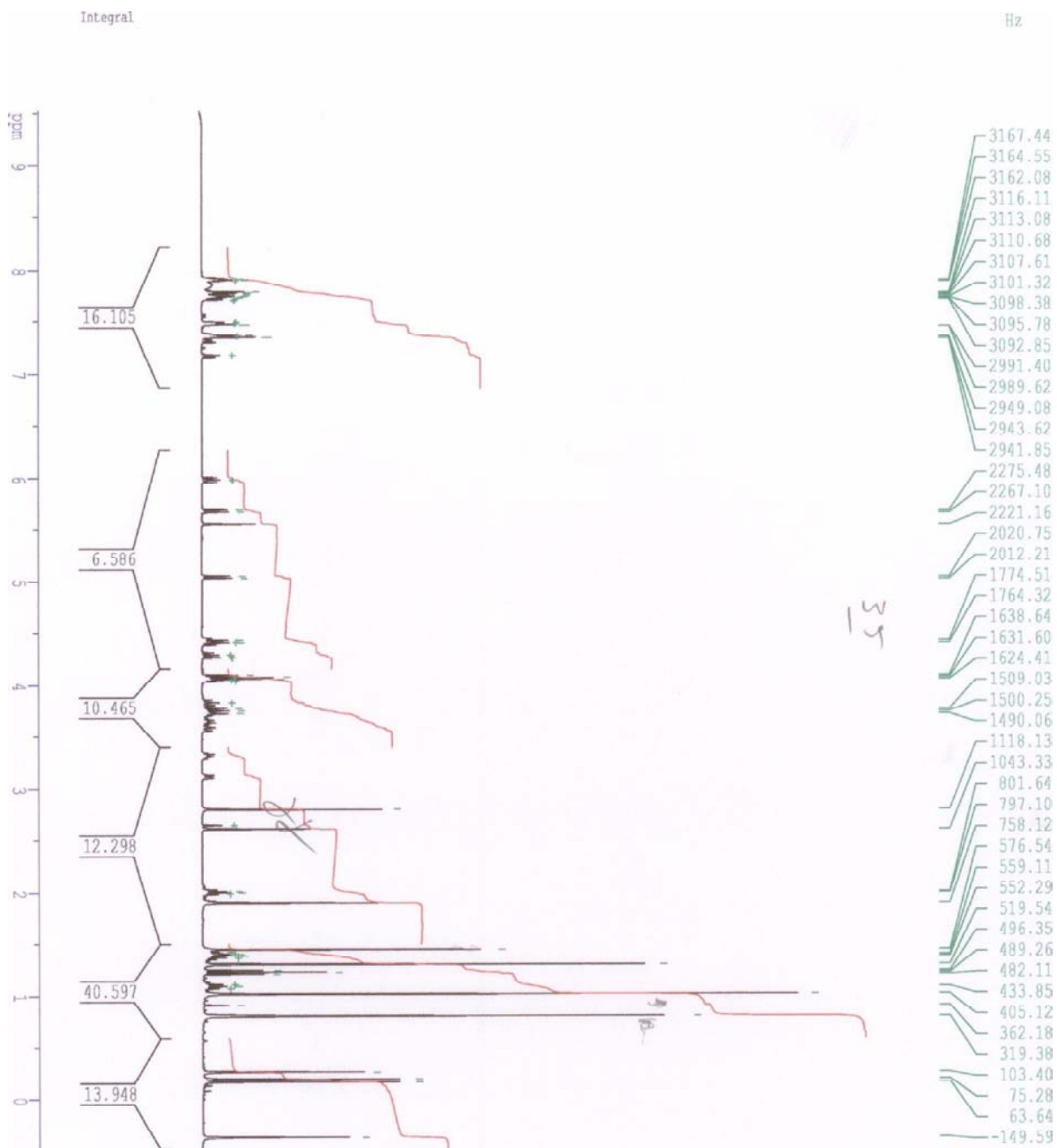
SMH 24154.598 Hz
FIDRES 0.368570 Hz
AQ 1.356452 sec
RG 9195.2
DM 20.700 usec
DE 4.50 usec
TE 300.0 K
P1 16.00 usec
DELTA 0.000204 sec
D20 0.00714000 sec
P1.12 17.50 dB
DI 1.2999995 sec
CPDPRG2 waltz16
PCPD2 100.00 usec
SFO2 400.137600 MHz
NUC2 13C
P1.2 120.00 dB
DI3 0.0000300 sec
P2 32.00 usec
SFO1 100.6237964 MHz
NUC1 13C
P1.1 0.00 dB
DE 4.50 usec

F2 - Processing parameters
SI 32768
SF 100.6127830 MHz
KCM EM
SSB 0
IB 1.00 Hz
GB 0
PC 0.50

1D NMR plot parameters
CX 22.00 cm
FLP 210.000 ppm
F1 21128.69 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
FPCMH 10.00000 ppm/cm
H2CM 1006.12787 Hz/cm

34





28 JUL 2006

Current Data Parameters
NAME mayu1
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 50000
Time 10.46

INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG zg30
TD 16384
SOLVENT CDCl3

DS 0
SHE 4005.410 Hz
FIDRES 0.24532 Hz
AQ 2.0447731 sec

RG 28.5
SW 124.800 usec
DE 4.50 usec
TE 300.0 K

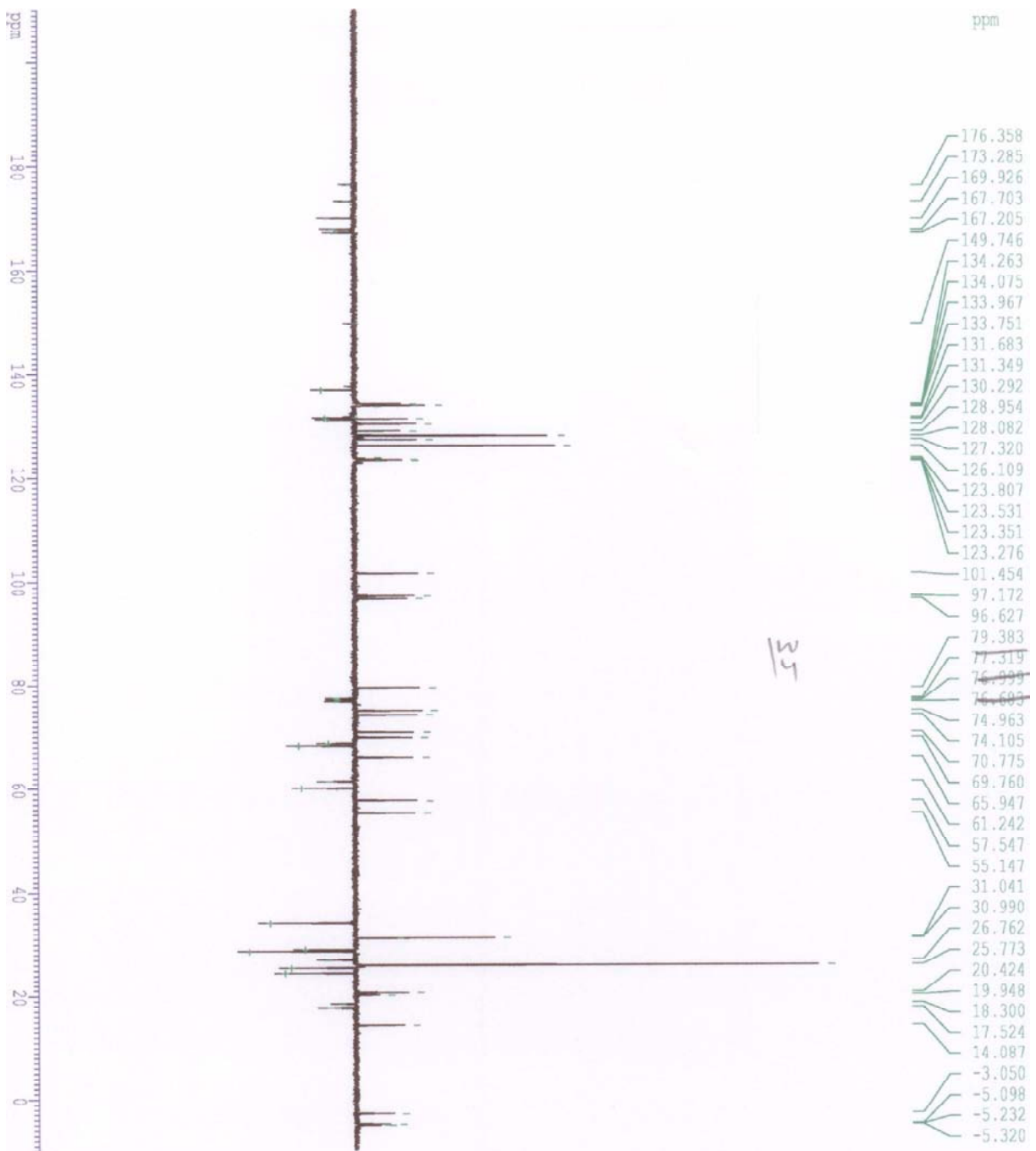
D1 0.10000000 sec
P1 9.50 usec
DE 4.50 usec
SFO1 400.138006 MHz

WOC1 1H
P11 -3.00 dB

F2 - Processing parameters
SI 8192
SF 400.129932 MHz
WDW GM
SSB 0
LB -0.30 Hz
GB 0.3
PC 0.01

ID NMR plot parameters
CX 22.00 cm
FLP 10.500 ppm
F1 4201.37 Hz
F2P -0.500 ppm

F2 -200.07 Hz
PPMCM 0.50000 ppm/cm
HZCM 200.06500 Hz/cm



Current Data Parameters
 NAME methylc
 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 28/11/2006
 Time_ 10.50
 INSTRUM spect
 PROBRD 5 mm 1H/13C
 FULPROG jmod
 TD 65536
 SOLVENT CDCl3
 NS 256
 DS 0
 SWH 24154.590 Hz
 FIDRES 0.368570 Hz
 AQ 1.3566452 sec
 RG 9195.2
 DW 20.700 usec
 DE 4.50 usec
 TE 300.0 K
 P1 16.00 usec
 DELTA 0.0000204 sec
 D20 0.00714000 sec
 PL12 17.50 dB
 D1 1.2999995 sec
 CEPPRG2 waltz16
 PCPD2 100.00 usec
 SFO2 400.1317000 MHz
 JMOD2 1H
 PL2 120.00 dB
 D13 0.00000330 sec
 P2 32.00 usec
 SFO1 100.6237964 MHz
 JMOD1 13C
 PL1 0.00 dB
 DE 4.50 usec

F2 - Processing Parameters
 SI 32768
 SF 100.6127830 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 0.30

1D NMR plot parameters
 CX 22.00 cm
 F1P 2.0.000 ppm
 F1 21.28.69 Hz
 F2P -10.000 ppm
 F2 -1006.13 Hz
 PPMCM 10.00000 ppm/cm
 HZCM 1006.12787 Hz/cm

[Mass Spectrum]

Date : COLLOT-MC388-FRB+-NBR-NR-HR0 Date : 02-Feb-2007 17:58

Sample: -

Note: -

Inlet : Direct Ion Mode : FRB+

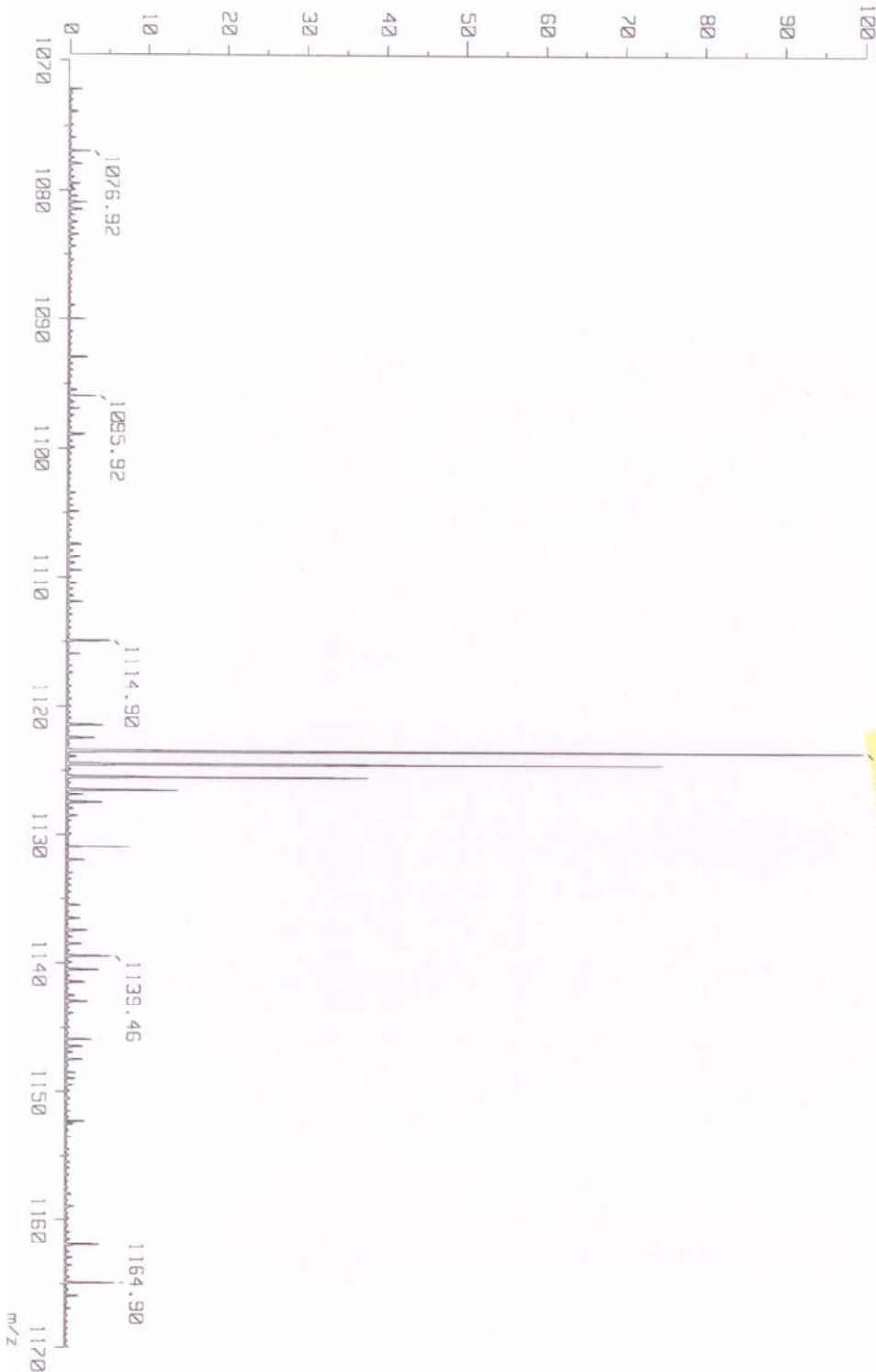
Spectrum Type : Normal Ion [CF-Linear]

RT : 1.52 min Scan# : (2,43)

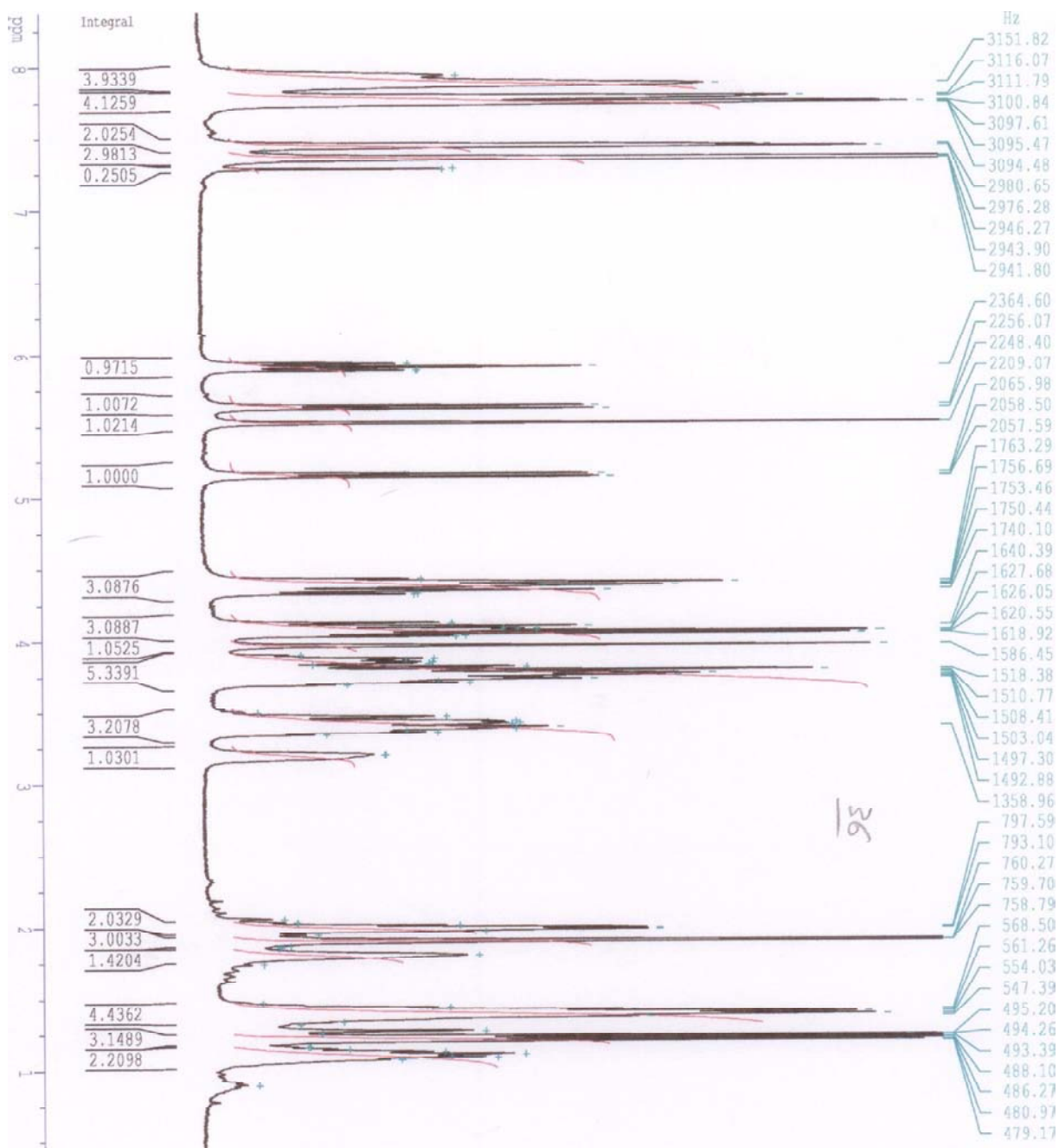
BP : m/z 1123.4564 Int. : 238.77

Output m/z range : 1070.0000 to 1170.0000 Cut Level : 0.00 %

105155448



35

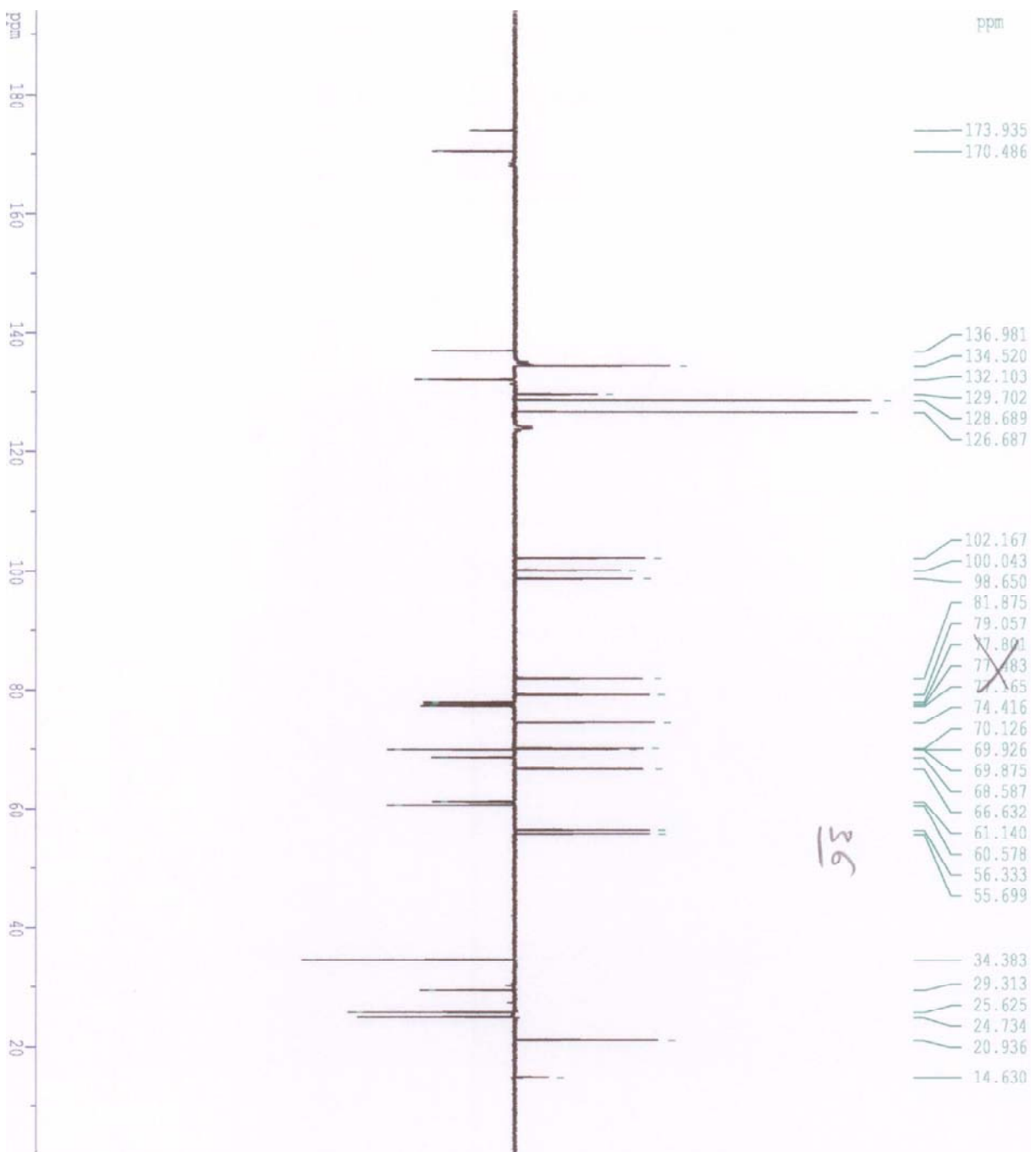


Current Data Parameters
NAME mayenimic-1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 500000
Time_ 22.10
INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 16
DS 2
SWH 4006.410 Hz
FIDRES 0.244537 Hz
AQ 2.0447731 sec
RG 128
DM 124.800 usec
DE 4.50 usec
TE 300.0 K
D1 0.10000000 sec
P1 9.50 usec
SFO1 400.136206 MHz
NOC1 1H
PL1 -3.00 dB

F2 - Processing parameters
SI 16384
SF 400.130000 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 0.10

1D NMR plot parameters
CX 22.00 cm
FLP 8.373 ppm
F1 3350.30 Hz
F2P 0.452 ppm
F2 180.93 Hz
EPWCF 0.36004 ppm/cm
HZCM 144.06258 Hz/cm



36

Current Data Parameters
NAME: mayhemulm1
EXPT: 2
PROCNO: 1

F2 - Acquisition Parameters
Date_: 300000
Time: 22.29

INSTRUM: spect
PROBHD: 5 mm 1H/13C
PULPROG: jmod2.php
TD: 65536
SOLVENT: CDCl3
NS: 4096
DS: 4

SWH: 24154.590 Hz
FIDRES: 0.368370 Hz
AQ: 1.3566452 sec
RG: 8192
DM: 20.700 usec
DE: 4.50 usec
TE: 300.0 K

PI: 26.50 usec
DELTA: 0.000169 sec
D20: 0.0071400 sec
P11: 17.50 dB
D1: 1.2999995 sec

CPDPRG2: Waltz16
PCPR2: 100.00 usec
SFO2: 400.131700 MHz
NUC2: 1H

P12: 120.00 dB
D13: 0.0000300 sec
SFO: 100.623764 MHz
NUC: 13C

P11: 0.00 dB
P2: 53.00 usec
DE: 4.50 usec

F2 - Processing parameters
SI: 65536
SF: 100.6127390 MHz
KCN: EX4
SSB: 0

LB: 0.30 Hz
GB: 0
PC: 0.30

1D NMR plot parameters
CX: 22.00 cm
F1P: 193.953 ppm
F1: 19514.16 Hz

F2P: 1.668 ppm
F2: 167.80 Hz
PFGM: 8.74025 ppm/cm
RGCM: 879.38013 Hz/cm

[Mass Spectrum]
Data : COLLOT-MC448B-FRB+-NBA-Na-HR Date : 23-Feb-2007 16:28

Sample : -

Note : -

Inlet : Direct Ion Mode : FRB+

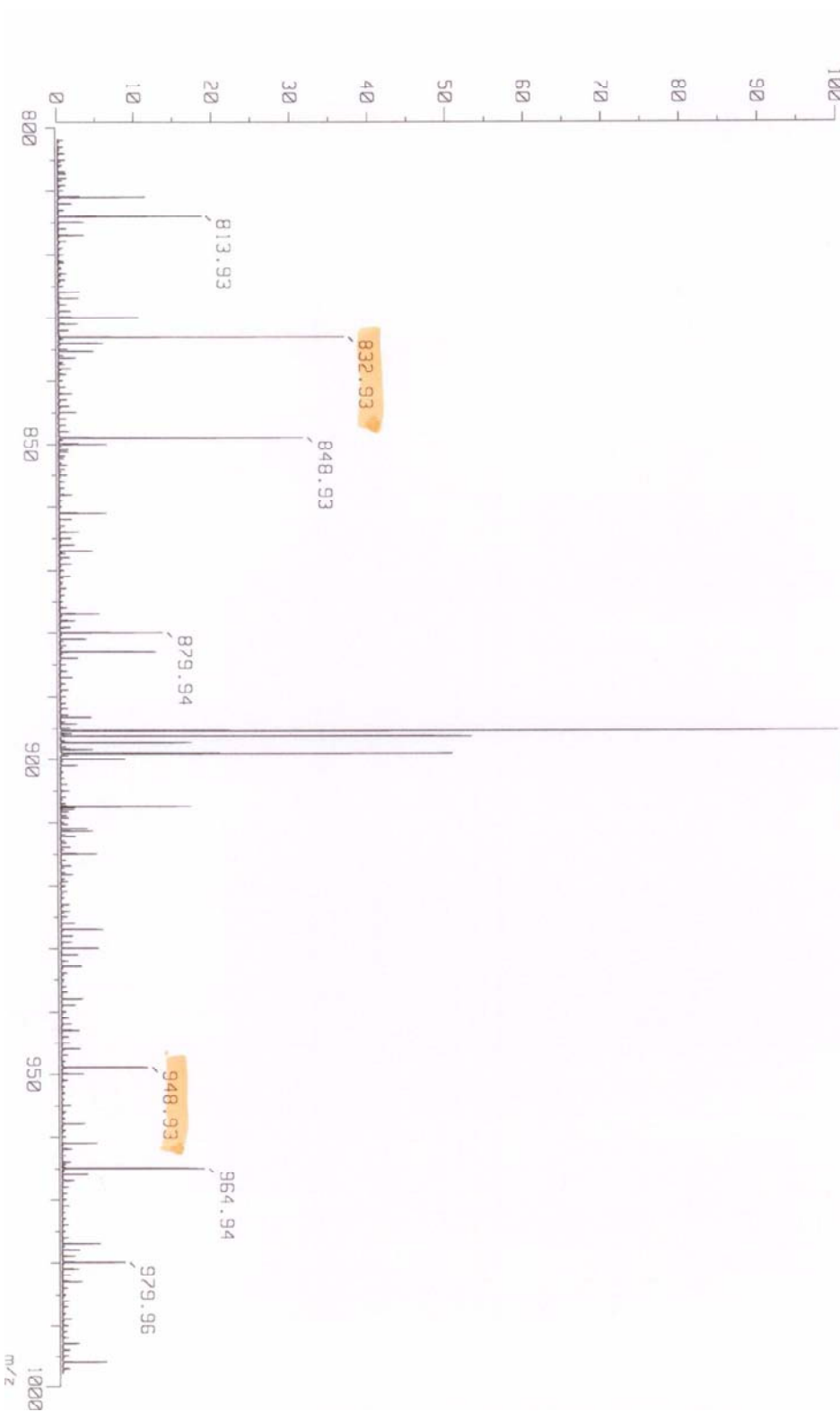
Spectrum Type : Normal Ion [EF-Linear]

RT : 4.09 min Scan# : (12,55)

BP : m/z 895.3104 Int. : 20.43

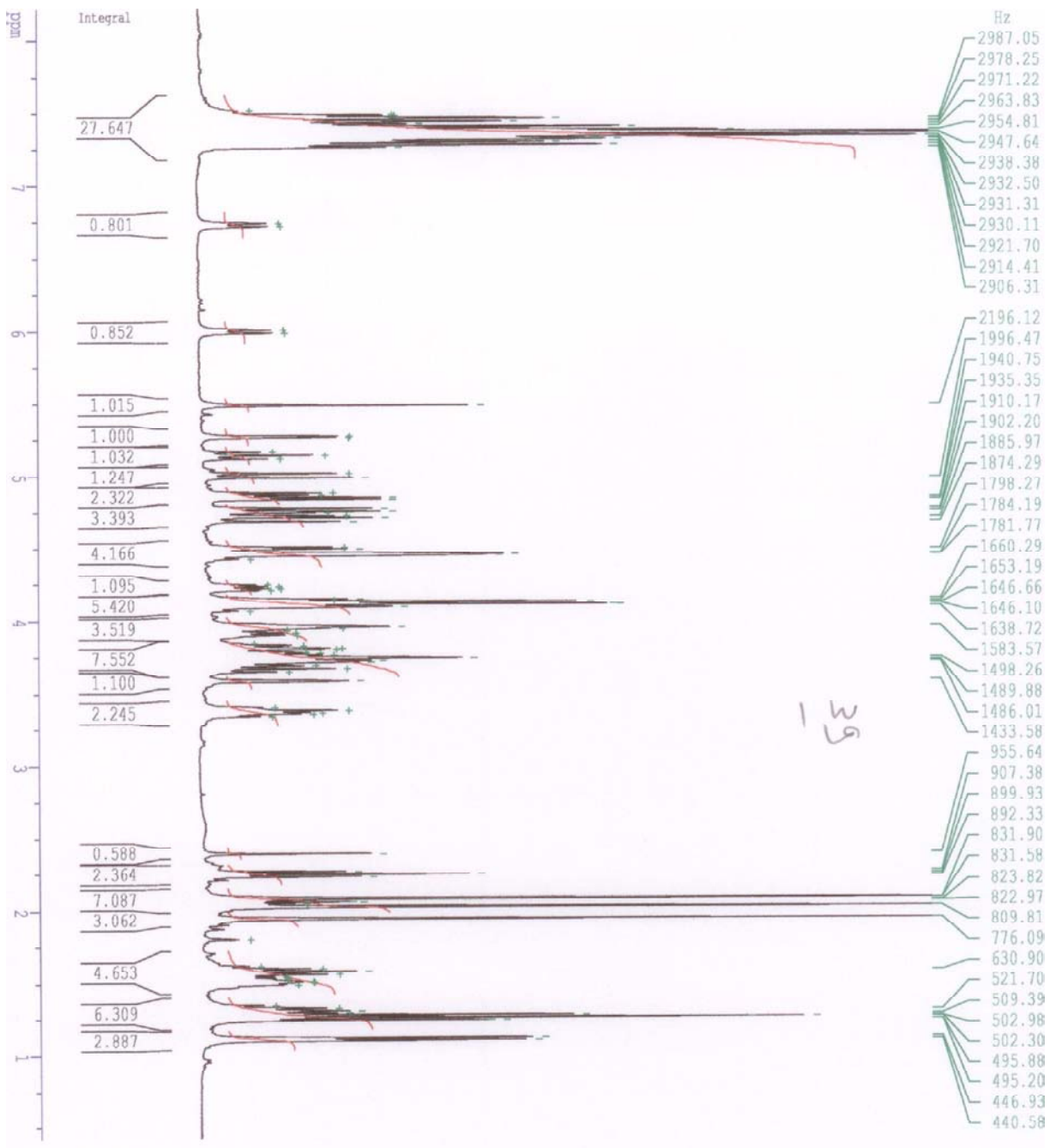
Output m/z range : 800.0000 to 1000.0000

Cut Level : 0.00 %



10 MAI 2007

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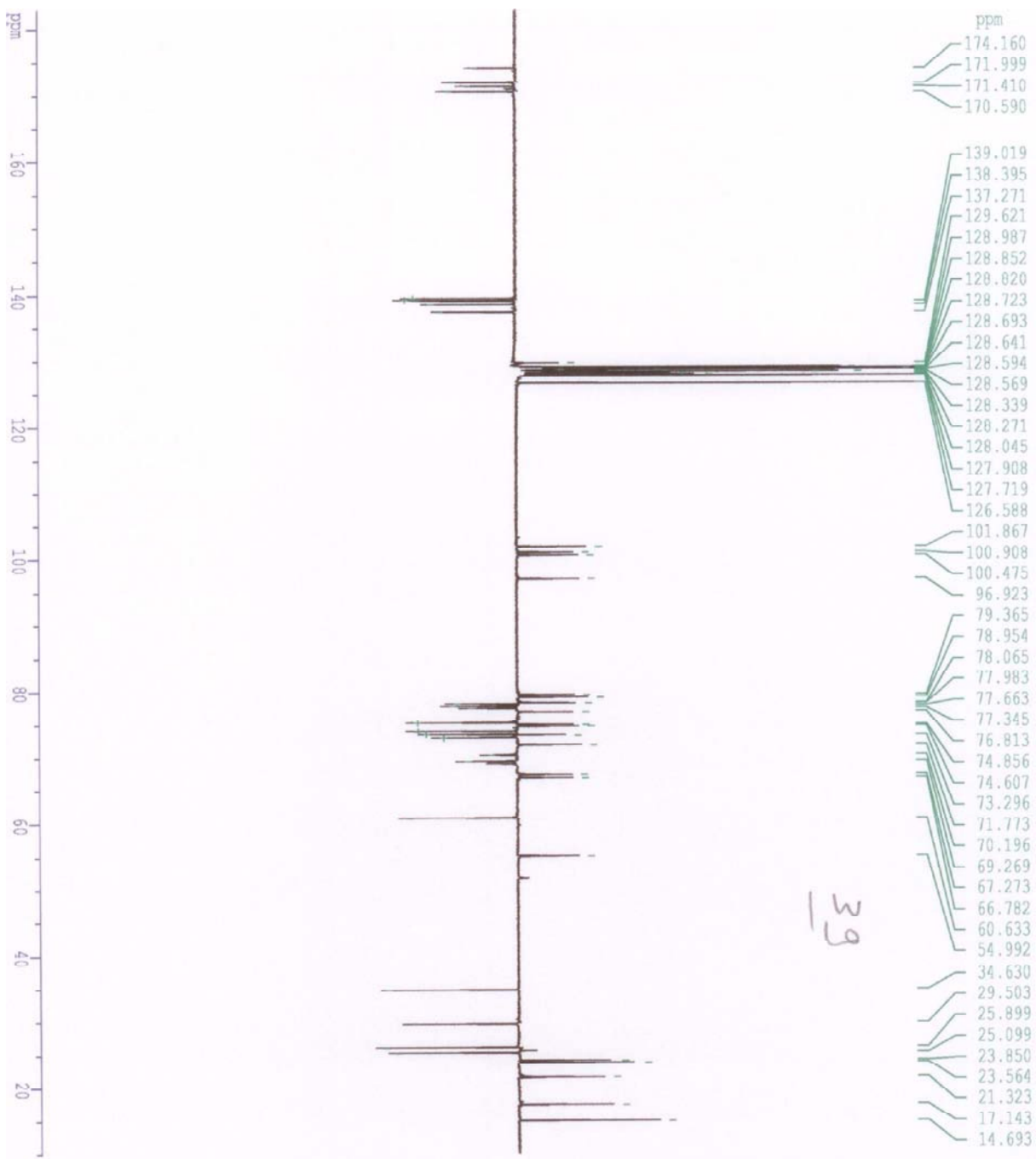


Current Data Parameters
NAME maywellm1c1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 500009
Time_ 21.19
INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 16
DS 2
SWH 4006.410 Hz
FIDRES 0.244532 Hz
AQ 2.044731 sec
RG 32
DM 124.800 usec
DE 4.50 usec
TE 300.0 K
D1 0.1000000 sec
P1 9.50 usec
DE 4.50 usec
SFO1 400.1319206 MHz
NUC1 13
ELI -3.00 dB

F2 - Processing parameters
SI 16384
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 0.10

1D NMR plot parameters
CX 22.00 cm
FLP 3.212 ppm
F1 3235.88 Hz
F2P 0.422 ppm
F2 158.86 Hz
PPMCM 0.35409 ppm/cm
HZCM 141.68248 Hz/cm



Current Data Parameters
 NAME mayhemilit
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 500000
 Time 21.31

INSTRUM spect
 PROBD 5 mm 1H/13C
 PULPROG jmod2.php
 TD 65536
 SOLVENT CDCl3
 NS 4096
 DS 4

SWH 24154.590 Hz
 FIDRES 0.368570 Hz
 AQ 1.356452 sec
 RG 4096
 DM 20.700 usec
 DE 4.50 usec
 TE 300.3 K
 P1 17.00 usec
 P2 34.0 usec

DELTA 0.0000109 sec
 D20 0.0074000 sec
 PL12 17.50 dB
 D1 1.2999995 sec
 CPDPRG2 waltz16
 EPCPD 160.00 usec
 SFO2 400.1317000 MHz
 NUC2 1H

PL2 120.00 dB
 D13 0.0000300 sec
 SFO1 100.6237964 MHz
 NUC1 13C
 PL1 0.00 dB
 DE 4.50 usec

F2 - Processing parameters
 SI 55536
 SF 100.6127250 MHz
 WCN EX
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 0.30

1D NMR plot parameters
 CX 22.00 cm
 FIP 182.870 ppm
 F1 18399.09 Hz
 F2 9.836 ppm

F2 989.65 Hz
 FWHM 7.86519 ppm/cm
 HZCN 791.33801 Hz/cm

10 MAY 2007

[Mass Spectrum]

Data : COLLOT-MC521-FRB+-NBR-Na-HR0 Date : 31-May-2007 15:03

Sample: -

Note: -

Inlet: Direct

Ion Mode: FRB+

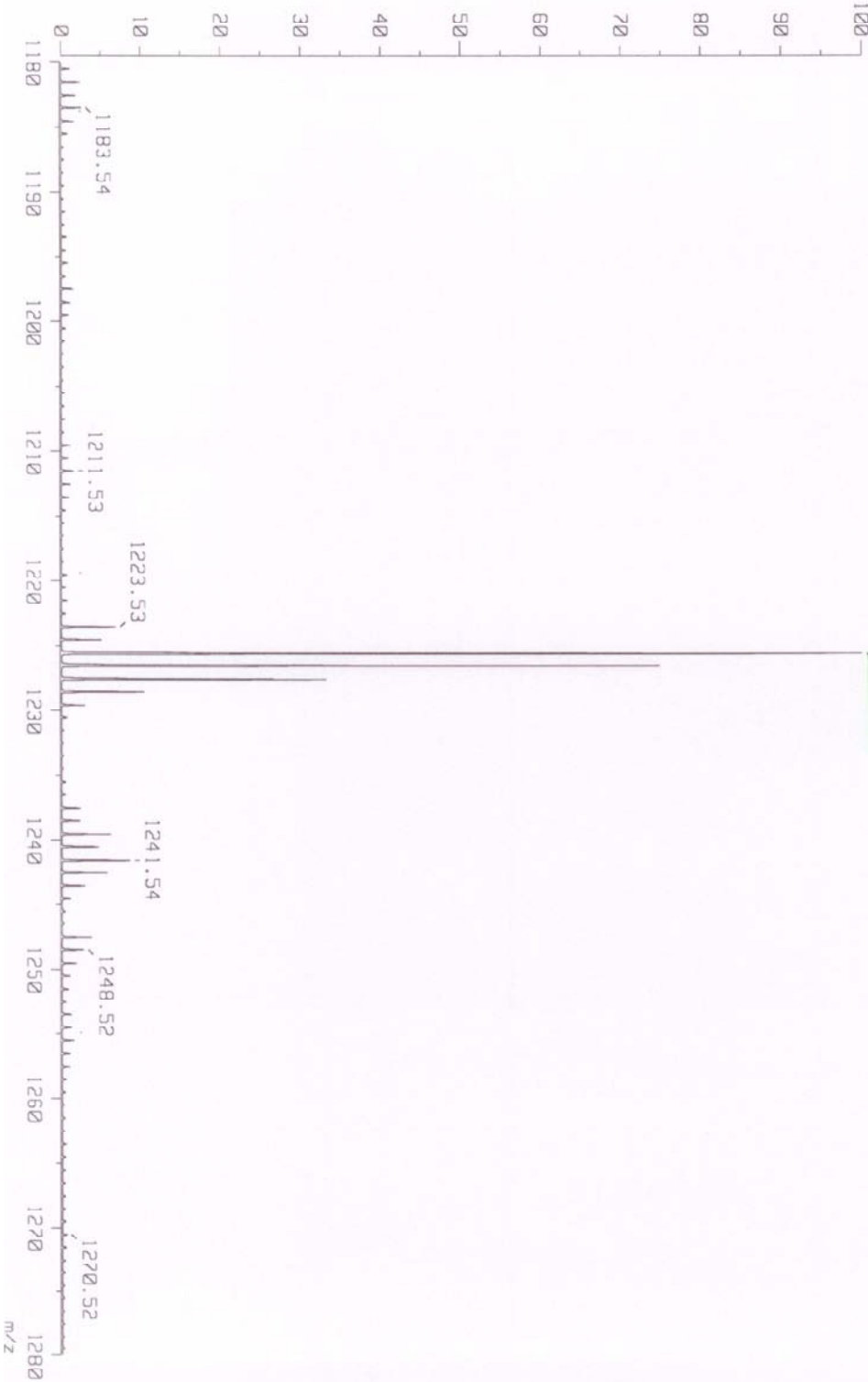
Spectrum Type: Normal Ion [EF-Linear]

RT: 7.82 min Scan#: (42,45)

BP: m/z 1225.5458 Int.: 681.08

Output m/z range: 1180.0000 to 1280.0000 Cut Level: 0.00 %

28565564 1225.55



39

27 NOV. 2005

Current Data Parameters
NAME mayenmulti
EXENO 1
PROCNO 1

F2 - Acquisition Parameters

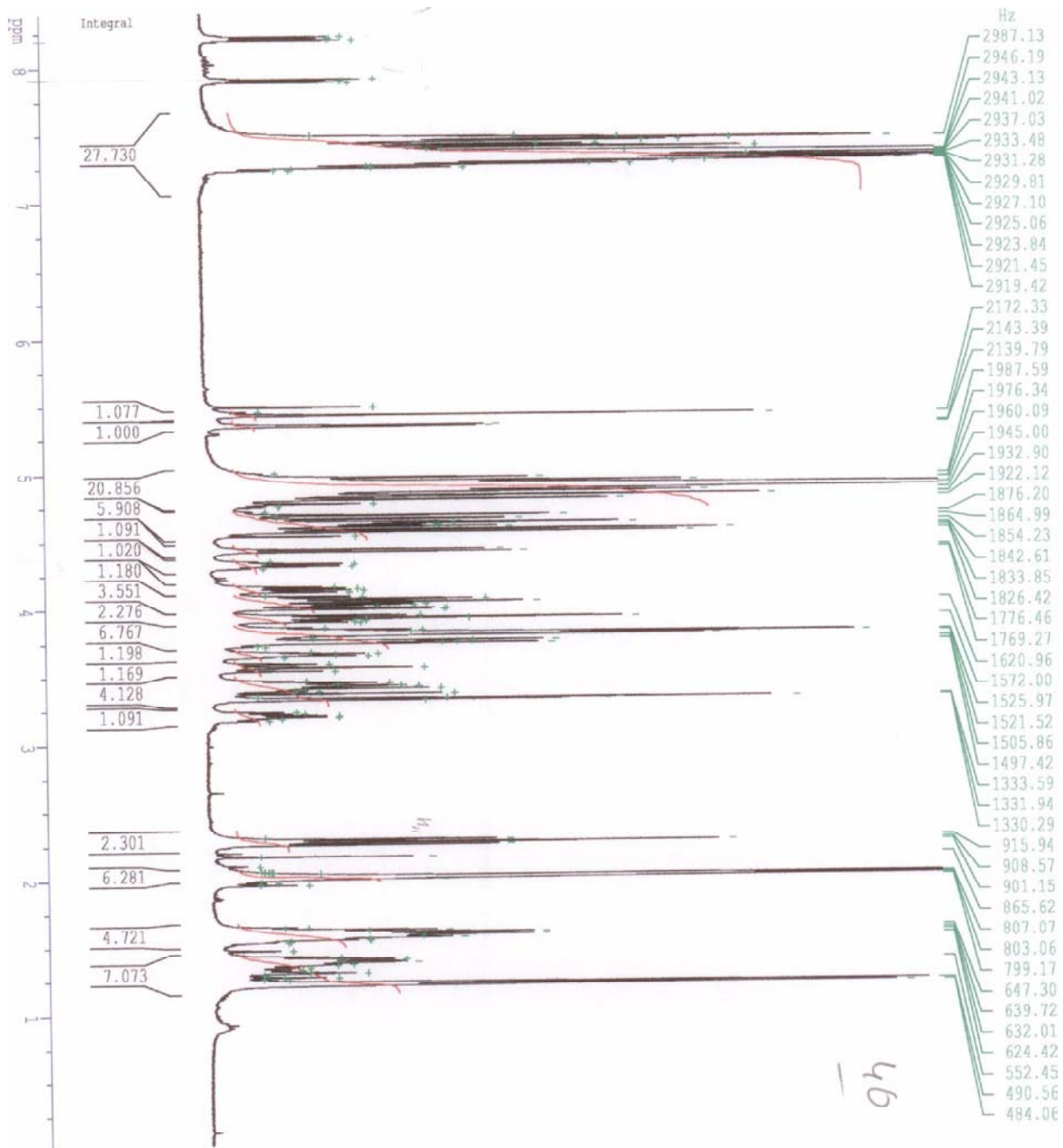
Date 500000
Time 21.10
INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 16
DS 2
SWH 4006.410 Hz
FIDRES 0.24532 Hz
AQ 2.044731 sec
RG 114
DM 124.800 usec
DE 4.50 usec
TE 300.0 K
D1 0.1000000 sec
D11 9.50 usec
DE 4.50 usec
SFO1 400.131206 MHz
NUC1 1H
P11 -1.00 dB

F2 - Processing parameters

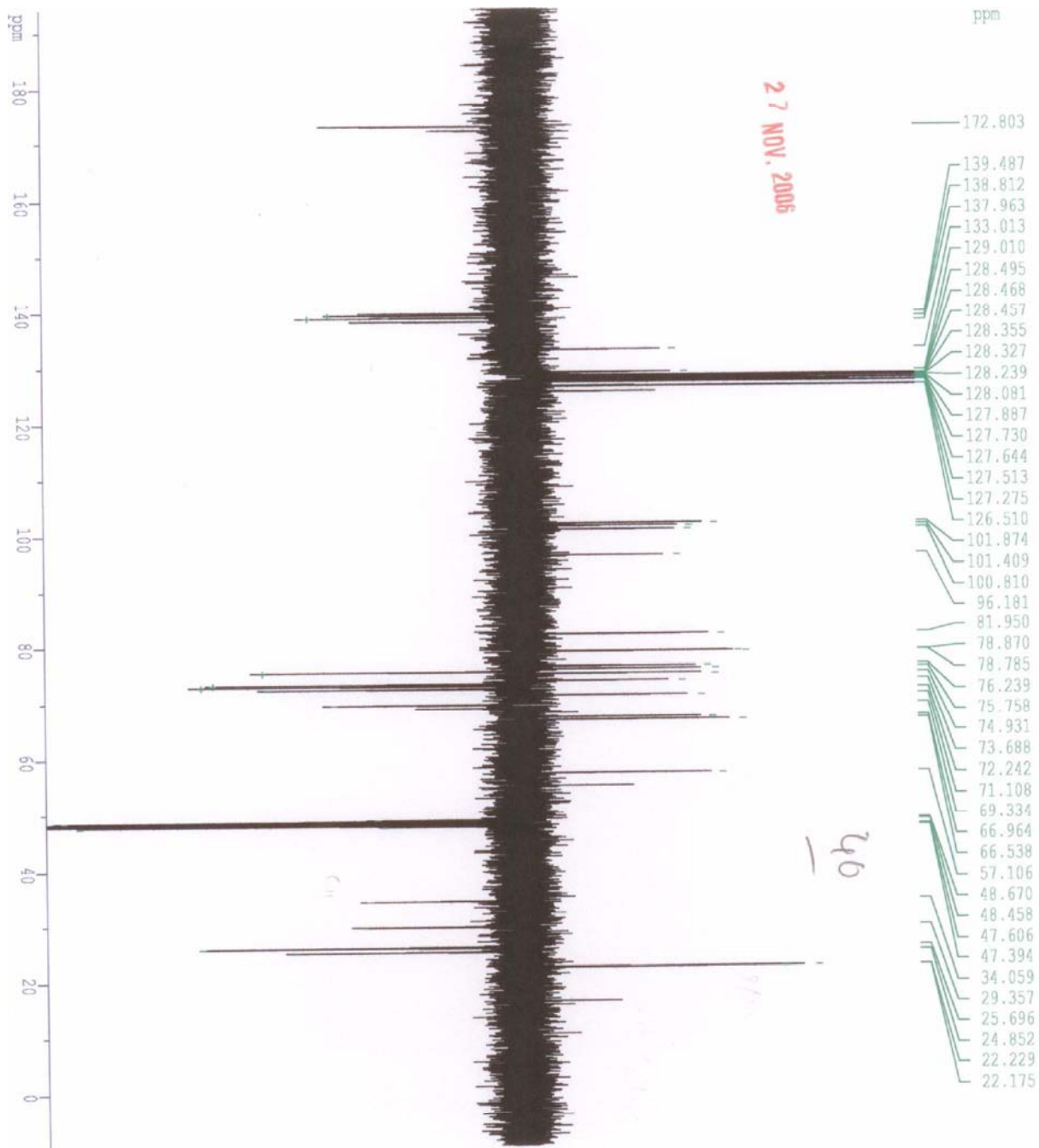
SI 16384
SF 400.130000 MHz
WDW EM
SSB 0
GB 0.00 Hz
PC 0.10

1D NMR plot parameters

CX 22.00 cm
ETP 8.402 ppm
F1 3361.88 Hz
F2P 0.026 ppm
F2 10.40 Hz
PRMCK 0.38071 ppm/cm
HZCM 152.33987 Hz/cm



ppm



Current Data Parameters

NAME mayenimici

EXPNO 2

PROCNO 1

F2 - Acquisition Parameters

Date_ 500000

Time 21.29

INSTRUM spect

PROBHD 5 mm 1H/13C

PULPROG jmod2.php

TD 65536

SOLVENT CDCl3

NS 128

DS 4

SWH 24154.590 Hz

FTIDRES 0.368570 Hz

AQ 1.356452 sec

RG 4096

DW 20.700 usec

DE 4.50 usec

TE 300.0 K

P1 26.50 usec

DELTA 0.000069 sec

D20 0.0071400 sec

PL12 17.50 dB

D1 1.29999995 sec

CPDPRG2 waltz16

PCPD2 100.00 usec

SE02 400.131700 MHz

NUC2 1H

PL2 128.00 dB

D13 0.0000300 sec

SE01 100.623784 MHz

NUC1 13C

PL1 0.00 dB

P2 53.00 usec

DE 4.50 usec

F2 - Processing parameters

SI 65536

SF 100.6127290 MHz

WCMW EN

SSB 0

LB 0.30 Hz

GB 0

PC 0.30

1D NMR plot parameters

CK 22.00 cm

FLP 194.039 ppm

F1 19522.81 Hz

F2P -10.031 ppm

F2 -1009.90 Hz

PRNCH 9.27621 ppm/cm

HCCH 933.34499 Hz/cm

[Mass Spectrum]

Data : COLLOT-MC437-FRB+-NBR-Na-HR0 Date : 23-Feb-2007 17:05

Sample : -

Note : -

Inlet : Direct

Ion Mode : FRB+

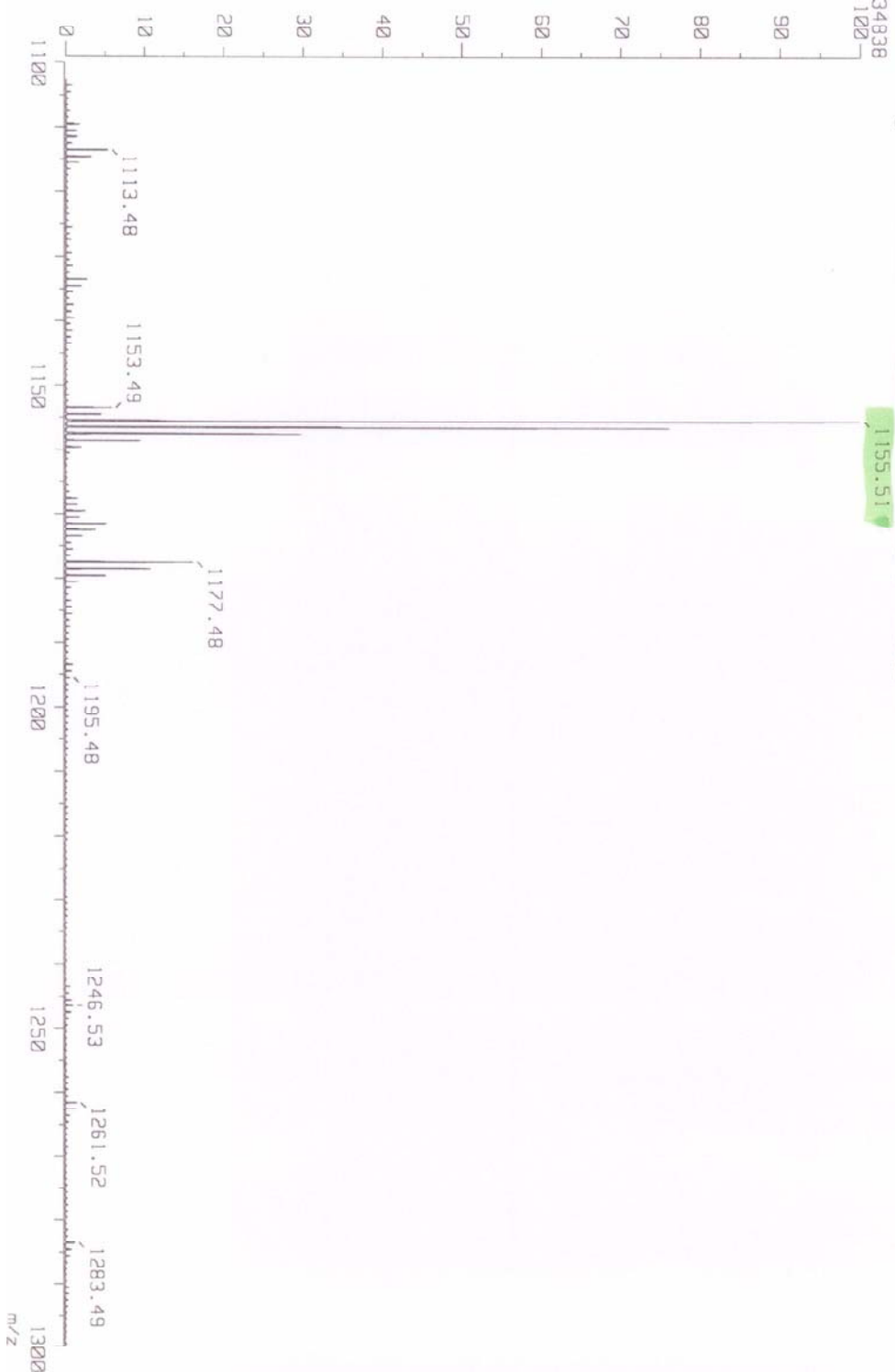
Spectrum Type : Normal Ion [EF-Linear]

RT : 1.14 min Scan# : 12

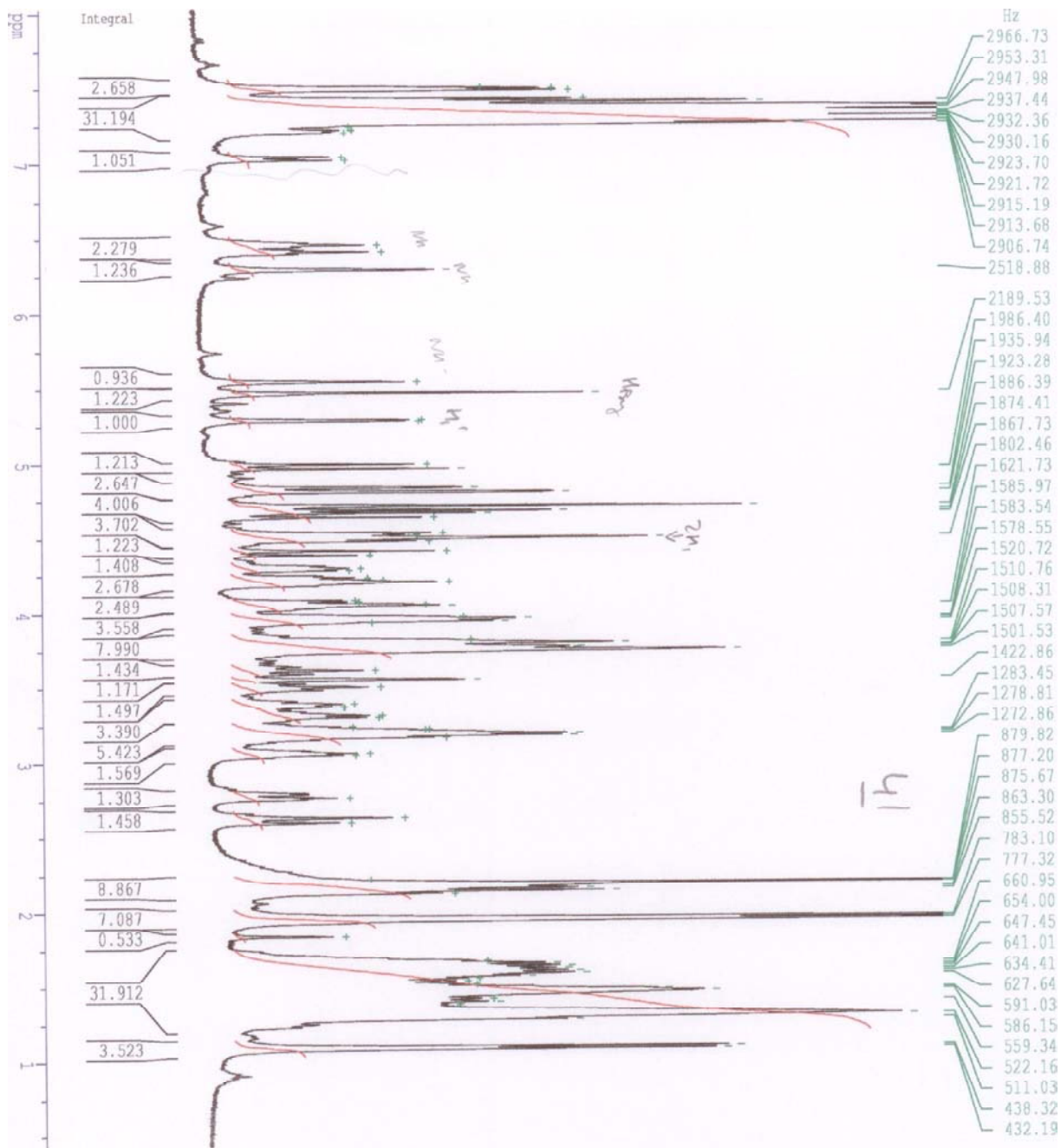
BP : m/z 1155.5056 Int. : 651.82

Output m/z range : 1100.0000 to 1300.0000 Cut Level : 0.00 %

6834838



07 DEC. 2006

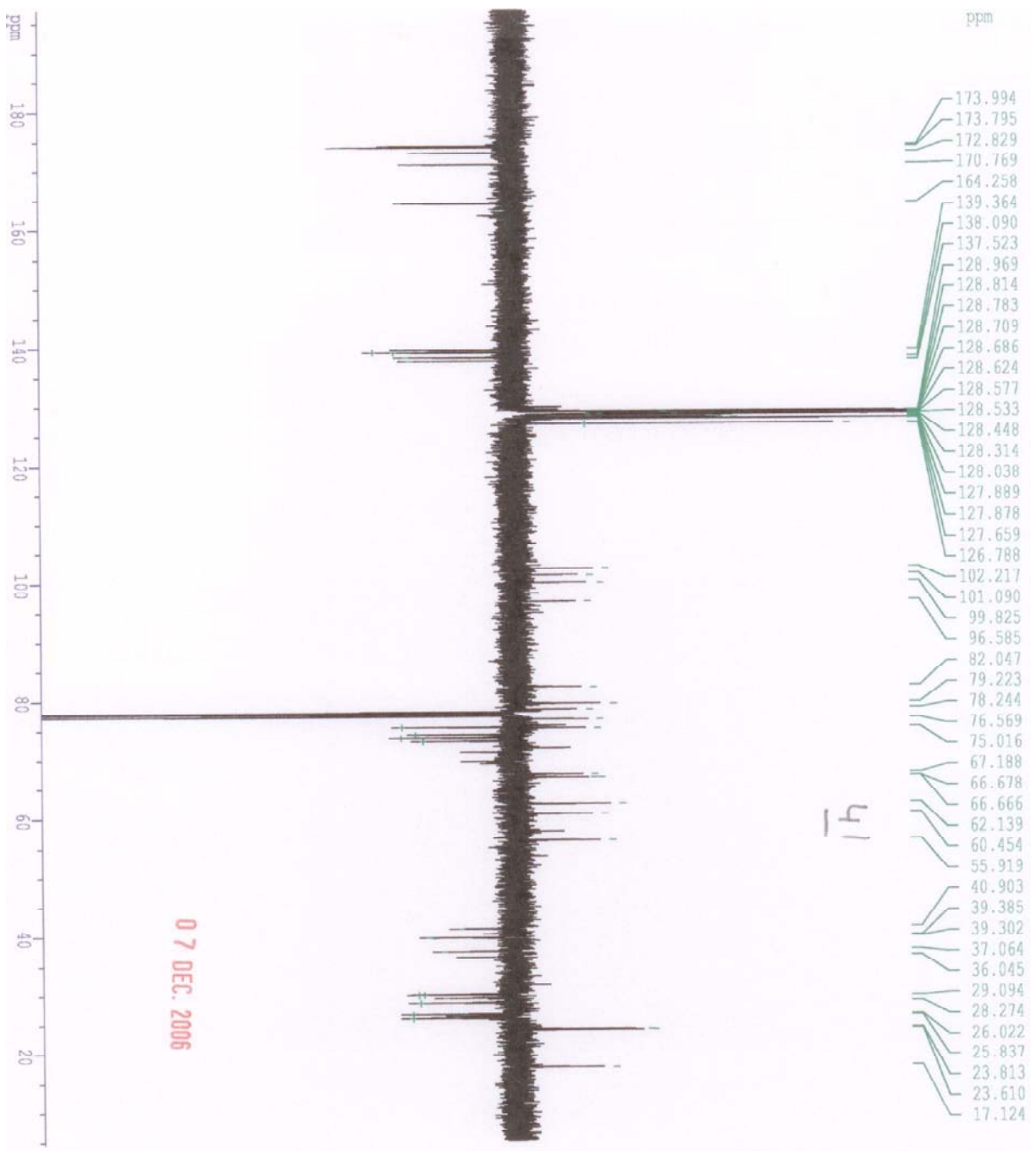


Current File Parameters
NAME mayenite
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 500000
Time 11.06
INSTRUM spect
PROBHD 5 mm H₁/13C
PULPROG zg30
TD 16384
SOLVENT CHCl₃
NS 32
DS 2
SWH 4006.410 Hz
FIDRES 0.24452 Hz
AQ 2.041731 sec
RG 288.1
RW 124.800 usec
TE 300.0 K
DE 1.50 usec
D1 0.1000000 sec
P1 9.50 usec
DE 1.50 usec
SFO1 400.131204 MHz
SFO2 101.626126 MHz
PC 0.10

F2 - Processing parameters
SI 16384
SF 400.130000 MHz
WDW EN
SSB 0
LB 0.00 Hz
GB 0
PC 0.10

1D NMR 90° parameters
CX 22.00 cm
FLP 8.027 ppm
F1 3212.03 Hz
F2 0.425 ppm
F2 170.58 Hz
EPHPCW 0.34551 ppm/cm
HSCW 139.24780 Hz/cm



173.994
173.795
172.829
170.769
164.258
139.364
138.090
137.523
128.969
128.814
128.783
128.709
128.686
128.624
128.577
128.533
128.448
128.314
128.038
127.889
127.878
127.659
126.788
102.217
101.090
99.825
96.585
82.047
79.223
78.244
76.569
75.016
67.188
66.678
66.666
62.139
60.454
55.919
40.903
39.385
39.302
37.064
36.045
29.094
28.274
26.022
25.837
23.813
23.610
17.124

41

Current Data Parameters
NAME mayenimil
EXNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 500000
Time_ 11.26

INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG jmod2.php
TD 65536
SOLVENT CDCl3
NS 4096

DS 4
SMH 2415.590 Hz
FIDRES 0.368570 Hz
AQ 1.356452 sec
RG 8192

TM 20.700 usec
DE 4.50 usec
TE 300.0 K
P1 25.50 usec
DELTA 0.000169 sec

D20 0.0071400 sec
P112 17.50 dB
D1 1.2989995 sec
CDEPRG2 waltz16

PCPD2 100.00 usec
SFO2 400.1317000 MHz
NUC2 1H
P12 120.00 dB

D13 0.00000300 sec
SFO1 100.6237964 MHz
NUC1 13C
P11 0.00 dB

P2 53.00 usec
DE 4.50 usec
F2 - Processing parameters
SI 65536

SF 100.617290 MHz
WPM EX
SSB 0
LB 0.30 Hz
GB 0
PC 0.30

07 DEC. 2006

1D NMR plot parameters
CX 22.00 cm
F1P 197.100 ppm
F1 19850.80 Hz
F2P 4.601 ppm
F2 462.95 Hz
PRCKM 8.14996 ppm/cm
ECOM 880.35706 Hz/cm

41

[Mass Spectrum]

Data : COLLOT-MC443-FRB+-NBA-NA-HR0 Date : 27-Feb-2007 17:51

Sample: -

Note: -

Ion Mode: FRB+

Inlet: Direct

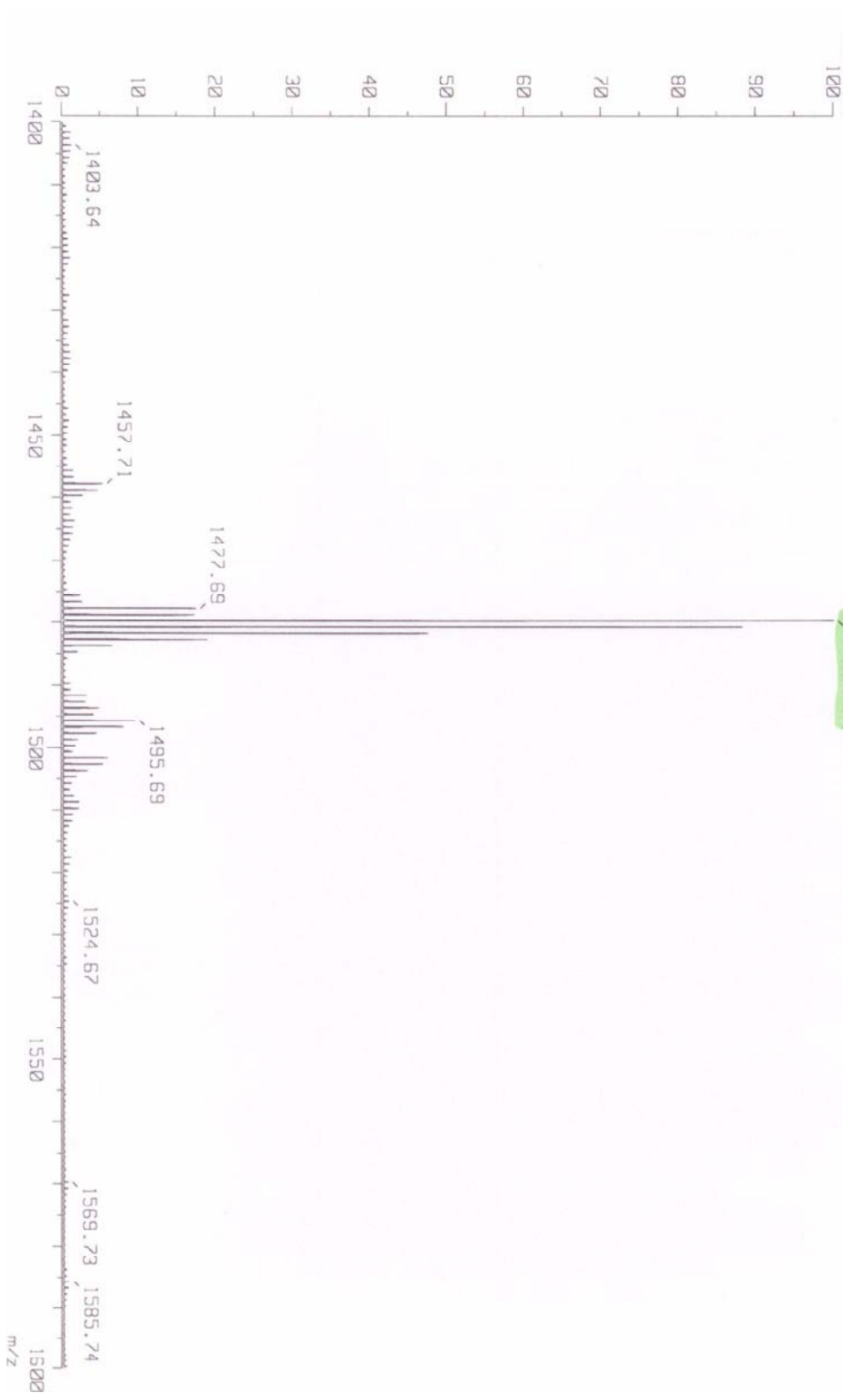
Spectrum Type: Normal Ion [EF-Linear]

RT: 3.61 min Scan#: (13,15)

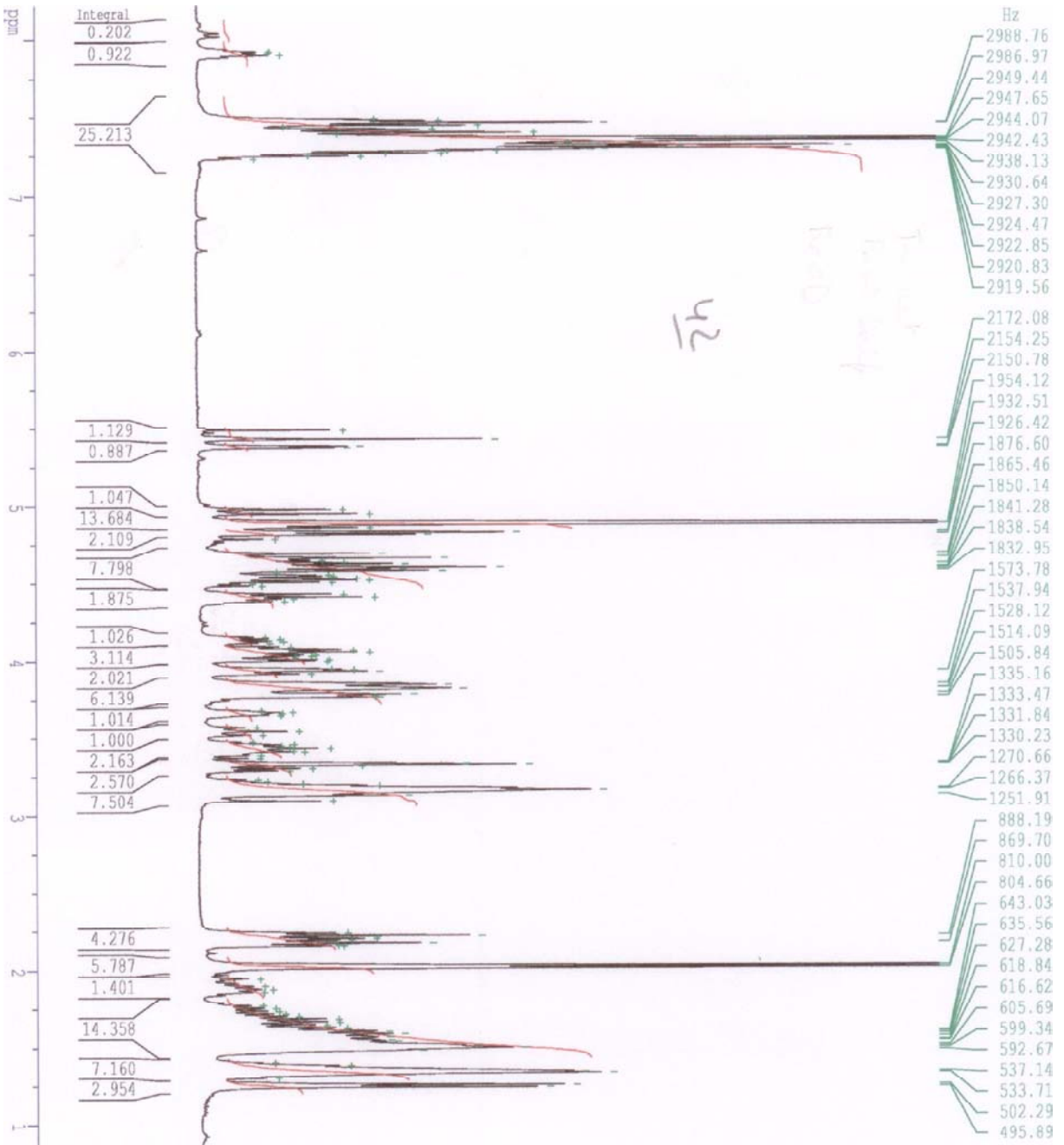
BP: m/z 1479.7040 Int.: 125.45

Output m/z range: 1400.0000 to 1600.0000

Cut Level: 0.00 %



07 APR. 2007

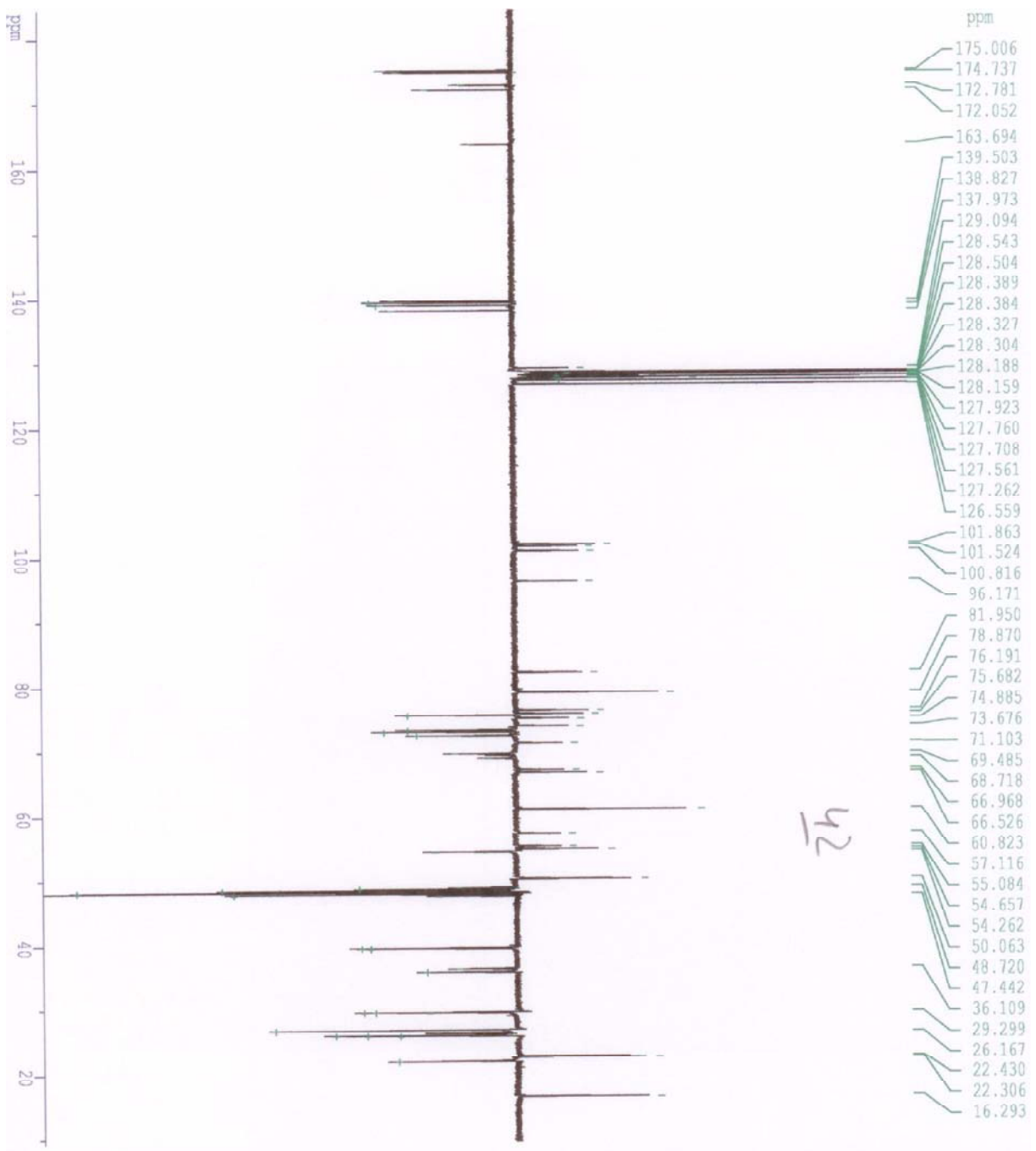


Current Data Parameters
NAME mayulic
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 5/00/00
Time 20.44
INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG zg30
TD 16384
FIDRES 0.24452 Hz
AQ 2.0447131 sec
RG 45.3
RW 124.800 usec
DE 4.50 usec
TE 300.0 K
D1 0.10000000 sec
F1 9.50 usec
DE 4.50 usec
SFO1 400.1319206 MHz
NUC1 1H
E11 -3.00 dB

F2 - Processing parameters
SI 16384
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 0.10

1D NMR plot parameters
CX 22.00 cm
F1P 3.217 ppm
F1 3287.16 Hz
F2P 0.856 ppm
F2 342.65 Hz
PFGM 0.33456 ppm/cm
HZCN 133.86890 Hz/cm



Current Data Parameters

NAME	mayulic
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	500000
Time	21.35
INSTRUM	spect
PROBHD	5 mm 1H/13C
PULPROG	jmod2.php
TD	65536
SOLVENT	CDCl3
NS	4096
DS	4
SWH	2415.590 Hz
FIDRES	0.36970 Hz
AQ	1.356452 sec
RG	4096
TM	20.700 usec
DE	4.50 usec
TE	300.0 K
PI	17.00 usec
P2	34.0 usec
DELTA	0.0000108 sec
D20	0.00714000 sec
PI12	17.50 dB
D1	1.29999995 sec
CDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.131700 MHz
NVC2	1H
PI2	120.00 dB
D13	0.0000308 sec
SFO1	100.627964 MHz
NVC1	13C
PL1	0.00 dB
DE	4.50 usec

F2 - Processing parameters

SI	65536
SF	100.617290 MHz
WFM	EM
SSB	0
LB	0.30 Hz
GB	0
PC	0.30

1D NMR plot parameters

CX	22.00 cm
F1P	184.410 ppm
F1	13553.96 Hz
F2P	9.252 ppm
F2	930.83 Hz
PRCKM	7.36173 ppm/cm
ECM	801.05139 Hz/cm

07 AVR. 2007

[Mass Spectrum]

Data : COLLOT-MC43-FRB+-NBR-Na-HR2 Date : 27-Feb-2007 17:26

Sample : -

Note : -

Inlet : Direct Ion Mode : FRB+

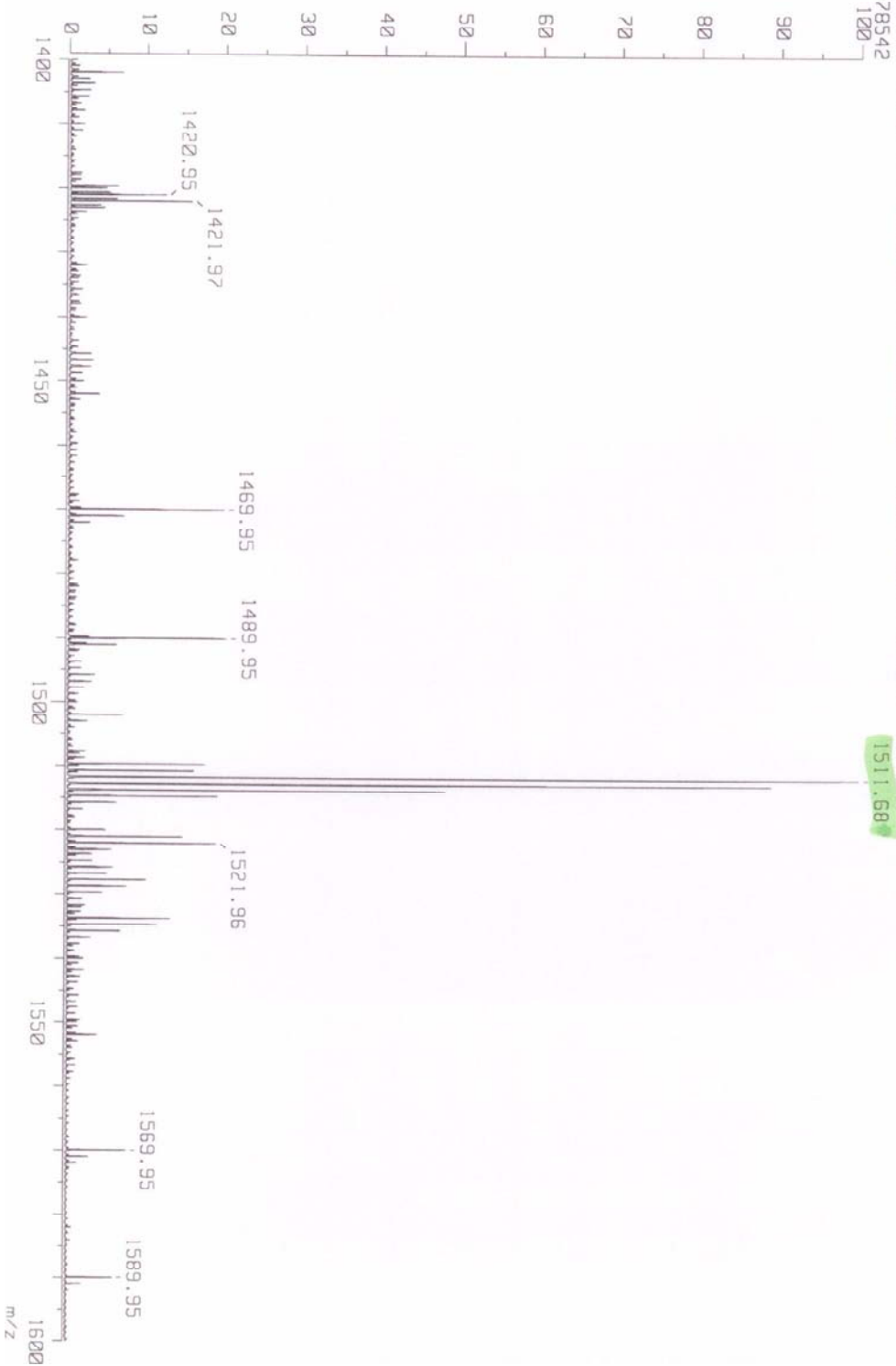
Spectrum Type : Normal Ion [FF-Linear]

RT : 6.53 min Scan# : (9,40)

BP : m/z 1511.6808 Int. : 32.12

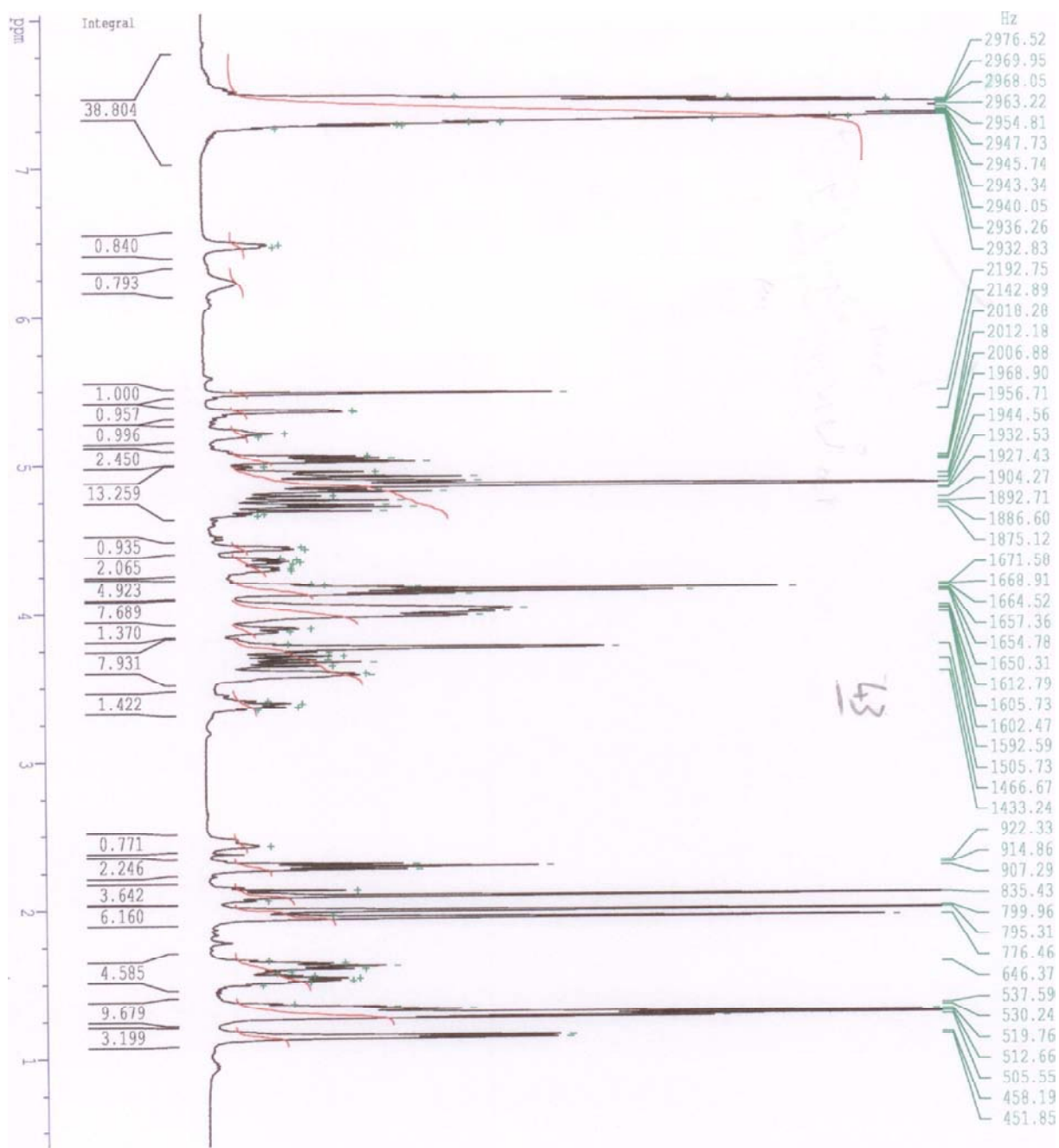
Output m/z range : 1400.0000 to 1600.0000 Cut Level : 0.00 %

10778542



42

16 MARS 2007

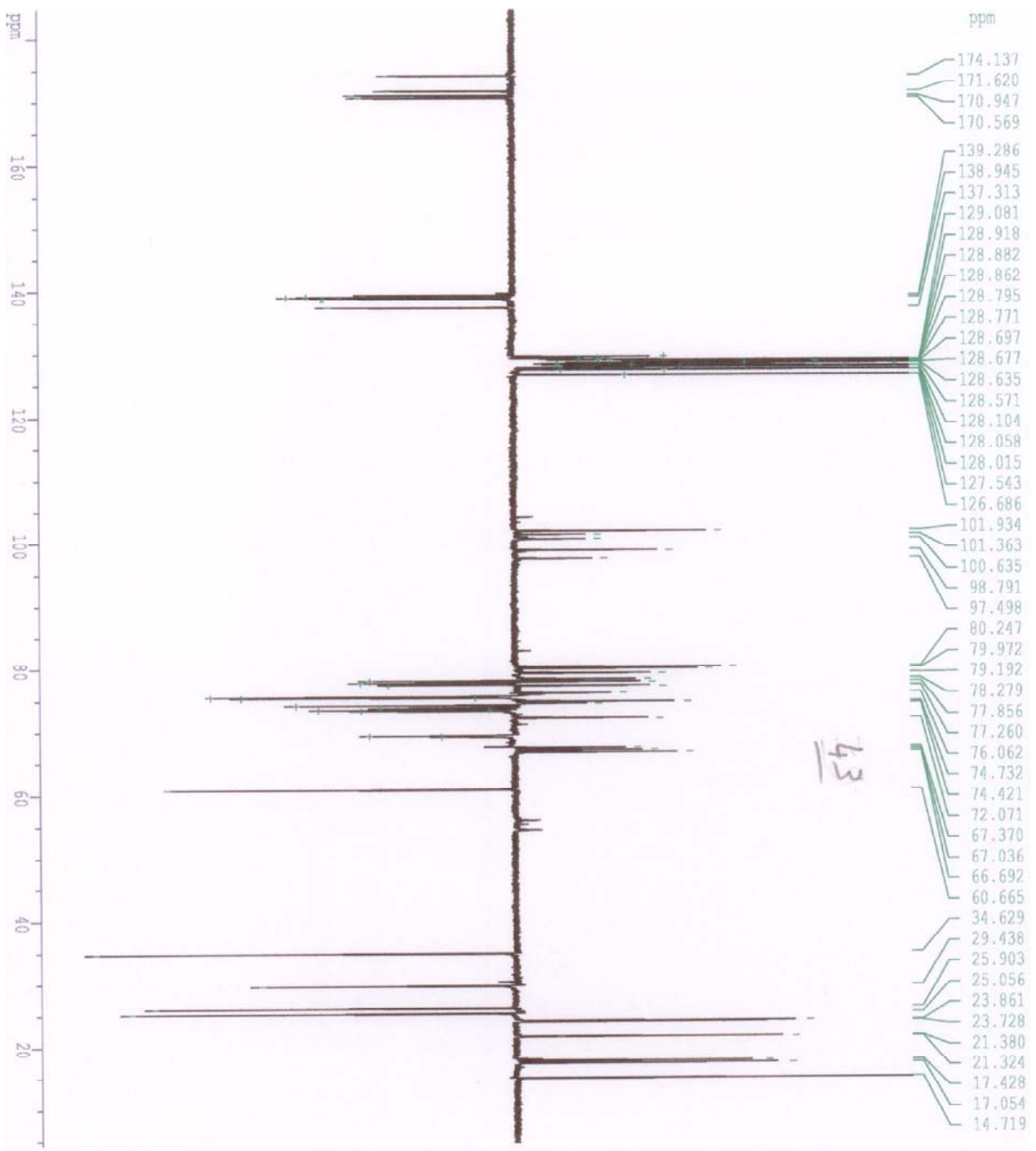


Current Data Parameters
NAME mayenimulti
EXNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 500000
Time_ 20.33
INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG zg30
TD 16384
SOLVENT CDCl3
NS 16
DS 2
SWH 4006.410 Hz
FIDRES 0.24532 Hz
AQ 2.041731 sec
RG 32
DM 124.800 usec
DE 4.50 usec
TE 300.0 K
D1 0.10000000 sec
P1 9.50 usec
DE 4.50 usec
SFO1 400.131206 MHz
NUC1 1H
P11 -1.00 dB

F1 - Processing parameters
SI 16384
SF 400.1305000 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 0.10

1D NMR plot parameters
CX 22.00 cm
FLP 8.034 ppm
F1 3214.61 Hz
F2 0.399 ppm
F2 159.63 Hz
PPMCK 0.34704 ppm/cm
HZCM 138.86276 Hz/cm



Current Data Parameters

NAME	rayeulm1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	500000
Time	20.58
INSTRUM	spect
PROBHD	5 mm 1H/13C
PULPROG	zgpg2
TD	65536
SOLVENT	MeOH
NS	4096
DS	4
SWH	24154.596 Hz
FIDRES	0.368576 Hz
AQ	1.3566452 sec
RG	2298.8
DM	20.700 usec
DE	4.50 usec
TE	300.0 K
PI	17.00 usec
P2	34.0 usec
DELTA	0.0000108 sec
D20	0.00714003 sec
PI12	17.50 dB
D1	1.29999995 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1317000 MHz
NPC2	1H
PI2	120.00 dB
D13	0.0000300 sec
SFO1	100.627964 MHz
NPC1	13C
PL1	0.00 dB
DE	4.50 usec

F2 - Processing parameters

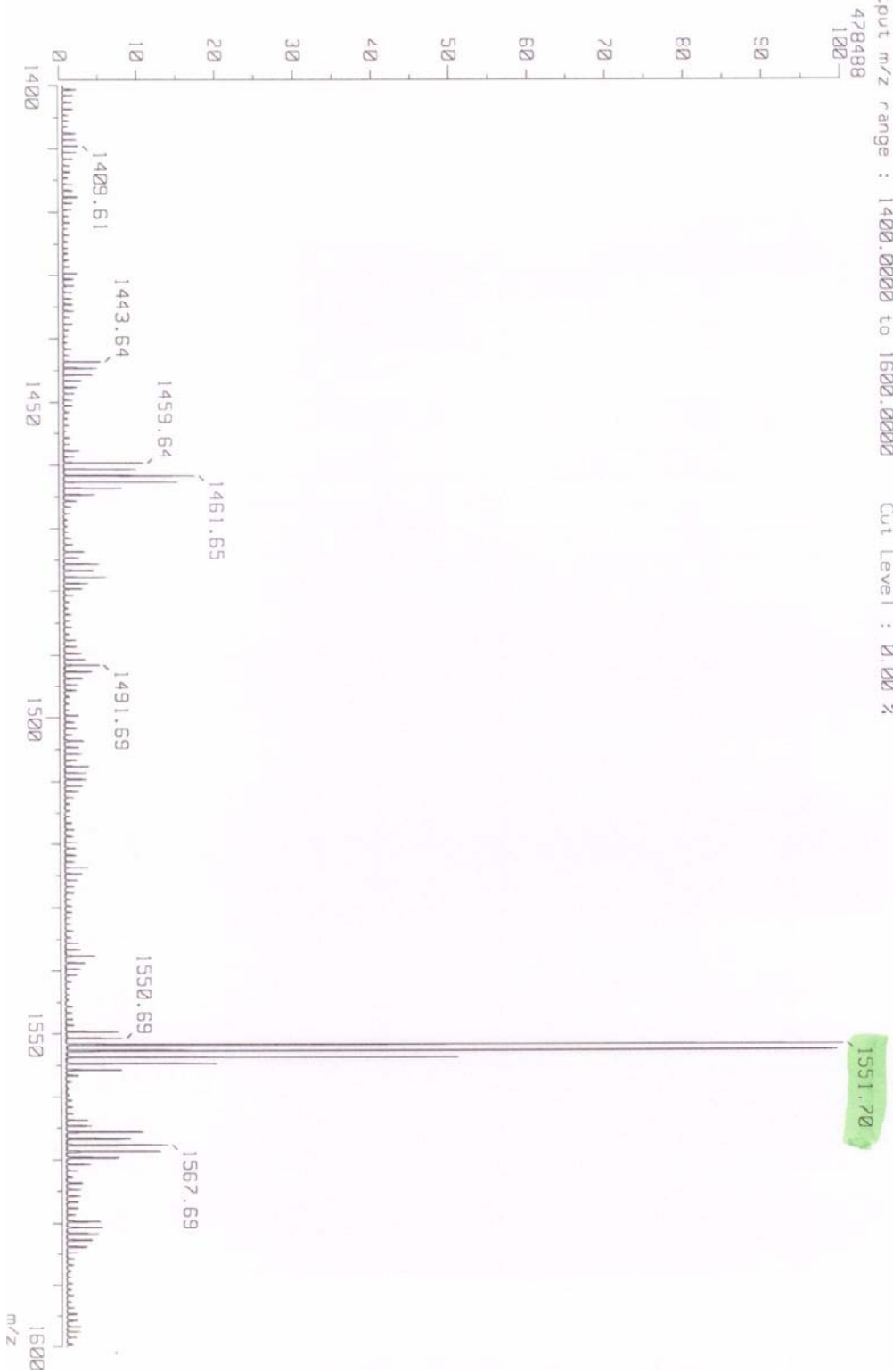
SI	65536
SP	100.617250 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	0.30

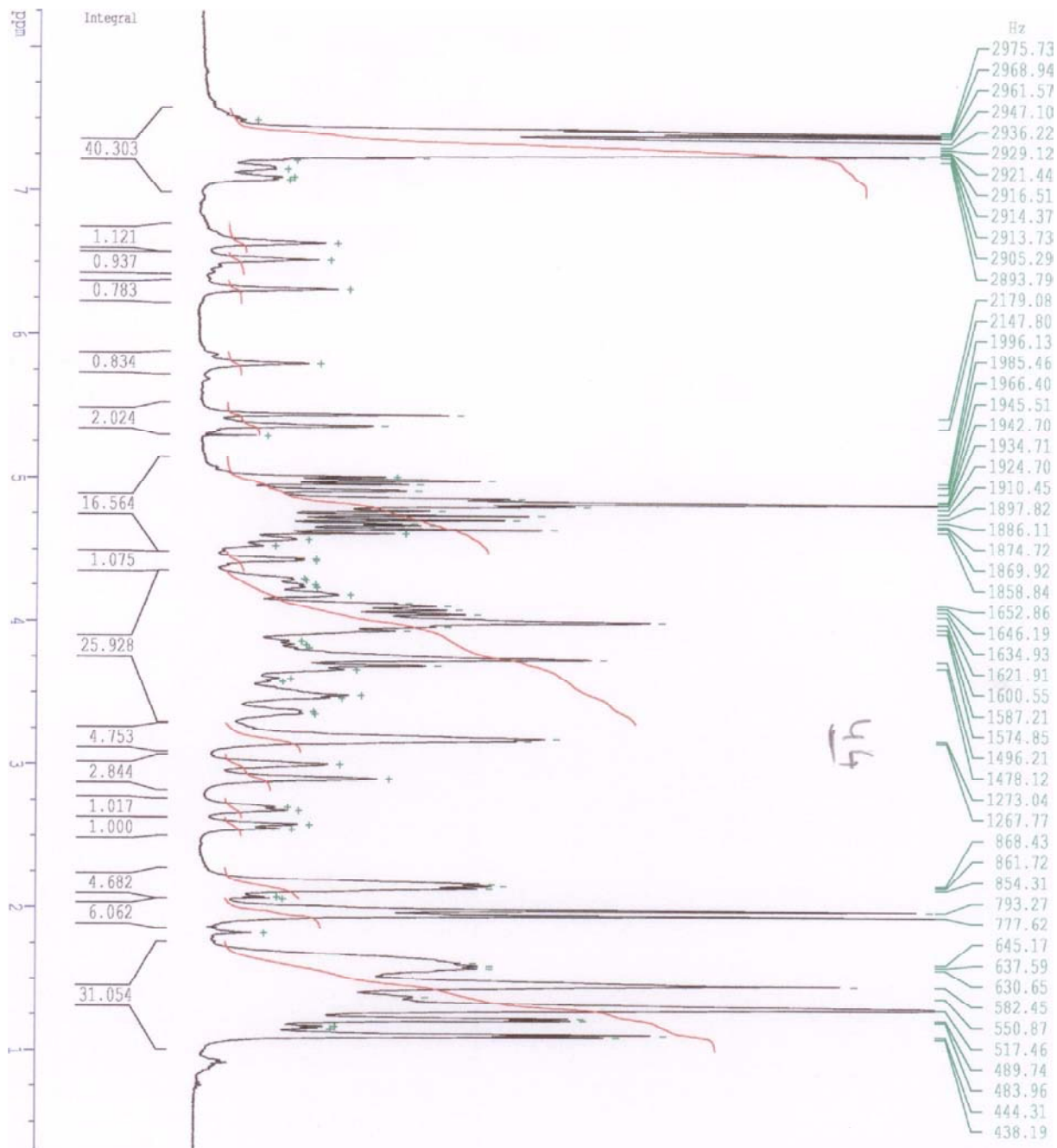
1D NMR plot parameters

CX	22.00 cm
F1P	181.602 ppm
F1	18573.32 Hz
F2P	4.312 ppm
F2	433.61 Hz
FEPCW	8.19501 ppm/cm
HZCW	824.52263 Hz/cm

43

[Mass Spectrum]
Data : COLLOT-MC454-FRB+-NB3-Na-HR0 Date : 26-Feb-2007 18:47
Sample: -
Note : -
Inlet : Direct Ion Mode : FRB+
Spectrum Type : Normal Ion [EF-Linear]
Scan# : 7
RT : 1.67 min
BP : m/z 1551.6390 Int. : 45.63
Output m/z range : 1400.0000 to 1600.0000 Cut Level : 0.00 %
478488



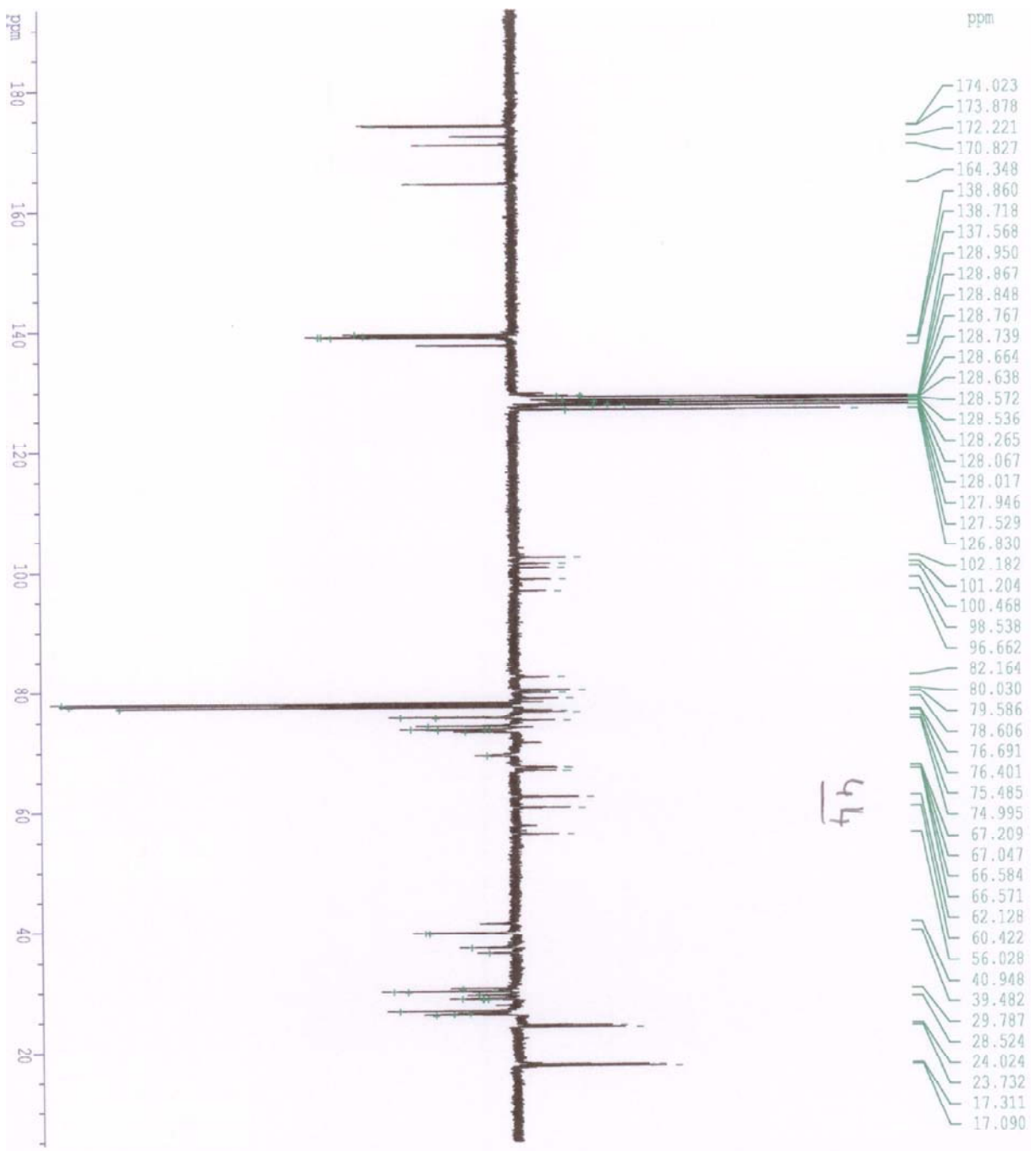


Current Data Parameters
 NAME mayenmulti
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 500000
 Time_ 20.57
 INSTRUM spect
 PROSD 5 mm 1H/13C
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 4006.410 Hz
 FIDRES 0.24652 Hz
 AQ 2.047731 sec
 RG 40.3
 DW 124.800 usec
 DE 4.50 usec
 TE 300.0 K
 D1 0.10000000 sec
 p1 9.50 usec
 DE 4.50 usec
 SFO: 400.119206 MHz
 HUC: 1H
 PL1 -3.00 dB

F2 - Processing parameters
 SI 16384
 SF 400.1100000 MHz
 PCWD EM
 SSB 0
 LB 0.00 Hz
 GB 0
 FC 0.10

1D NMR plot parameters
 CX 22.00 cm
 F1P 8.254 ppm
 F1 3102.53 Hz
 F2P 0.236 ppm
 F2 118.62 Hz
 PPMQCM 0.36169 ppm/cm
 HZCM 144.72282 Hz/cm



Current Data Parameters
NAME mayenimiliti
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 500000
Time 21.24
INSTRUM spect
PROBHD 5 mm 1H/13C
PULPROG jmod2.php
TD 65536
SOLVENT CDCl3
NS 4096
DS 4
SHE 2415.590 Hz
FIDRES 0.368570 Hz
AQ 1.356452 sec
RG 1625.5
TM 20.700 usec
DE 4.50 usec
TE 300.0 K
P1 17.00 usec
P2 34.0 usec
DELTA 0.0000108 sec
D20 0.00714000 sec
P112 17.50 dB
D112 1.29999993 sec
CDEPRG2 waltz16
PCPD2 100.00 usec
SFO2 400.131700 MHz
NUC2 1H
P12 120.00 dB
D13 0.0000308 sec
SFO1 100.627964 MHz
NUC1 13C
P11 0.00 dB
DE 4.50 usec

F2 - Processing parameters
SI 65536
SF 100.617290 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.30

1D NMR plot parameters
CX 22.00 cm
F1P 193.301 ppm
F1 19448.59 Hz
F2P 4.512 ppm
F2 453.97 Hz
FPCMH 8.58134 ppm/cm
FZCM 863.39166 Hz/cm

44

[Mass Spectrum]

Data : COLLECT-MC501-FRB+-NBR-NR-hr0 Date : 04-May-2007 14:05

Sample: -

Note: -

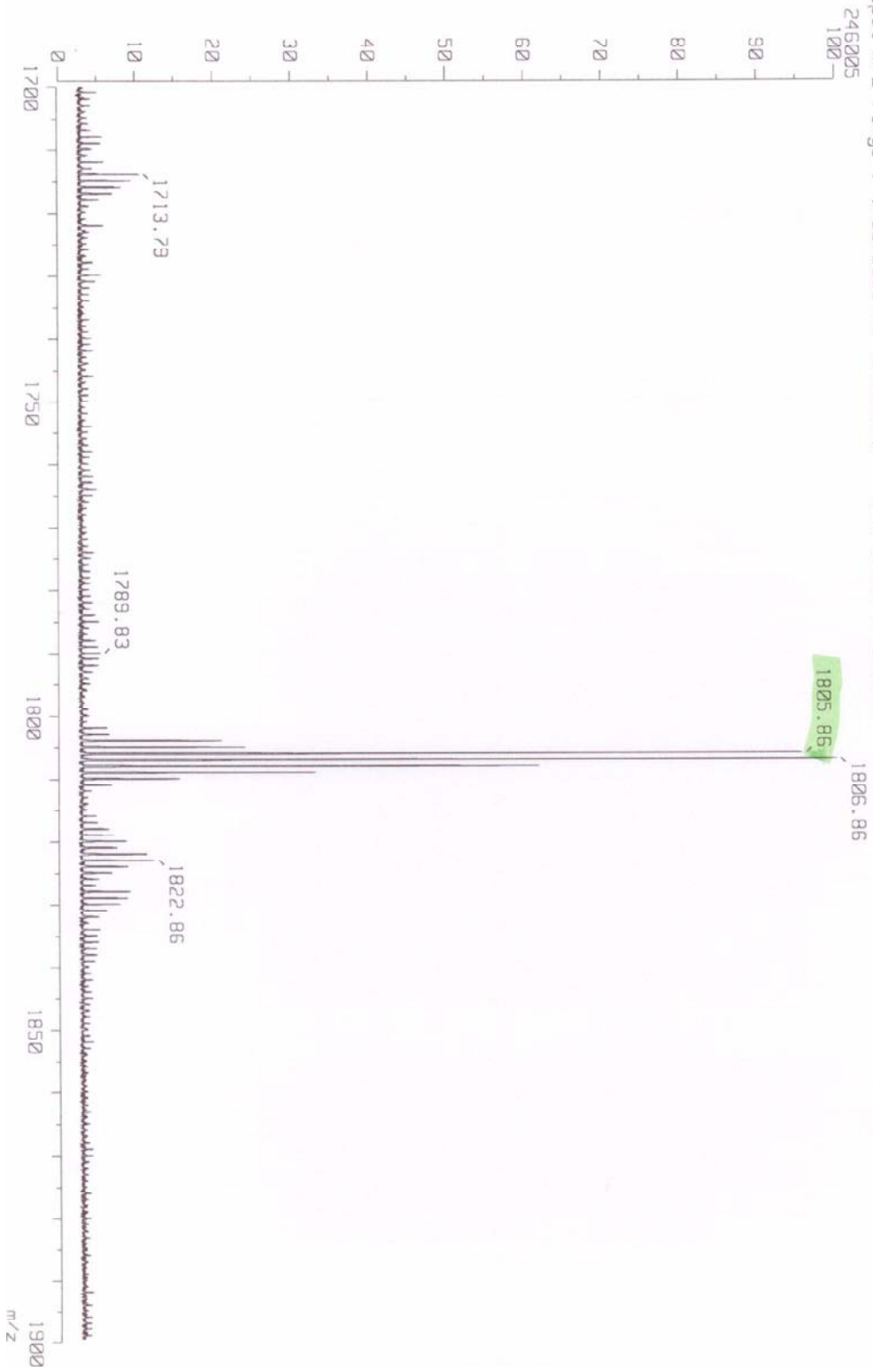
Inlet: Direct Ion Mode: FRB+

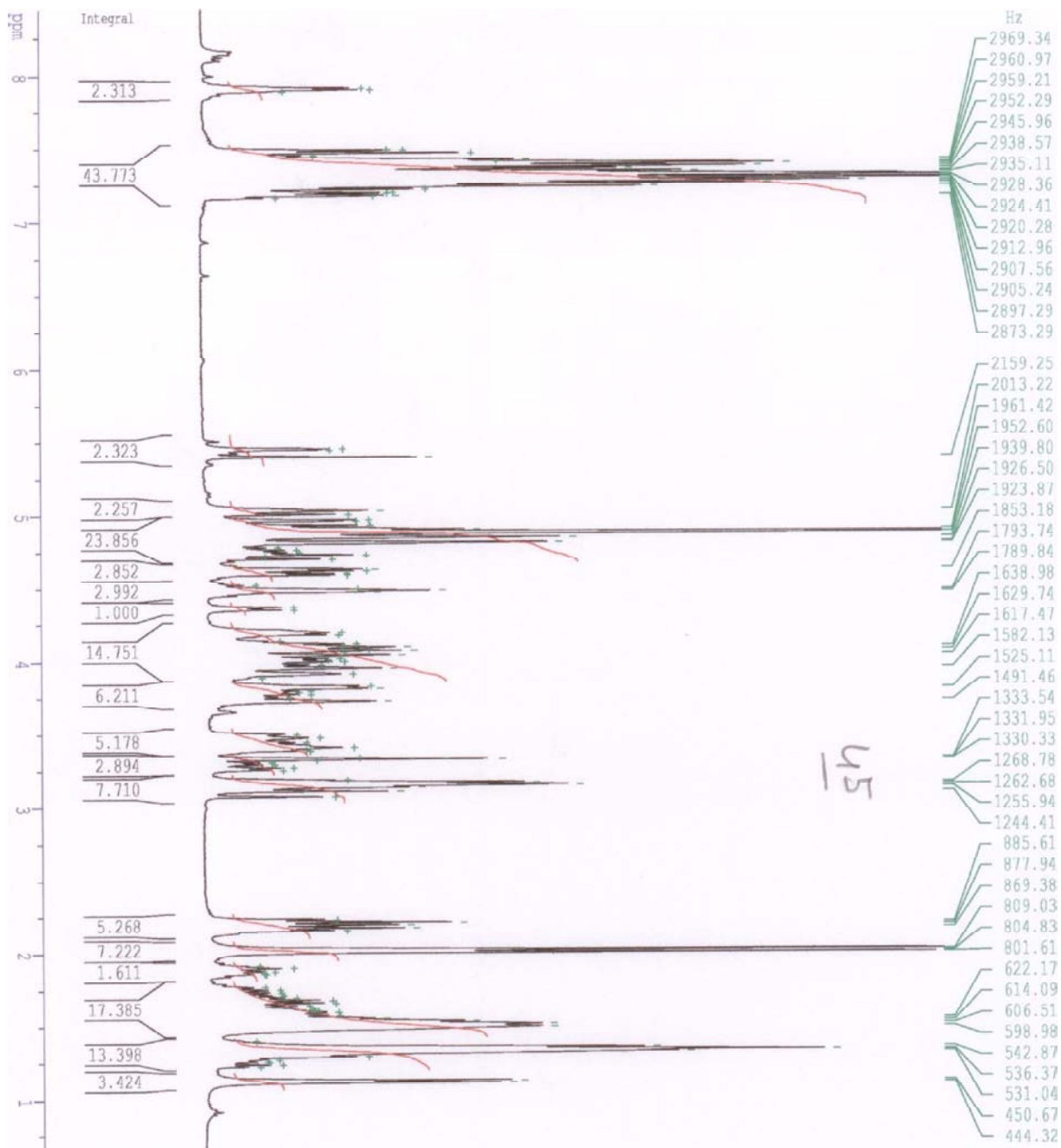
Spectrum Type: Normal Ion [EF-Linear]

RT: 7.51 min Scan#: (30,35)

BP: m/z 1806.8635 Int.: 3.91

Output m/z range: 1700.0000 to 1900.0000 Cut Level: 0.00 %





Current Data Parameters

NAME mayenimul

EXPNO 1

PROCNO 1

F2 - Acquisition Parameters

Date_ 5/06/03

Time 14.12

INSTRUM spect

PROBHD 5 mm 1H/13C

PULPROG zg30

TD 16384

SOLVENT CDCl3

NS 16

DS 2

SWH 4006.410 Hz

FIDRES 0.244522 Hz

AQ 2.0417731 sec

RG 32

DM 124.8000 usec

DE 4.50 usec

TE 300.0 K

D1 0.10000000 sec

E1 9.50 usec

DE 4.50 usec

SFO1 400.139206 MHz

NUC1 1H

EL1 -3.00 dB

F2 - Processing parameters

SI 16384

SE 400.1300000 MHz

KCM EX

SSB 0

LB 0.00 Hz

GB 0

PC 0.10

1D NMR plot parameters

CX 22.00 cm

F1P 3.443 ppm

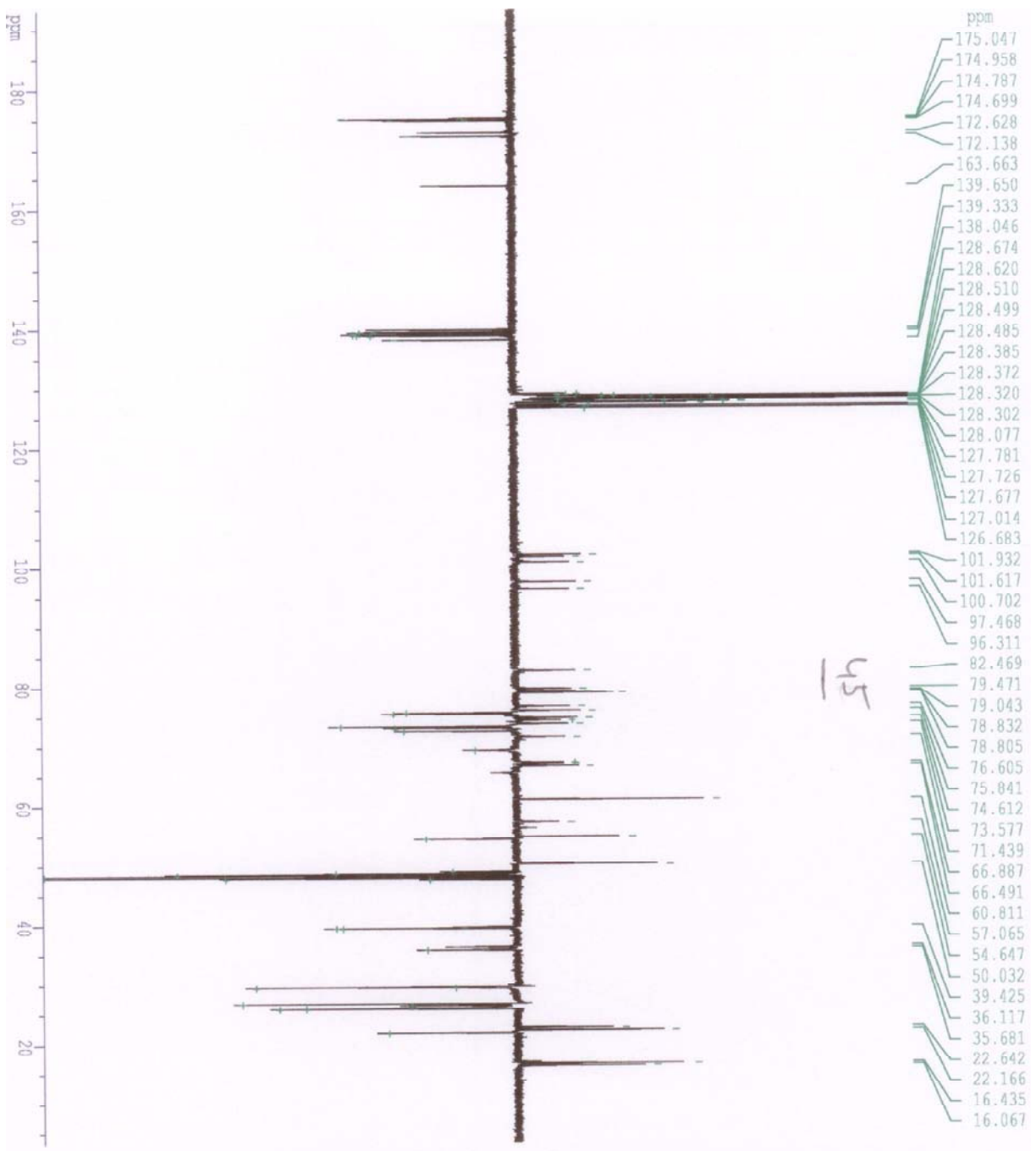
F1 3378.38 Hz

F2P 0.647 ppm

F2 259.02 Hz

PPMCM 0.35436 ppm/cm

HZCM 141.78893 Hz/cm



ppm

175.047
174.958
174.787
174.699
172.628
172.138
163.663
139.650
139.333
138.046
128.674
128.620
128.510
128.499
128.485
128.385
128.372
128.320
128.302
128.077
127.781
127.726
127.677
127.014
126.683
101.932
101.617
100.702
97.468
96.311
82.469
79.471
79.043
78.832
78.805
76.605
75.841
74.612
73.577
71.439
66.887
66.491
60.811
57.065
54.647
50.032
39.425
36.117
35.681
22.642
22.166
16.435
16.067

ppm

180
160
140
120
100
80
60
40
20

Current Data Parameters

NAME	mayhem1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	5/06/00
Time	17.48
INSTRUM	spect
PROBHD	5 mm 1H/13C
PULPROG	jmod2.php
TD	65536
SOLVENT	CDCl3
NS	16384
DS	4
SWH	2415.590 Hz
FIDRES	0.368570 Hz
AQ	1.356452 sec
RG	2580.3
DM	20.700 usec
DE	4.50 usec
TE	300.0 K
PI	17.00 usec
P2	34.0 usec
DELTA	0.0000108 sec
D20	0.00714000 sec
PI12	17.50 dB
D1	1.2999995 sec
CPDPRG2	waltz16
PCPD2	100.00 usec
SFO2	400.1317006 MHz
NUC2	1H
PL2	120.00 dB
D13	0.0000300 sec
SFO1	100.6237964 MHz
NUC1	13C
PL1	0.00 dB
DE	4.50 usec

F2 - Processing parameters

SI	65536
SF	100.617290 MHz
WDM	EX
SSB	0
LB	0.30 Hz
GB	0
PC	0.30

1D NMR plot parameters

CX	22.00 cm
F1P	193.205 ppm
F1	19498.86 Hz
F2P	3.212 ppm
F2	323.14 Hz
PPMCM	8.53605 ppm/cm
HZCM	868.39650 Hz/cm

[Mass Spectrum]

Data : COLLOT-MC506-FRB+ NBr-Na HR0 Date : 04-May-2027 14:50

Sample: -

Note: -

Inlet : Direct

Ion Mode : FRB+

Spectrum Type : Normal Ion [EF-Linear]

RT : 9.89 min Scan# : (39,45)

BP : m/z 1838.8486 Int. : 25.92

Output m/z range : 1700.0000 to 1900.0000 Cut Level : 0.00 %

45

