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The UDP-Gal*p* mutase catalyzed isomerization: Synthesis and Evaluation of 1,4-anhydro-β-D-galactopyranose and its [2.2.2] methylene homologue

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Methyl α-D-galactopyranoside (2 g, 10.3 mmol) and camphor-10-sulfonic acid (30 mg, 0.13 mmol) were suspended in anhydrous chloroform (150 ml). Distilled benzaldehyde dimethyl acetal (2 ml, 14.2 mmol) was added dropwise to this suspension. The reaction mixture (initially a suspension) was distilled at 65 °C for 2 h. The distillate (*ca.* 60 ml) was collected as a mixture of chloroform and methanol. The residue (pale yellow solution) was neutralized by addition of triethylamine (1 ml, 7 mmol), washed with water (50 ml) and concentrated *in vacuo* to give a yellow solid. This solid was then washed with hexanes (20 ml) and EtOAc (20 ml) to give a white solid (2.8 g, 100%). Based on NMR and TLC analysis, the sample was free of any other impurities and was used without further purification in the next step. For analytical purposes a fraction of the sample was purified by column chromatography on silica gel (ethyl acetate–ethanol, 11:1) and crystallized very slowly as fine white needles from hot water on storage at 4 °C. R_f 0.4 (ethyl acetate–ethanol, 9:1); mp 166-168 °C (lit.,[82] 171.0-171.5 °C, lit.,[83] 168.9-170.5 °C); $[\alpha]_D^{25}$ +133.9 (*c* 1 in $CHCl_3$), (lit.,[82] +141, *c* 0.59 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 3566m sharp (hydrogen bonded OH), 2910m (C-H), 2840 (OC-H), 1950w, 1870w, 1810w, 1730w (overtone, comb, Ar), 1602w, 1496w (C-C, Ar), 1454m sharp (CH_2), 1144m, 1090vs, 1072vs, 1042vs, 980s; δ_H ($CDCl_3$) 2.12 (2H, br. s, O*H*-2 and O*H*-3), 3.41 (3H, s, -OCH_3), 3.66 (1H, app. d, *J* 1.3, 5-H), 3.84 (1H, dd, $J_{3,2}$ 9.9 and $J_{3,4}$ 3.2, 3-H), 3.88 (1H, dd, $J_{2,3}$ 9.9 and $J_{2,1}$ 3.1, 2-H), 4.04 (1H, dd, $J_{6a,6b}$ 12.6 and $J_{6a,5}$ 1.8, 6a-H), 4.22 (1H, dd, $J_{4,3}$ 3.2 and $J_{4,5}$ 1.2, 4-H), 4.24 (1H, dd, $J_{6b,6a}$ 12.6 and $J_{6b,5}$ 1.5, 6b-H), 4.88 (1H, d, $J_{1,2}$ 3.1, 1-H), 5.51 (1H, s, C*H*Ph), 7.30-7.33 (3H, m, *meta*- and *para*-Ph), 7.43-7.46 (2H, m, *ortho*-Ph); δ_C ($CDCl_3$) 55.7 (CH_3, -OCH_3), 62.7 (CH, C-5), 69.4 (CH_2, C-6), 69.7 and 69.8 (each CH, C-2 or C-3), 76.0 (CH, C-4), 100.3 (CH, C-1), 101.3 (CH, *C*HPh), 126.3 (2xCH, *meta*-Ph), 128.3 (2xCH, *ortho*-Ph), 129.2 (CH, *para*-Ph), 137.6 (C, Ph); *m/z* (70 ev, EI) 282 (29%, M^+), 251 (10, M-OMe), 179 (33, M-$C_4H_7O_3$), 133 (31) and 107 (100, OBn); HRMS (ESI): found M^+ 282.1102, $C_{14}H_{18}O_6$ requires M^+ 282.1103.

Methyl 3,4-*O*-benzylidene-α-D-galactopyranosides 6&7

Methyl α-D-galactopyranoside (2.91 g, 15 mmol) was added to a mixture of benzaldehyde dimethyl acetal (2.25 ml, 15.2 mmol) and *p*-toluenesulfonic acid (14.55 mg, 0.08 mmol) in anhydrous DMF (14.5 ml). The suspension was rotated at 60-70 °C on a rotary evaporator under a moderate vacuum to remove the methanol generated in the reaction. After 2 h, 4 Å molecular sieves (*ca.* 20) were added and the reaction mixture refluxed in an oil bath under nitrogen for 18 h. The resulting mixture was filtered, concentrated *in vacuo* and neutralised with solid sodium carbonate (20 mg) and diluted with water (50 ml). The solution was extracted with ethyl acetate (2 x 100 ml). The organic extracts were washed with brine (25 ml), dried over anhydrous sodium sulfate, evaporated *in vacuo* and purified by silica gel (pre-treated with triethylamine) column chromatography (EtOAc-EtOH, 9:1). Without attempting a quantitative recovery, the first fraction (R_f 0.7) was identified as a diastereomeric mixture of **6** and **7**. HRMS (ESI): found $(M+Na)^+$ 305.1017, $C_{14}H_{18}O_6$ requires $(M+Na)^+$ 305.1001. The ratio of diastereoisomers in $CDCl_3$ was determined by NMR spectroscopy, *exo*/*endo* 2.5/1. The second fraction (R_f 0.4) was identified as **5** (30% yield). Another unknown by-product (~ 5% yield, R_f 0.3) also formed and was separated from the reaction mixture under these conditions, HRMS (ESI^+): found 337.1251.

***Exo* 6**

δ_H ($CDCl_3$) 3.43 (3H, s, -OCH_3), 3.81 (1H, dd, $J_{6a,6b}$ 11.8 and $J_{6a,5}$ 4.2, 6a-H), 3.89 (1H, dd, $J_{2,3}$ 7.2 and $J_{2,1}$ 3.9, 2-H), 3.94 (1H, dd, $J_{6b,6a}$ 11.8 and $J_{6b,5}$ 6.6, 6b-H), 4.01 (1H, ddd, $J_{5,6b}$ 6.6, $J_{5,6a}$ 4.2 and $J_{5,4}$ 2.2, 5-H), 4.2 (1H, dd, $J_{4,3}$ 5.6 and $J_{4,5}$ 2.2, 4-H), 4.4 (1H, dd, $J_{3,2}$ 7.2 and $J_{3,4}$ 5.6, 3-H), 4.83 (1H, d, $J_{1,2}$ 3.9, 1-H), 6.11 (1H, s, C*H*Ph), 7.31-7.37 (5H, m, Ph); δ_C ($CDCl_3$) 55.8 (CH_3, -OCH_3), 62.8 (CH_2, C-6), 67.8 and 68.1 (each CH, C-5 or C-2), 74.2 (CH, C-4), 77.8 (CH, C-3), 98.9 (CH, C-1), 103.5 (CH, *C*HPh), 126.2-129.3 (all CH, Ph), 138.6 (C, Ph).

***Endo* 7**

δ_H ($CDCl_3$) 3.45 (3H, s, -OCH_3), 3.81-3.97 (3H, m, 6a-H, 2-H and 6b-H), 4.11 (1H, ddd, $J_{5,6b}$ 6.7, $J_{5,6a}$ 4.3 and $J_{5,4}$ 2.3, 5-H), 4.28 (1H, dd, $J_{4,3}$ 6.6 and $J_{4,5}$ 2.4, 4-H), 4.36 (1H, dd, $J_{3,2}$ ~ 6.6 and $J_{3,4}$ 6.6, 3-H), 4.78 (1H, d, $J_{1,2}$ 3.9, 1-H), 5.83 (1H, s, C*H*Ph), 7.38-7.47 (5H, m, Ph); δ_C ($CDCl_3$) 55.7 (CH_3, -OCH_3), 62.7 (CH_2, C-6), 68.4 and 69.2 (each CH, C-5 or C-2), 75.5 (CH, C-4), 76.2 (CH, C-3), 98.3 (CH, C-1), 104.4 (CH, *C*HPh), 126.2-129.3 (all CH, Ph), 129.7 (C, Ph).

Methyl 2,3-di-*O*-benzyl-4,6-*O*-(*S*)-benzylidene-α-D-galactopyranoside 8

Methyl 4,6-*O*-benzylidene-α-D-galactopyranoside **5** (4.5 g, 15.9 mmol) was added to a stirred suspension of sodium hydride (2.5 g, 60% dispersion in oil, 62.5 mmol) in anhydrous DMF (60 ml) at room temperature. After stirring for 30 min, the reaction mixture was cooled to 0 °C and tetrabutylammonium iodide (1.85 g, 4.9 mmol) was added, followed by benzyl bromide (6 ml, 49 mmol) in a dropwise fashion. The resulting suspension was stirred at room temperature for 18 h. The reaction was then quenched by the addition of methanol (50 ml) and evaporated to dryness. Water (100 ml) was added and the resulting mixture was extracted with DCM (3 × 100 ml). The combined organic extracts were successively washed with water (40 ml) and brine (20 ml), dried (anhydrous Na_2SO_4) and filtered. The filtrate was concentrated *in vacuo* to give a yellow solid which was crystallised from methanol to afford **8** (6.27 g, 85% yield) as white blocks (CCDC 287123‡, X-ray diffraction data). R_f 0.24 (hexanes-EtOAc, 7:3); mp 175-176 °C (lit.,[84] 174-175 °C); $[\alpha]_D^{25}$ +76 (*c* 1 in $CHCl_3$), (lit.,[84] +77, *c* 2.4 in $CHCl_3$); [Found: C, 72.60; H, 6.44%; $(M+Na)^+$ 462.2055. $C_{28}H_{30}O_6$ requires C, 72.70; H, 6.54%; $(M+Na)^+$ 462.2042]; ν_{max} ($CHCl_3$)/cm^{-1} 2910m (C-H), 2862m (OC-H), 1950w, 1870w, 1810w, 1730w (overtone, comb, Ph), 1602w, 1454m sharp (CH_2), 1361m, 1151m, 1096vs, 1049vs, 986s; δ_H ($CDCl_3$) 3.40 (3H, s, -OCH_3), 3.60 (1H, app. br. d, *J* 1.2, 5-H), 4.00 (1H, dd, $J_{2,3}$ 10.1 and $J_{2,1}$ 3.5, 2-H), 4.02 (1H, dd, $J_{6a,6b}$ 12.4 and $J_{6a,5}$ 1.8, 6a-H), 4.08 (1H, dd, $J_{3,2}$ 10.1 and $J_{3,4}$ 3.5, 3-H), 4.19 (1H, dd, $J_{4,3}$ 3.5 and $J_{4,5}$ 0.9,

4-H), 4.23 (1H, dd, $J_{6b,6a}$ 12.4 and $J_{6b,5}$ 1.6, 6b-H), 4.70 and 4.90 (AB, each 1H, d, $J_{A,B}$ 12.0, CH_AH_BPh), 4.76 and 4.85 (AB, each 1H, d, $J_{A,B}$ 12.3, CH_AH_BPh), 4.79 (1H, d, $J_{1,2}$ 3.5, 1-H), 5.41 (1H, s, C*H*Ph), 7.25-7.44 (15H, m, 3xPh); δ_C ($CDCl_3$) 55.6 (CH_3, -OCH_3), 62.5 (CH, C-5), 69.5 (CH_2, C-6), 72.2 and 73.9 (each CH_2, 2xCH_2Ph), 74.9 (CH, C-4), 75.5 (CH, C-3), 76.1 (CH, C-2), 99.6 (CH, C-1), 101.2 (CH, *C*HPh), 126.4, 127.6, 127.7, 127.8, 128.1, 128.2, 128.4, 128.9 (all CH, 3xPh), 137.9, 138.7, 138.9 (each C, 3xPh); *m/z* (MeOH, EI) 462 (1%, M^+), 430 (8, M-OMe), 371 (26), 177 (52), 121 (37), 91 (100).

Crystallographic Data

Crystal data for methyl-2,3-di-*O*-benzyl-4,6-*O*-(S)-benzylidene-α-D-galactopyranoside **8** (CCDC 287123): C28H30O6, M = 462.52, monoclinic, space group $P2_1$, a = 11.497(Å), b = 9.1335(12) (Å), c = 11.666(2) (Å), β = 101.688(2)°, U = 1199.6(3) (Å)^3, Z=2, D_c =1.280 Mg/m^3, μ(Mo-$K\alpha$) = 0.089 mm^{-1}, T = 150(2) K. 2758 unique reflections (R_{int} = 0.035). Final R_1 [2731 $I > 2\sigma(I)$] = 0.0409, wR_2 (all data) = 0.101. This was recorded on a Bruker SMART1000 CCD area-detector diffractometer.

Methyl 2,3,6-tri-*O*-benzyl-α-D-galactopyranoside 9

To a round bottom flask containing the benzylidene acetal **8** (2 g, 4.3 mmol) and 3Å molecular sieves (*ca.* 40), was added anhydrous THF (60 ml) followed by sodium cyanoborohydride (2.84 g, 43 mmol). The resulting suspension was stirred at room temperature until the sodium cyanoborohydride had completely dissolved, it was then cooled to 0 °C. Hydrogen chloride in diethyl ether (2 M) was added (*ca*. 20 ml) until gas evolution had ceased. After 10 min at room temperature TLC (hexanes-EtOAc, 1:1) indicated that all the starting material had been consumed. The mixture was diluted with DCM (50 ml), filtered and washed successively with cold water (2 x 30 ml), a saturated solution of $NaHCO_3$ (20 ml) and dried over $MgSO_4$. The sample was filtered and concentrated *in vacuo.* The resulting syrup was purified by column chromatography on silica (hexanes-EtOAc, 4:1) to give **9** (1.4 g, 70%) as a pale yellow oil. R_f 0.56 (hexanes-EtOAc, 3:2); $[\alpha]_D^{25}$ +30.9 (*c* 1.8 in $CHCl_3$), (lit.,[85] +34, c 3 in $CHCl_3$), (lit.,[86] +33.4, c 1.67 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 3570m (hydrogen bonded OH in 5-membered ring), ~3500sh,w (hydrogen bonded OH in 6-membered ring), 2912s (CH), 2872s (OC-H), 1951w, 1870w, 1810w, 1730w (overtone, comb, Ph), 1603w, 1496w (C-C, Ar), 1454m sharp (CH_2), 1354m, 1090vs, 1049vs; δ_H ($CDCl_3$) 2.56 (1H, app. t, $J_{OH\text{-}4,4} \sim J_{OH\text{-}4,5}$ 1.3, 4-O*H*), 3.35 (3H, s, -OCH_3), 3.63 (1H, dd, $J_{6a,6b}$ 10 and $J_{6a,5}$ 6.3, 6a-H), 3.70 (1H, dd, $J_{6b,6a}$ 10 and $J_{6b,5}$ 5.4, 6b-H), 3.84$_1$ (1H, obscured dd, $J_{3,2}$ 10 and $J_{3,4}$ 2.9, 3-H), 3.84 (1H, obscured dd, $J_{2,3}$ 10 and $J_{2,1}$ 1.9, 2-H), 3.86 (1H, app. br. t, J 5.9, 5-H), 4.01 (1H, ddd, $J_{4,3}$ 2.9 and $J_{4,5} \sim J_{4,4\text{-}OH}$ 1.3, 4-H), 4.51 and 4.56 (AB, each 1H, d, $J_{A,B}$ 11.9, CH_AH_BPh), 4.63 and 4.78 (AB, each 1H, d, $J_{A,B}$ 12.1, CH_AH_BPh), 4.64 (1H, obscured d, $J_{1,2}$ 1.9, 1-H), 4.67 and 4.76 (AB, each 1H, d, $J_{A,B}$ 11.6, CH_AH_BPh), 7.27-7.32 (15H, m, 3xPh); δ_C ($CDCl_3$) 55.4 (CH_3, -OCH_3), 68.2 (CH, C-4), 68.4 (CH, C-5), 69.7 (CH_2, C-6), 72.8, 73.6, 73.7 (each CH_2, 3xCH_2Ph), 75.8 (CH, C-3), 77.7 (CH, C-2), 98.7 (CH, C-1), 127.7, 127.9, 128.1, 128.4$_6$, 128.5 (all CH, 3xPh), 138.1, 138.3, 138.5 (each C, 3xPh); HRMS (ESI): found $(M+Na)^+$ 487.2052. $C_{28}H_{32}O_6$ requires $(M+Na)^+$, 487.2097.

Methyl 2,3,4-tri-*O*-benzyl-α-D-galactopyranoside 10

Compound **10** was separated as a by-product in the synthesis of **9**. Column chromatography on silica (hexanes-EtOAc, 4:1) gave **10** (0.2 g, 10%) as a colourless oil. R_f 0.3 (hexanes-EtOAc, 2:3); $[\alpha]_D^{25}$ +1.8 (*c* 1 in $CHCl_3$), (lit.,[75] +4, *c* 1.38 in $CHCl_3$), (lit.,[87] +7, *c* 1 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 3592m (free OH), 3500sh,w (hydrogen bonded OH in 6-membered ring), 2912m (CH), 2900m (OC-H), 1950w, 1870w, 1810w, 1730w (overtone, comb, Ph), 1496w (C-C, Ar), 1454m sharp (CH_2), 1350m, 1090vs, 1048vs; δ_H ($CDCl_3$) 1.6 (1H, br. s, 6-O*H*), 3.25 (3H, s, -OCH_3), 3.44 (1H, ddd, $J_{6a,6b}$ 15, $J_{6a,5}$ 6.5 and $J_{6a,6\text{-}OH}$ 2, 6a-H), 3.66 (1H, obscured dd, $J_{5,6a} \sim J_{5,6b}$ 6.5 and $J_{5,4}$ 0, 5-H), 3.68 (1H, obscured ddd, $J_{6b,6a}$ 15, $J_{6b,5}$ 6.5 and $J_{6b,6\text{-}OH}$ 1, 6b-H), 3.83 (1H, br. d, $J_{4,3}$ 2.8 and $J_{4,5}$ 0, 4-H), 3.90 (1H, dd, $J_{3,2}$ 10 and $J_{3,4}$ 2.8, 3-H), 4.01 (1H, dd, $J_{2,3}$ 10 and $J_{2,1}$ 3.6, 2-H), 4.59 and 4.93 (AB, each 1H, d, $J_{A,B}$ 11.6, CH_AH_BPh), 4.65 and 4.80 (AB, each 1H, d, $J_{A,B}$ 12.1, CH_AH_BPh), 4.66 (1H, obscured d, $J_{1,2}$ 3.4, 1-H), 4.71 and 4.85 (AB, each 1H, d, $J_{A,B}$ 11.8, CH_AH_BPh), 7.23-7.37 (15H, m, 3xPh); δ_C ($CDCl_3$) 55.4 (CH_3, -OCH_3), 62.5 (CH_2, C-6), 70.3 (CH, C-5), 73.6$_6$, 73.7$_0$, 74.5 (each CH_2, 3xCH_2Ph), 75.1 (CH, C-4), 76.6 (CH, C-2), 79.2 (CH, C-3), 98.9 (CH, C-1), 127.6, 127.7, 127.8, 128.1, 128.2, 128.4, 128.5$_1$,128.5$_5$, 128.7 (all CH, 3xPh), 138.2, 138.5, 138.8 (each C, 3xPh); HRMS (ESI): found $(M+Na)^+$ 487.2107. $C_{28}H_{32}O_6$ requires $(M+Na)^+$, 487.2097.

Methyl 2,3-di-*O*-benzyl-α-D-galactopyranoside 11

Compound **11** was separated as a by-product in the synthesis of **9**. Column chromatography on silica (hexanes-EtOAc, 4:1) gave **11** (0.1 g, 6%) as a colourless oil. R_f 0.1 (hexanes-EtOAc, 1:1), R_f 0.38 (EtOAc); $[\alpha]_D^{25}$ +43.0 (*c* 0.74 in $CHCl_3$), (lit.,[88] +47, *c* 3.7 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 3578m br (hydrogen bonded OH in 5-membered ring), 2905m (CH), 2850m (OC-H), 1954w, 1882w, 1810w, 1730w (overtone, comb, Ph), 1602w, 1496w (C-C, Ar), 1454m sharp (CH_2), 1355s, 1141s, 1092vs, 1048vs; δ_H ($CDCl_3$) 3.39 (3H, s, -OCH_3), 3.69-3.73 (2H, m, $J_{5,6a}$ 2.4, 5-H and 6a-H), 3.78 (1H, dd, $J_{2,3}$ 9.8 and $J_{2,1}$ 3.1, 2-H), 3.82 (1H, dd, $J_{3,2}$ 9.8 and $J_{3,4}$ 3.1, 3-H), 3.85 (1H, dd, $J_{6b,6a}$ 12.9 and $J_{6b,5}$ 7.0, 6b-H), 4.0 (1H, dd, $J_{4,3}$ 3.1 and $J_{4,5}$ 2.0, 4-H), 4.68 and 4.83 (AB, each 1H, d, $J_{A,B}$ 12.5, CH_AH_BPh), 4.71 (1H, d, $J_{1,2}$ 3.1, 1-H), 4.71 and 4.83 (AB, each 1H, d, $J_{A,B}$ 11.7, CH_AH_BPh), 7.29-7.39 (10H, m, 2xPh); δ_C ($CDCl_3$) 55.4 (CH_3, -OCH_3), 63.1 (CH_2, C-6), 68.8 (CH, C-5), 69.2 (CH, C-4), 72.9, 73.5 (each CH_2, CH_2Ph), 75.5 (CH, C-3), 77.3 (CH, C-2), 98.6 (CH, C-1), 127.8, 127.9, 128.0, 128.1, 128.4, 128.6 (all CH, 2xPh), 138.0, 138.2 (each C, 2xPh); HRMS (ESI): found $(M+Na)^+$ 397.1632. $C_{21}H_{26}O_6$ requires $(M+Na)^+$ 397.1627.

Methyl 4,6-*O*-(*R*)-benzylidene-α-D-glucopyranoside 13

This compound was prepared using the same procedure as **5** (see above) from methyl-α-D-glucopyranoside (8.0 g; 41 mmol) to get a yellow solid, which was recrystallised from EtOAc to produce **13** as a colourless lath (10.6 g, 92%). R_f 0.6 (EtOAc-MeOH, 21:4); mp 165-166 ºC (crystallised from H_2O), (lit.,[83] 165.4-166.8 ºC, lit.,[89] 156-158 ºC); $[\alpha]_D^{25}$ +114.1 (*c* 1.06, in $CHCl_3$), (lit.,[89] +111.5, *c* 2 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 3592m sharp (free OH), 2937m (C-H), 2842m (OC-H), 1954w, 1882w, 1810, 1730w (overtone, comb, Ar), 1602w, 1456m sharp (CH_2), 1141m, 1067vs, 1044vs, 993vs (lit.,[90] 3574, 3462, 3005, 2941, 1467); δ_H ($CDCl_3$) 2.72 and 3.11 (each 1H, br. s, O*H*-2 and O*H*-3), 3.48 (3H, s, -OCH_3), 3.51 (1H, app. t, $J_{4,3} \sim J_{4,5}$ 9.2, 4-H), 3.65 (1H, dd, $J_{2,3}$ 9.2 and $J_{2,1}$ 4, 2-H), 3.76 (1H, dd, $J_{6a,5}$ 10 and $J_{6a,6b}$ 9.6, 6a-H), 3.83 (1H, ddd, $J_{5,6a}$ 10, $J_{5,4}$ 9.2 and $J_{5,6b}$ 3.6, 5-H), 3.95 (1H, app. t, $J_{3,4} \sim J_{3,2}$ 9.2, 3-H), 4.31 (1H, dd, $J_{6b,6a}$ 9.6 and $J_{6b,5}$ 3.6, 6b-H), 4.82 (1H, d, $J_{1,2}$ 4, 1-H), 5.55 (1H, s, C*H*Ph), 7.36-7.40 (3H, m, *meta*- and *para*-Ph), 7.48-7.52 (2H, m, *ortho*-Ph); δ_C ($CDCl_3$) 55.3 (CH_3, -OCH_3), 62.0 (CH, C-5), 68.6 (CH_2, C-6), 71.5 (CH, C-3), 72.6 (CH, C-2), 80.6 (CH, C-4), 99.4 (CH, C-1), 101.6 (CH, *C*HPh), 126.0, 128.0, 129.0 (all CH, Ph), 136.7 (C, Ph); HRMS (ESI): found $(M+Na)^+$ 305.0983. $C_{14}H_{18}O_6$ requires $(M+Na)^+$ 305.1001.

Methyl 2,3-di-*O*-benzyl-4,6-*O*-(*R*)-benzylidene-α-D-glucopyranoside 14

This compound was prepared using the same procedure as **8** (see above) from **13** (6.0 g; 21 mmol). The solid obtained was crystallised from MeOH to give **14** as a white solid (8.3 g, 84%). R_f 0.39 (hexanes-EtOAc, 3:2); mp 94-95 ºC (crystallised from MeOH), (lit.[91] 93 ºC (crystallised from aq-EtOH)); $[\alpha]_D^{25}$ –29.6 (*c* 1.31 in $CHCl_3$), (lit.,[92] –30, *c* 0.25 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 2934m (C-H), 2869 (OC-H), 1954w, 1883w, 1811w, 1730w (overtone, comb, Ar), 1602w, 1496w (C-C, Ar), 1454m sharp (CH_2), 1369s, 1087vs, 1053vs, 995vs; δ_H ($CDCl_3$) 3.42 (3H, s, -OCH_3), 3.57 (1H, dd, $J_{2,3}$ 9.2 and $J_{2,1}$ 3.6, 2-H), 3.62 (1H, app. t, $J_{4,3} \sim J_{4,5}$ 9.2, 4-H), 3.72 (1H, app. t, $J_{6a,5} \sim J_{6a,6b}$ 10, 6a-H), 3.84 (1H, ddd, $J_{5,6a}$ 10 and $J_{5,6b}$ 4.8, 5-H), 4.06 (1H, app. t, $J_{3,2} \sim J_{3,4}$ 9.2, 3-H), 4.28 (1 H, dd, $J_{6b,6a}$ 10 and $J_{6b,5}$ 4.8, 6b-H), 4.61 (1H, d, $J_{1,2}$ 3.6, 1-H), 4.71 and 4.87 (AB, each 1H, d, $J_{A,B}$ 12.0, CH_AH_BPh), 4.85 and 4.93 (AB, each 1H, d, $J_{A,B}$ 11.4, CH_AH_BPh), 5.56 (1H, s, C*H*Ph), 7.30-7.41 (3H, m, *meta*- and *para*-Ph), 7.49-7.51 (2H, m, *ortho*-Ph); δ_C ($CDCl_3$) 55.8 (CH_3, -OCH_3), 62.7 (CH, C-5), 69.5 (CH_2, C-6), 74.2, 75.8 (each CH_2, *C*H_2Ph), 79.0 (CH, C-3), 79.6 (CH, C-2), 82.6 (CH, C-4), 99.7 (CH, C-1), 101.7 (CH, *C*HPh), 126.5, 128.0, 128.4, 128.5, 128.6, 128.7, 128.8, 128.9, 129.4 (all CH, 3xPh), 137.8, 138.6, 139.1 (each C, 3xPh); HRMS (ESI): found $(M+Na)^+$ 485.1929. $C_{28}H_{30}O_6$ requires $(M+Na)^+$ 485.1940.

Methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside 15

This compound was prepared using the same procedure as **9** (see above) from **14** (6.0 g; 13 mmol). The resulted syrup was purified by column chromatography on silica gel eluting with pet. ether-EtOAc (from 99:1 to 2:3), to yield **15** (5.0 g; 10.8 mmol; 83%). R_f 0.53 (hexanes-EtOAc, 1:1); $[\alpha]_D^{25}$ +15.1 (*c* 1.04 in $CHCl_3$), (lit.,[88] +14, *c* 1.1 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 3603m (free OH), 3500sh,w (hydrogen bonded OH in 6-membered ring), 2915s (CH), 2870s (OC-H), 1952w, 1882w, 1815w, ~1730w (overtone, comb, Ph), 1602m, 1496w (C-C, Ar), 1454m sharp (CH_2), 1363m, 1090vs, 1054vs; δ_H ($CDCl_3$) 2.37 (1H, br. s, 4-O*H*), 3.40 (3H, s, -OCH_3), 3.55 (1H, dd, $J_{2,3}$ 9.6 and $J_{2,1}$ 3.6, 2-H), 3.6 (1H, app. t, $J_{4,3} \sim J_{4,5}$ 9.2, 4-H), 3.68-3.74 (3H, m, 5-H , 6a-H and 6b-H), 3.80 (1H, app. t, $J_{3,2}$ 9.6 and $J_{3,4}$ 9.2, 3-H), 4.55 and 4.60 (AB, each 1H, d, $J_{A,B}$ 12.2, CH_AH_BPh), 4.64 (1H, d, $J_{1,2}$ 3.6, 1-H), 4.67 and 4.79 (AB, each 1H, d, $J_{A,B}$ 12.1, CH_AH_BPh), 4.75 and 5.02 (AB, each 1H, d, $J_{A,B}$ 11.4, CH_AH_BPh), 7.30-7.39 (15H, m, 3xPh); δ_C ($CDCl_3$) 55.2 (CH_3, -OCH_3), 69.3 (CH_2, C-6), 69.8 (CH, C-5), 70.6 (CH, C-4), 73.1, 73.5, 75.4 (each CH_2, 3x*C*H_2Ph), 79.5 (CH, C-2), 81.4 (CH, C-3), 98.1 (CH, C-1), 127.5$_4$, 127.5$_6$, 127.8, 127.8$_8$, 127.9$_3$, 128.1, 128.3, 128.4, 128.5 (all CH, 3xPh), 137.9, 138.0, 138.7 (each C, 3xPh); HRMS (ESI): found $(M^{\cdot}+Na)^+$ 487.2075. $C_{28}H_{32}O_6$ requires $(M^{\cdot}+Na)^+$ 487.2097.

Methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside 16

Compound **16** was a by-product in the synthesis of **15**, It was separated by column chromatography on silica gel eluting with pet. ether-EtOAc (from 99:1 to 2:3) as colourless oil (168 mg; 0.45 mmol; 3.5%). R_f 0.38 (hexanes-EtOAc, 1:1); mp 43-44 ºC (crystallised from H_2O), (lit.,[93] 53-54 ºC); δ_H ($CDCl_3$) 2.18 (1H, s, 6-O*H*), 3.38 (3H, s, -OCH_3), 3.51 (1H, dd, $J_{2,3}$ 9.6 and $J_{2,1}$ 3.6, 2-H), 3.53 (1H, obscured dd, $J_{4,5}$ 9.6 and $J_{4,3}$ 8.8, 4-H), 3.66 (1H, obscured ddd, $J_{5,4}$ 9.6, $J_{5,6a}$ 4 and $J_{5,6b}$ 2.8, 5-H), 3.70 (1H, obscured dd, $J_{6a,6b}$ 11.6 and $J_{6a,5}$ 4, 6a-H), 3.78 (1H, dd, $J_{6b,6a}$ 11.6 and $J_{6b,5}$ 2.8, 6b-H), 4.02 (1H, app. t, $J_{3,2}$ 9.6 and $J_{3,4}$ 8.8, 3-H), 4.57 (1H, d, $J_{1,2}$ 3.6, 1-H), 4.65 and 5.00 (AB, each 1H, d, $J_{A,B}$ 10.9, CH_AH_BPh), 4.67 and 4.81 (AB, each 1H, d, $J_{A,B}$ 12.1, CH_AH_BPh), 4.85 and 4.89 (AB, each 1H, d, $J_{A,B}$ 11.1, CH_AH_BPh), 7.29-7.38 (15H, m, 3xPh); δ_C ($CDCl_3$) 55.2 (-OCH_3), 61.9 (CH_2, C-6), 70.6 (CH, C-5), 73.5, 75.1, 75.8 (each CH_2, 3x*C*H_2Ph), 77.3 (CH, C-4), 79.9 (CH, C-2), 82.0 (CH, C-3), 98.2 (CH, C-1), 127.6, 127.89, 127.95, 127.97, 128.0, 128.1, 128.41, 128.47, 128.48 (all CH, 3xPh), 138.1, 138.7 (each C, 3xPh); HRMS (ESI): found $(M+Na)^+$ 487.2101. $C_{28}H_{32}O_6$ requires $(M+Na)^+$ 487.2097.

Methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside 17

Compound **17** was a by-product in the synthesis of **15**, It was separated as white solid (323 mg, 5.4%) by column chromatography (see above) followed by crystallisation from water. R_f 0.22 (EtOAc-hexanes, 1:1); HRMS (ESI): found $(M+Na)^+$ 397.1602, $C_{21}H_{26}O_6$ requires $(M+Na)^+$ 397.1627.

Methyl 2,3,6-tri-*O*-benzyl-α-D-*xylo*-4-hexulopyranoside 18

Dimethyl sulfoxide (DMSO) (1.08 ml; 15.1 mmol) was added to freshly distilled DCM (30 ml) and the solution was cooled to –78 ºC. Trifluoroacetic anhydride (TFAA) (1.52 ml; 10.8 mmol) was added dropwise to the cooled solution over 5 min period and allowed to react for 15 min. Methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside **15** (2.08 g; 4.48 mmol) dissolved in dry DCM (30 ml) was then added

dropwise over a 10 min period. The resulting solution was stirred for 8 h allowing the temperature to rise to –40 ºC whereupon Et_3N (2.12 ml; 15.1 mmol) was added. The reaction continued for other 13 h at rt before the organic phase was washed with water (40 ml). The organic layer was separated and the aqueous phase was extracted with DCM (3 x 40 ml). The combined organic phases were dried with $MgSO_4$, filtered and concentrated *in vacuo*. The resulting syrup was purified by silica gel column chromatography eluting with pet. ether-EtOAc (from 99:1 to 2:3). This yielded **18** as a clear oil (1.65 g, 80 %). R_f 0.44 (hexanes-EtOAc, 7:3); $[\alpha]_D^{25}$ +77.5 (*c* 0.97 in $CHCl_3$), (lit.,[77] +62º, *c* 1 in $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 2933s (CH), 2872s (OC-H), 1950w, 1880w, 1810w, 1730w (overtone, comb, Ph), 1736vs (C=O), 1496w (C-C, Ar), 1454m sharp (CH_2), 1367m, 1087vs, 1052vs; δ_H ($CDCl_3$) 3.50 (3H, s, -OCH_3), 3.68 (1H, dd, $J_{6a,6b}$ 10.8 and $J_{6a,5}$ 6.3, 6a-H), 3.81 (1H, dd, $J_{2,3}$ 10 and $J_{2,1}$ 3.5, 2-H), 3.91 (1H, dd, $J_{6b,6a}$ 10.8 and $J_{6b,5}$ 3.5, 6b-H), 4.29 (1H, dd, $J_{5,6a}$ 6.3 and $J_{5,6b}$ 3.5, 5-H), 4.44 (1H, d, $J_{3,2}$ 10, 3-H), 4.56 and 4.62 (AB, each 1H, d, $J_{A,B}$ 12, CH_AH_BPh), 4.68 and 4.87 (AB, each 1H, d, $J_{A,B}$ 12.1, CH_AH_BPh), 4.69 and 4.97 (AB, each 1H, d, $J_{A,B}$ 11.4, CH_AH_BPh), 4.81 (1H, d, $J_{1,2}$ 3.5, 1-H), 7.28-7.38 (3H, m, *meta*- and *para*-Ph), 7.41-7.45 (2H, m, *ortho*-Ph); δ_C ($CDCl_3$) 56.1 (CH_3, -OCH_3), 67.6 (CH_2, C-6), 72.7 (CH, C-5), 73.7, 74.0, 74.4 (each CH_2, 3xCH_2Ph), 80.0 (CH, C-2), 82.6 (CH, C-3), 98.4 (CH, C-1), 127.7, 127.8, 127.9, 128.0, 128.1, 128.35, 128.39, 128.5 (all CH, 3xPh), 137.7, 137.76, 137.82 (each C, 3xPh), 202.0 (C=O); HRMS (ESI): found $(M+Na)^+$ 485.1965. $C_{28}H_{30}O_6$ requires $(M+Na)^+$ 485.1940.

Enzyme Assay.[15-18]

The reactions were carried out in 100 mM MOPS buffer (pH 8.0), with fresh 20 mM sodium dithionite. The final volume of each reaction mixture was 30 μL. Initially, the enzyme concentration was adjusted for each different mutant to give a reasonable conversion (20-40%) within 2-3 min at 100 μM concentration (for example, wt UGM was used at a final concentration of 0.4 μM). Subsequent reactions, with varying substrate concentrations (5 μM to 5 mM) were carried out with the same enzyme concentration for all reactions. The time of each reaction was adjusted to have % conversion values between 30% and 40%. The reactions were quenched by the addition of 50 μL of *n*-butanol. The aqueous layer was removed and injected onto a Waters HPLC system. The column used was a Gemini 5 μ (C-18) column (Phenomenex), pre-equilibrated with 50 mM triethylammonium acetate (pH 6.9), 1.5% acetonitirile. The samples were eluted isocratically and absorbance readings were carried out at 262 nm.

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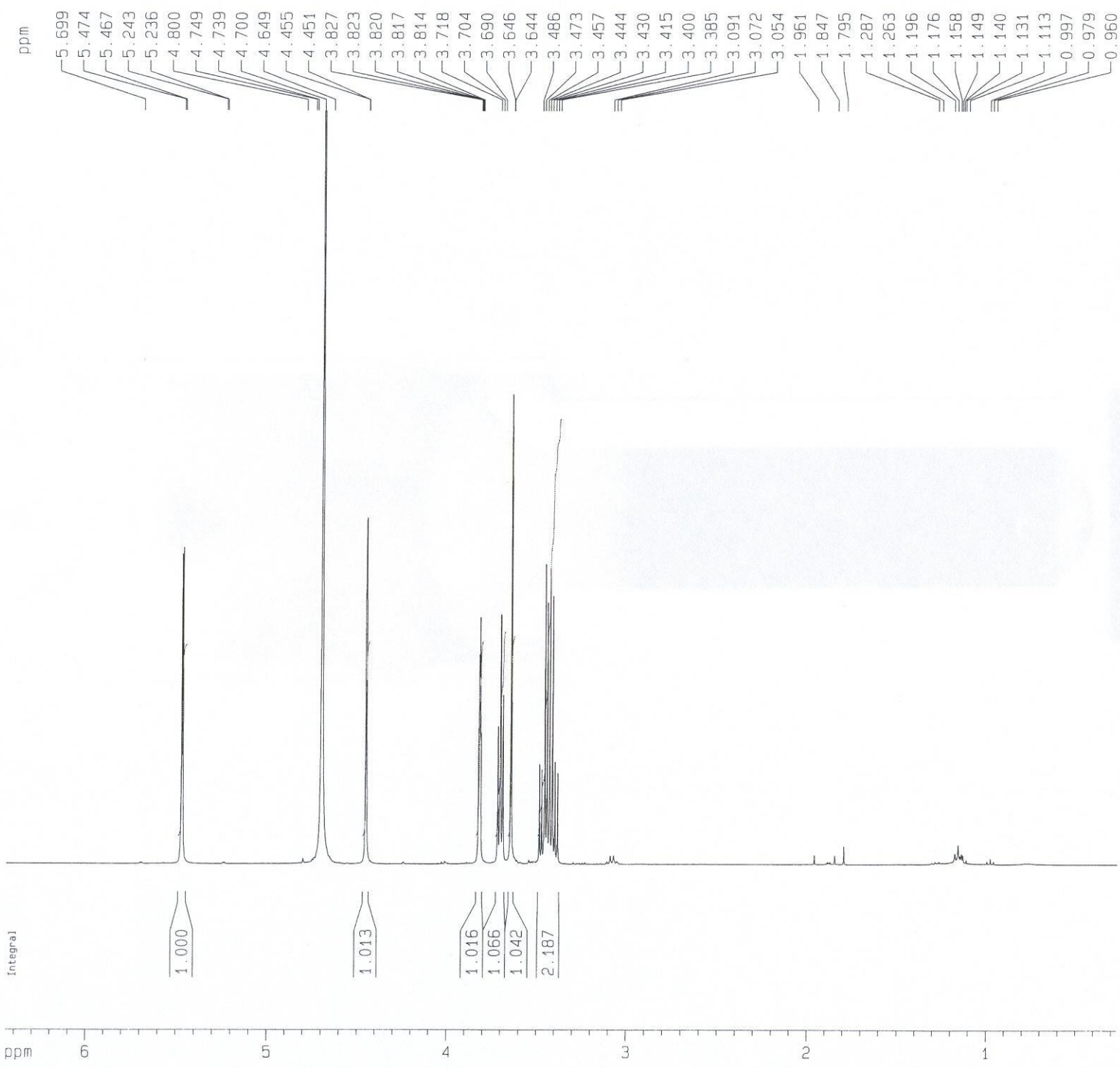

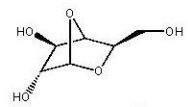

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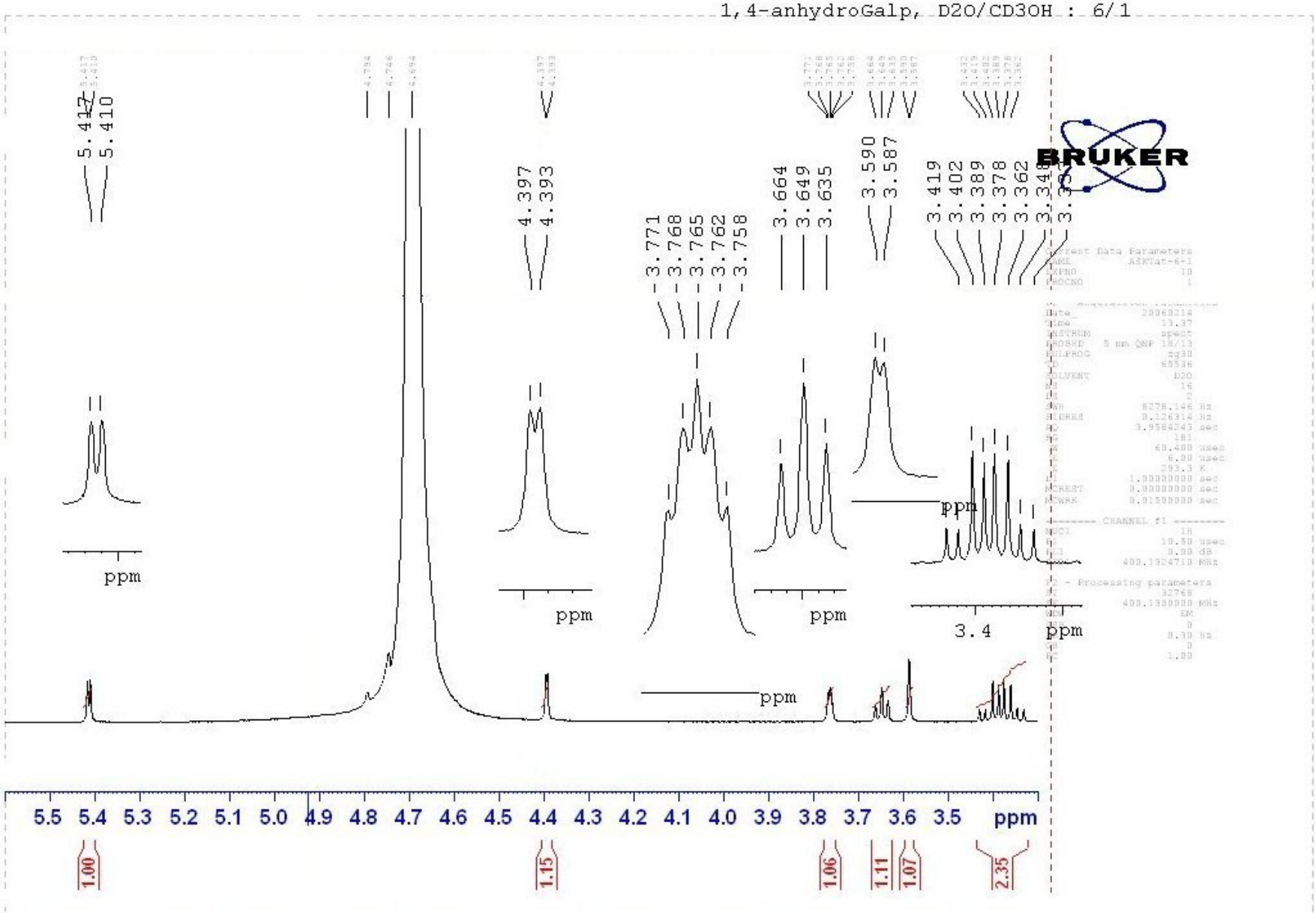
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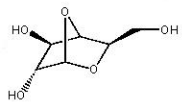

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BRUKER

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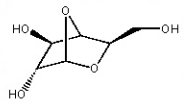
ASK4, Concentrated



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

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F2 - Processing parameters

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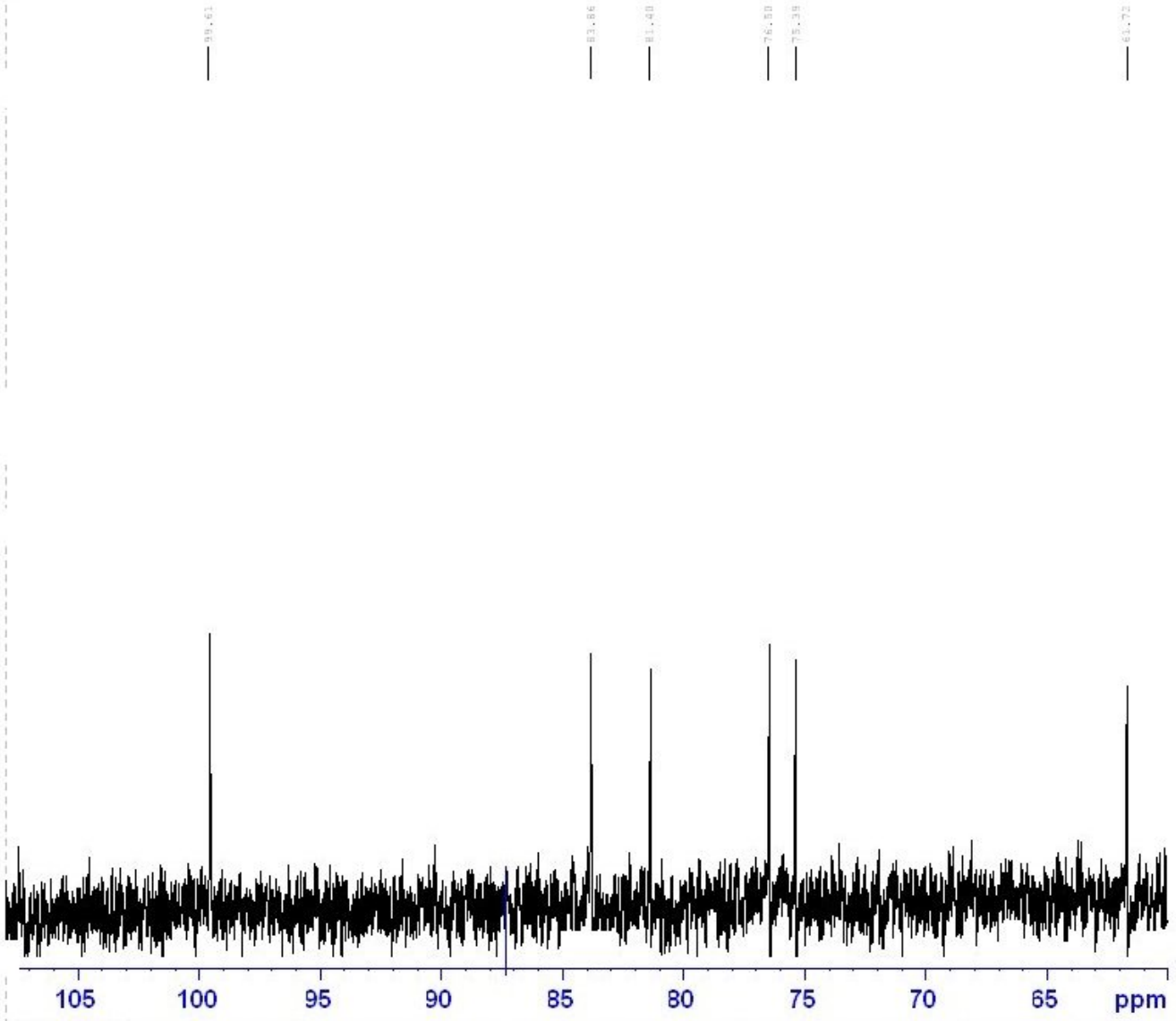

BRUKER

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======== CHANNEL f2 ========
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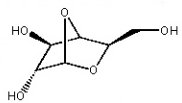
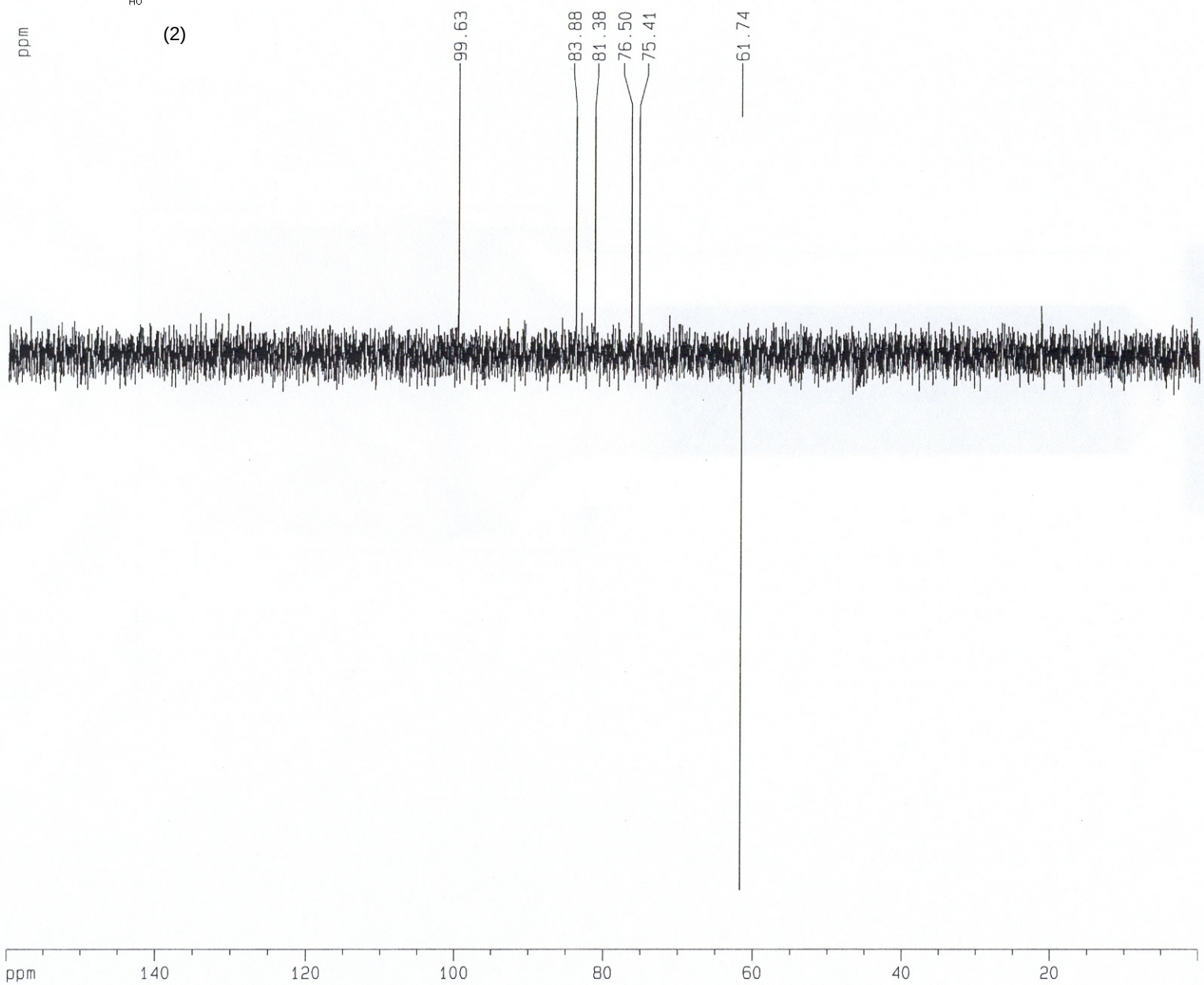
PL12              18.00 dB
PL13              21.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                32768
SF           100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```



(2)

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Current Data Parameters
NAME          tjf22_dept
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20040419
Time               12.57
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG          dept135
TD                65536
SOLVENT             D2O
NS                  256
DS                    4
SWH           23980.814 Hz
FIDRES         0.365918 Hz
AQ             1.3664756 sec
RG                16384
DW               20.850 usec
DE                6.00 usec
TE               294.7 K
CNST2        145.0000000
D1             2.00000000 sec
d2             0.00344828 sec
d12            0.00002000 sec
DELTA          0.00001034 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                 8.12 usec
p2                16.24 usec
PL1                0.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
P3                10.50 usec
p4                21.00 usec
PCPD2             80.00 usec
PL2                0.00 dB
PL12              18.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127690 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                20.00 cm
CY                 9.00 cm
F1P              160.000 ppm
F1             16098.04 Hz
F2P                0.000 ppm
F2                 0.00 Hz
PPMCM          8.00000 ppm/cm
HZCM         804.90216 Hz/cm
```
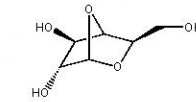
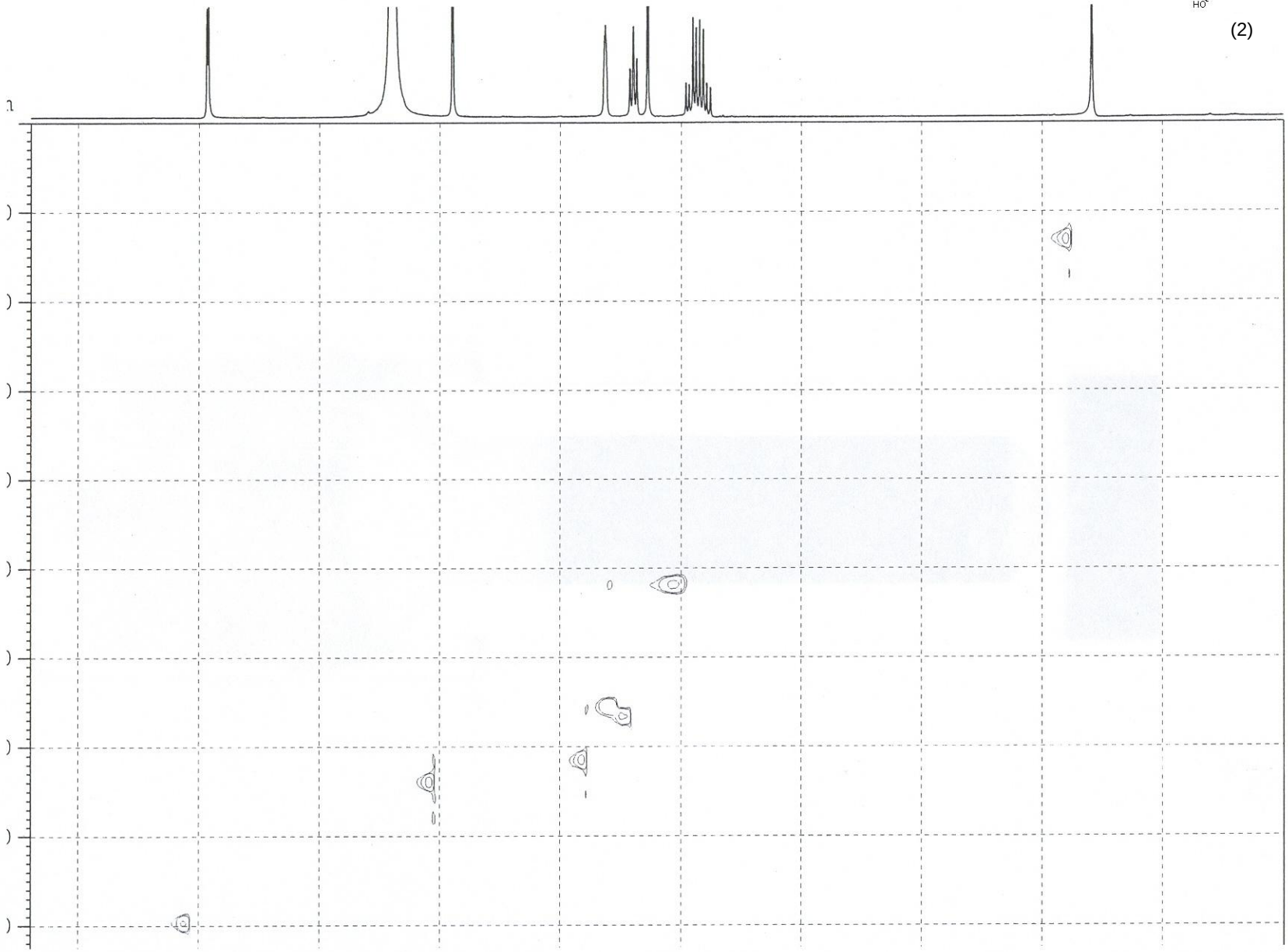
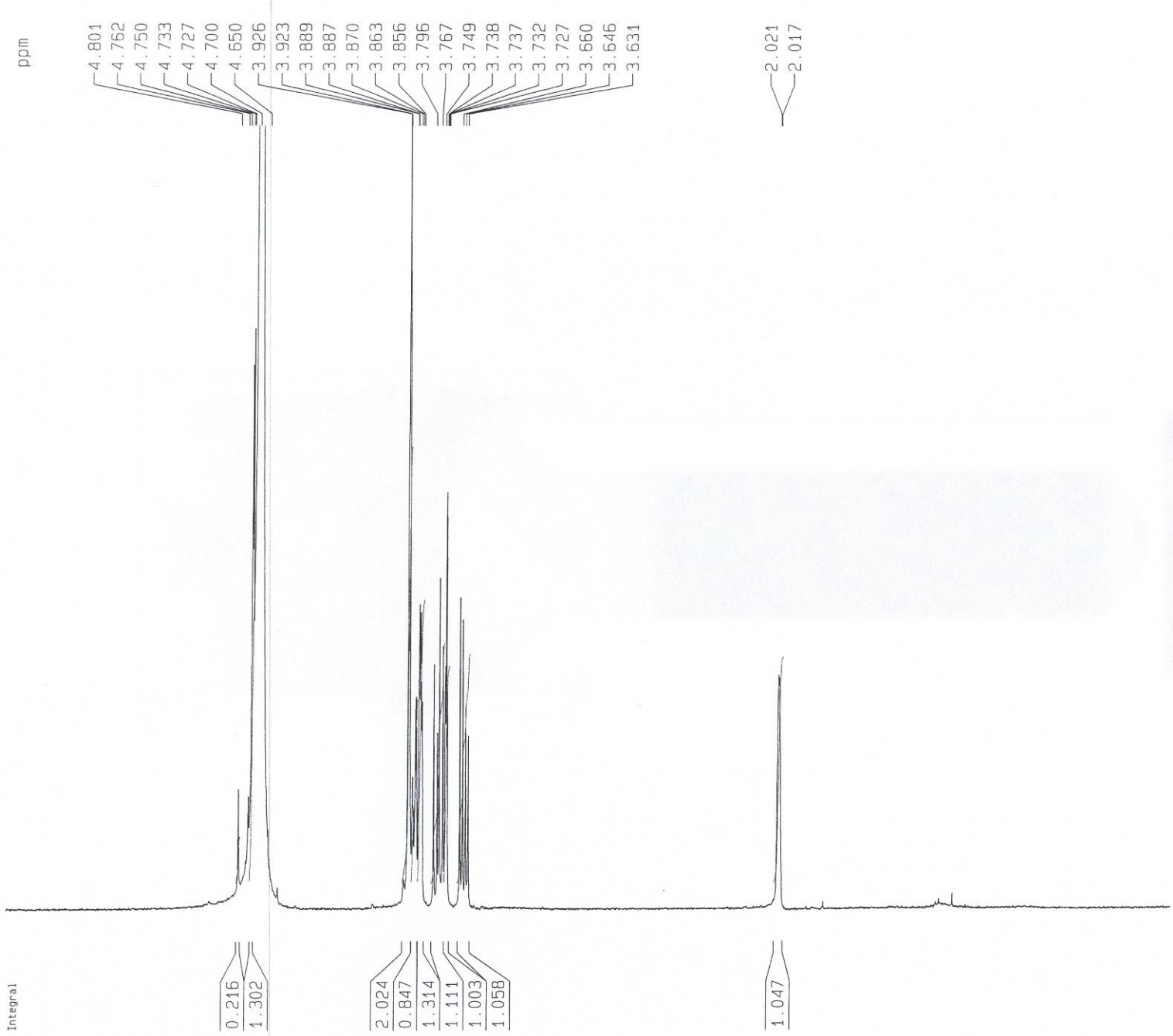
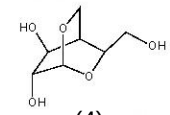



(2)







(4)

Current Data Parameters

NAME	tjf57f0to1c2
EXPNO	10
PROCNO	1

F2 - Acquisition Parameters

Date_	20040920
Time	12.09
INSTRUM	spect
PROBHD	5 mm QNP 1H/13
PULPROG	zg30
TD	65536
SOLVENT	D2O
NS	64
DS	2
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.9584243 sec
RG	256
DW	60.400 usec
DE	6.00 usec
TE	294.4 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

NUC1	1H
P1	10.50 usec
PL1	0.00 dB
SFO1	400.1324710 MHz

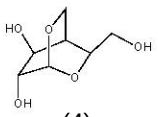
F2 - Processing parameters

SI	32768
SF	400.1299997 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

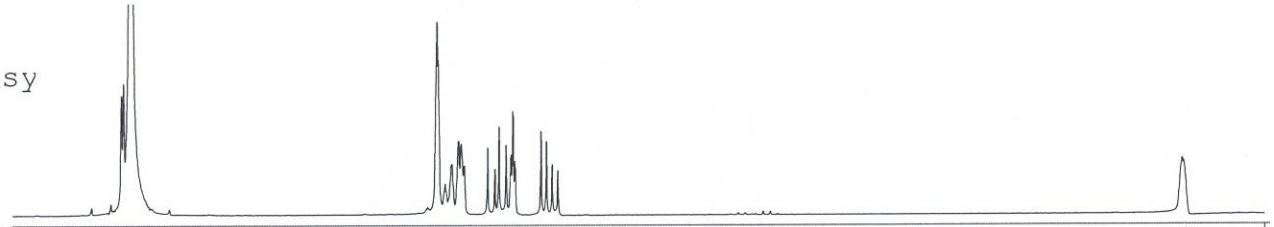
1D NMR plot parameters

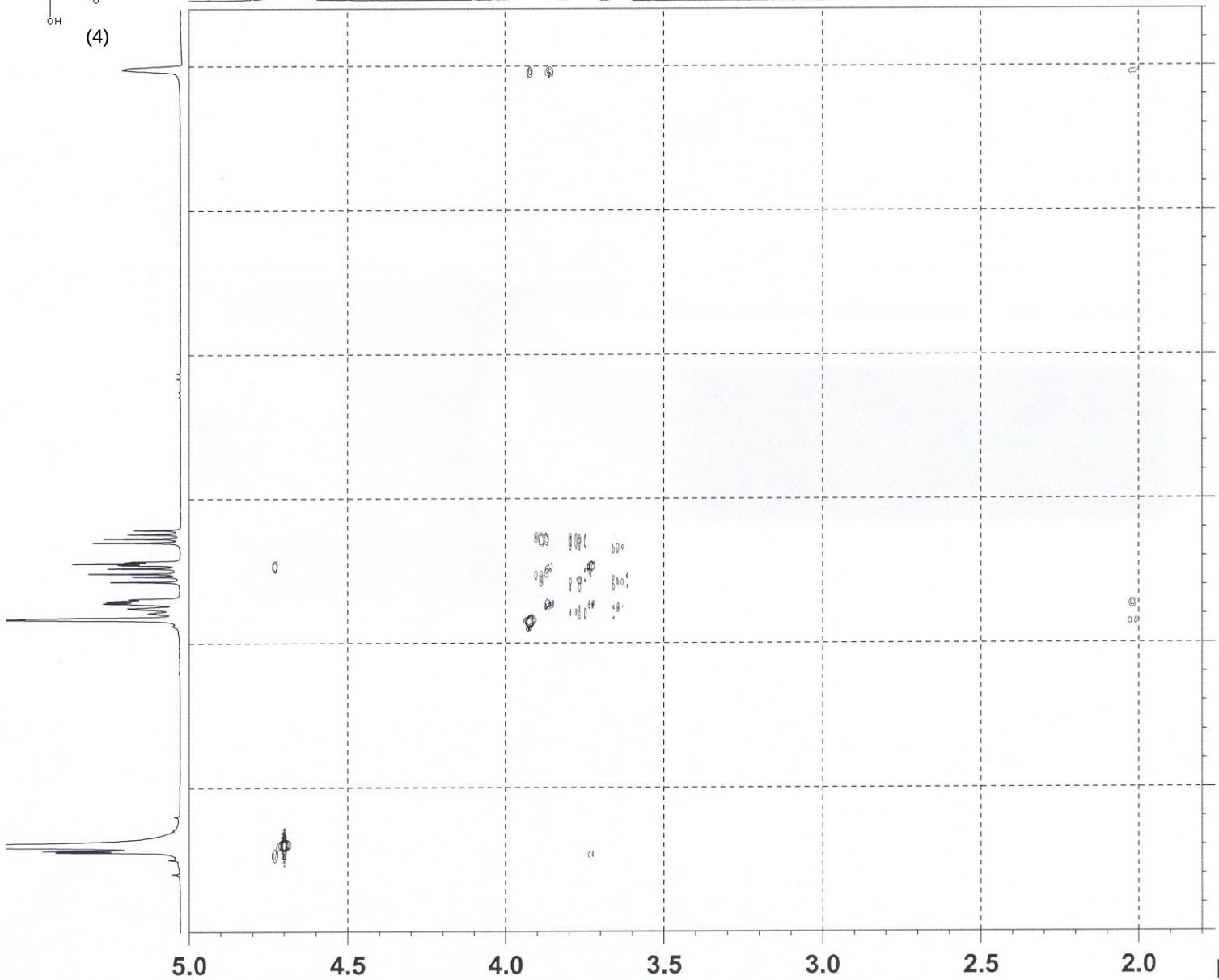
CX	20.00 cm
CY	0.00 cm
F1P	6.000 ppm
F1	2400.78 Hz
F2P	-0.000 ppm
F2	-0.00 Hz
PPMCM	0.30000 ppm/cm
HZCM	120.03900 Hz/cm

tjf56f4to10Cosy



(4)





BRUKER

Current Data Parameters
NAME tjf56f4to10
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20040911
Time 13.38
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG cosygpqf
TD 2048
SOLVENT D2O
NS 1
DS 8
SWH 1436.782 Hz
FIDRES 0.701554 Hz
AQ 0.7127540 sec
RG 256
DW 348.000 usec
DE 6.00 usec
TE 294.2 K
d0 0.00000300 sec
D1 0.96383268 sec
d13 0.00000400 sec
D16 0.00020000 sec
IN0 0.00069600 sec
MCREST 0.00000000 sec
MCWRK 0.96383268 sec

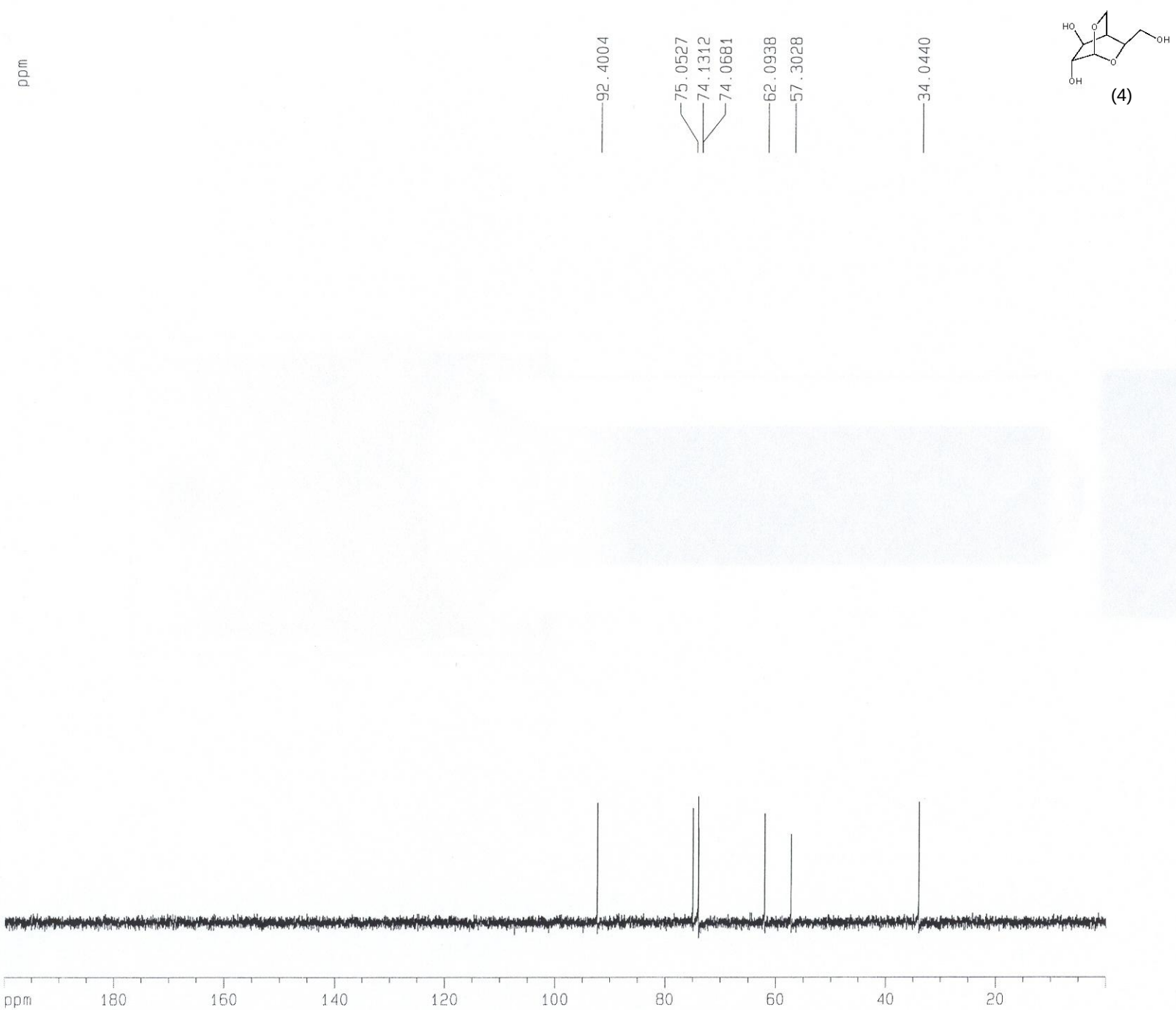
======== CHANNEL f1 ========
NUC1 1H
P0 10.50 usec
P1 10.50 usec
PL1 0.00 dB
SFO1 400.1313875 MHz

====== GRADIENT CHANNEL =====
GPNAM1 SINE.100
GPNAM2 SINE.100
GPX1 0.00 %
GPX2 0.00 %
GPY1 0.00 %
GPY2 0.00 %
GPZ1 10.00 %
GPZ2 10.00 %
P16 1000.00 usec

F1 - Acquisition parameters
ND0 1
TD 128
SFO1 400.1314 MHz
FIDRES 11.224856 Hz
SW 3.591 ppm
FnMODE QF

F2 - Processing parameters
SI 1024
SF 400.1300000 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
MC2 QF
SF 400.1300000 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0



Current Data Parameters

NAME	tjf56f4to10
EXPNO	14
PROCNO	1

F2 - Acquisition Parameters

Date_	20040911
Time	14.57
INSTRUM	spect
PROBHD	5 mm QNP 1H/13
PULPROG	zgpg30
TD	65536
SOLVENT	D2O
NS	1024
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664756 sec
RG	128
DW	20.850 usec
DE	6.00 usec
TE	294.5 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

NUC1	13C
P1	8.12 usec
PL1	0.00 dB
SFO1	100.6228298 MHz

======== CHANNEL f2 ========

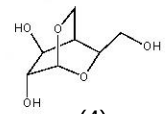
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	0.00 dB
PL12	18.00 dB
PL13	21.00 dB
SFO2	400.1316005 MHz

F2 - Processing parameters

SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	0.00 cm
F1P	200.000 ppm
F1	20122.55 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	10.00000 ppm/cm
HZCM	1006.12769 Hz/cm



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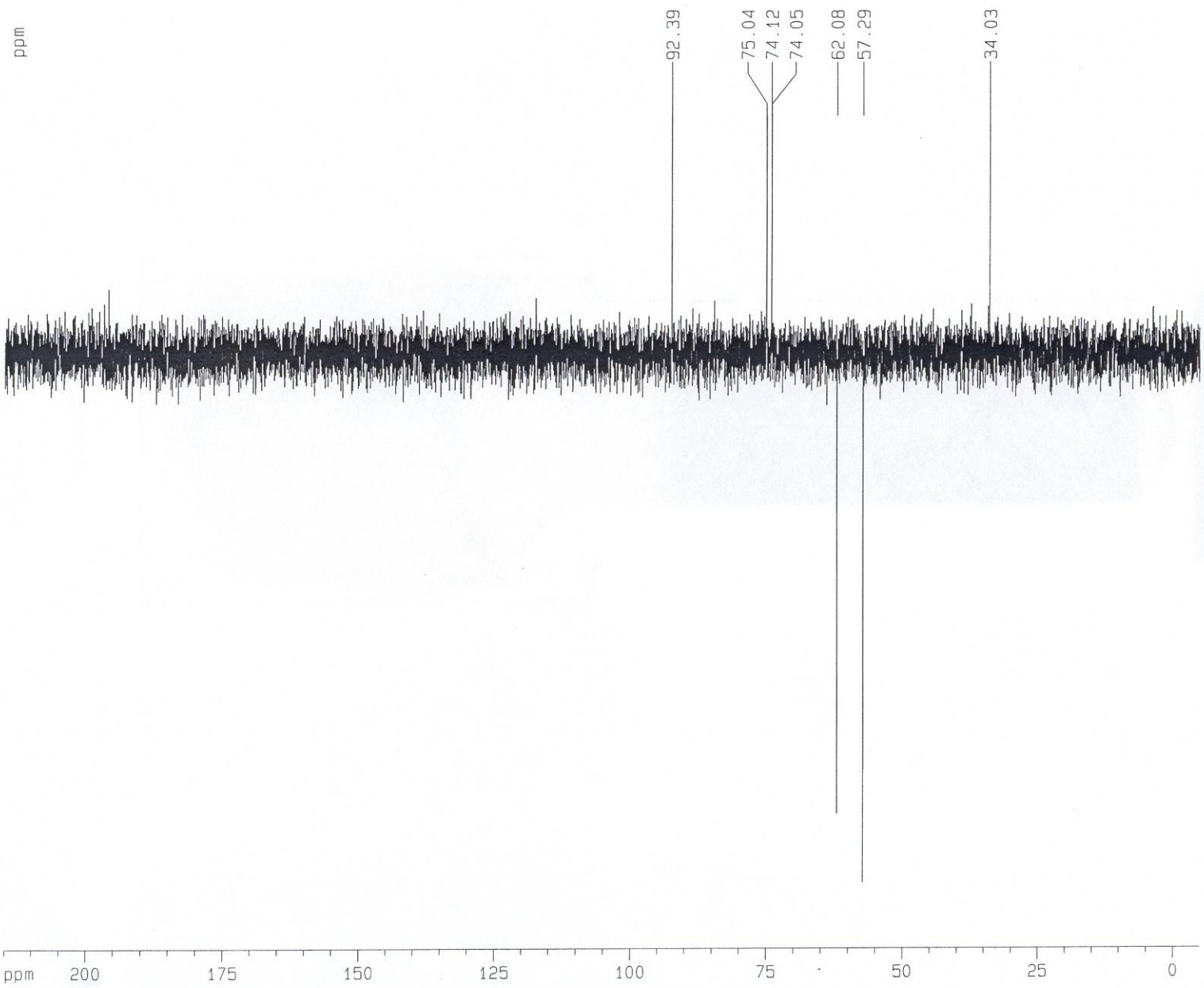


Current Data Parameters

NAME	tjf56f4to10
EXPNO	11
PROCNO	1

F2 - Acquisition Parameters

Date_	20040911
Time	13.37
INSTRUM	spect
PROBHD	5 mm QNP 1H/13
PULPROG	dept135
TD	65536
SOLVENT	D20
NS	256
DS	4
SWH	23980.814 Hz
FIDRES	0.365918 Hz
AQ	1.3664756 sec
RG	16384
DW	20.850 usec
DE	6.00 usec
TE	294.3 K
CNST2	145.0000000
D1	2.00000000 sec
d2	0.00344828 sec
d12	0.00002000 sec
DELTA	0.00001034 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

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

NUC1	13C
P1	8.12 usec
p2	16.24 usec
PL1	0.00 dB
SFO1	100.6228298 MHz

======== CHANNEL f2 ========

CPDPRG2	waltz16
NUC2	1H
P3	10.50 usec
p4	21.00 usec
PCPD2	80.00 usec
PL2	0.00 dB
PL12	18.00 dB
SFO2	400.1316005 MHz

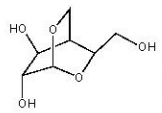
F2 - Processing parameters

SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
CY	9.00 cm
F1P	215.000 ppm
F1	21631.75 Hz
F2P	-5.000 ppm
F2	-503.06 Hz
PPMCM	11.00000 ppm/cm
HZCM	1106.74048 Hz/cm

tjf56f4to10HSQC



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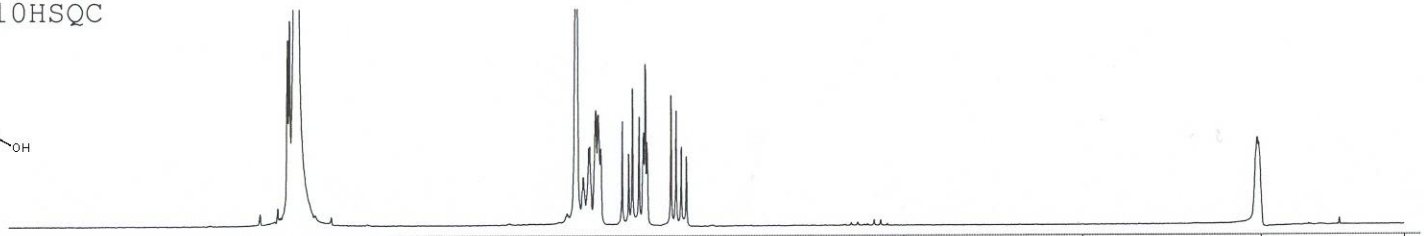
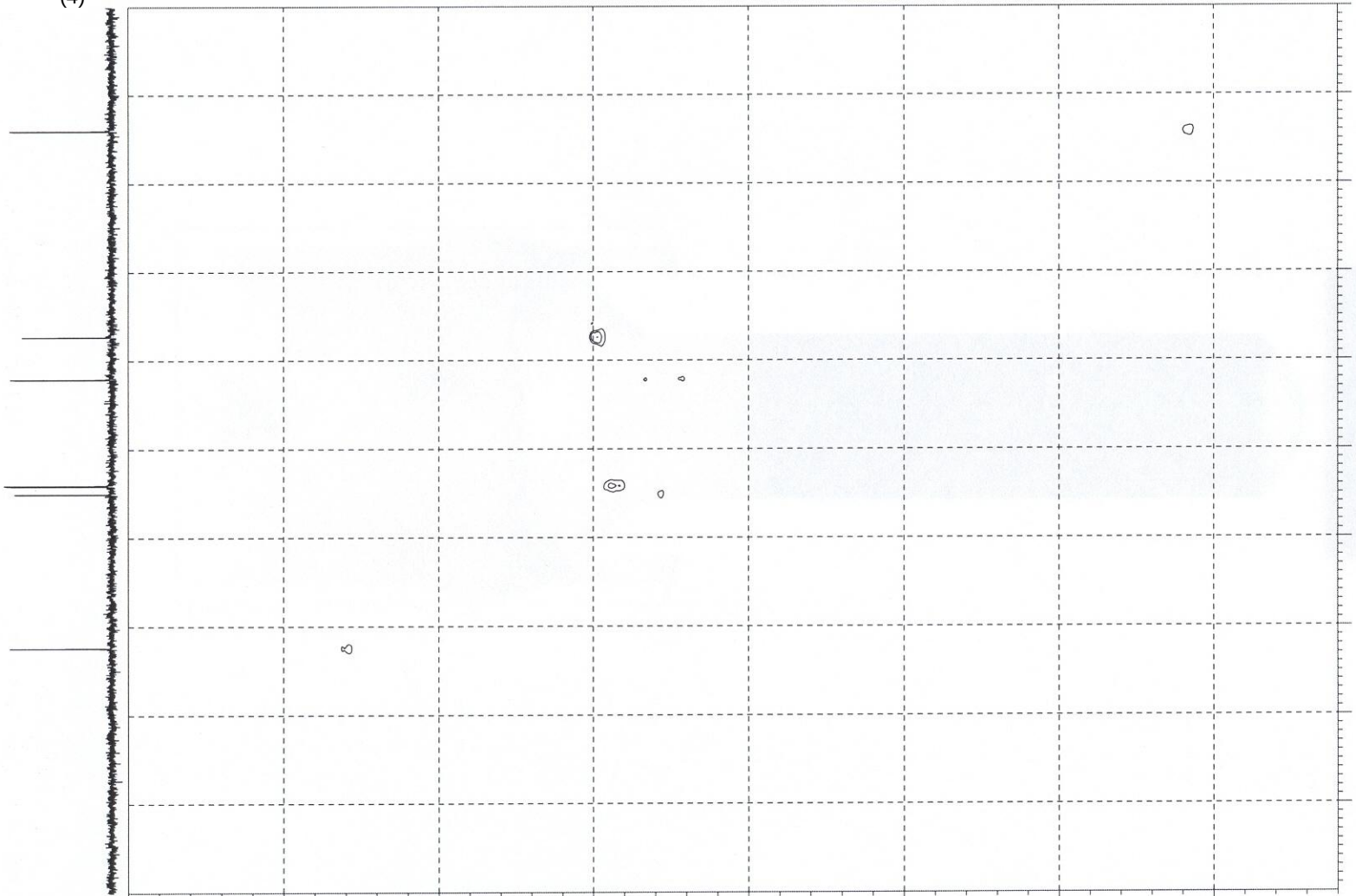
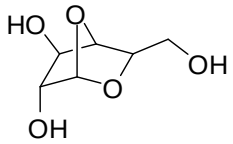
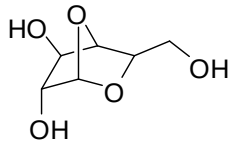
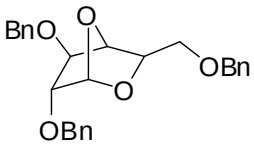
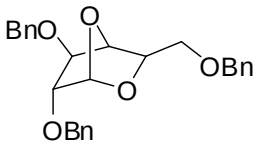
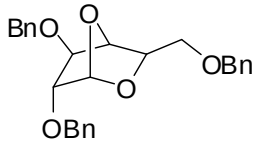
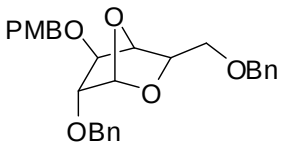
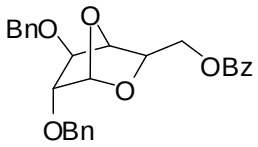
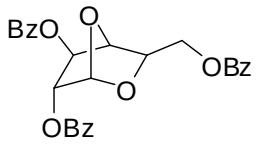
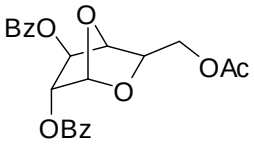
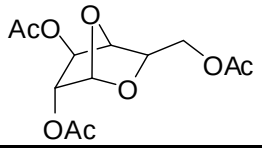
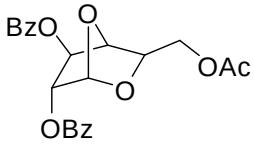
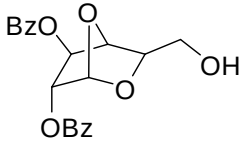


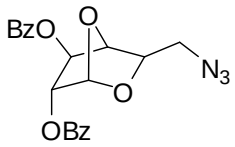
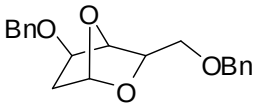
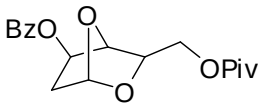
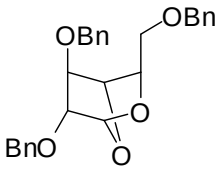
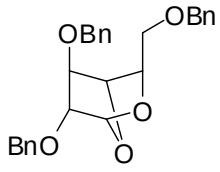


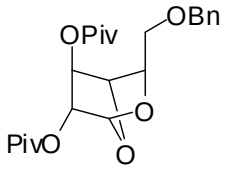
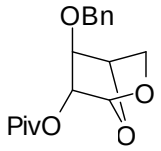

```
Current Data Parameters
NAME                  tjf56f4to10
EXPNO                          13
PROCNO                          1

F2 - Acquisition Parameters
Date                     20040911
Time                        13.43
INSTRUM                      spect
PROBHD     5 mm QNP 1H/13
PULPROG              hsqcetgpsi2
TD                            1024
SOLVENT                       D2O
NS                               4
DS                              16
SWH                    1436.782 Hz
FIDRES                 1.403107 Hz
AQ                     0.3564020 sec
RG                           16384
DW                       348.000 usec
DE                         6.00 usec
TE                         294.6 K
CNST2                145.0000000
d0                     0.00000300 sec
D1                     1.23846996 sec
d4                     0.00172414 sec
d11                    0.03000000 sec
d13                    0.00000400 sec
D16                    0.00020000 sec
D24                    0.00086207 sec
DELTA                  0.00127700 sec
DELTA1                 0.00120800 sec
DELTA2                 0.00006207 sec
DELTA3                 0.00052414 sec
IN0                    0.00003000 sec
MCREST                 0.00000000 sec
MCWRK                  0.20641208 sec
ST1CNT                        128

======== CHANNEL f1 ========
NUC1                          1H
P1                        10.50 usec
p2                        21.00 usec
P28                        0.00 usec
PL1                        0.00 dB
SFO1                400.1313875 MHz

======== CHANNEL f2 ========
CPDPRG2                    garp
NUC2                         13C
P3                         9.25 usec
p4                        18.50 usec
PCPD2                     72.00 usec
PL2                        0.00 dB
PL12                      17.82 dB
SFO2                100.6203124 MHz

====== GRADIENT CHANNEL =====
GPNAM1                  SINE.100
GPNAM2                  SINE.100
GPNAM3                  SINE.100
GPNAM4                  SINE.100
GPX1                       0.00 %
GPX2                       0.00 %
GPX3                       0.00 %
GPX4                       0.00 %
GPY1                       0.00 %
GPY2                       0.00 %
GPY3                       0.00 %
GPY4                       0.00 %
GPZ1                      80.00 %
GPZ2                      20.10 %
GPZ3                      11.00 %
GPZ4                      -5.00 %
P16                     1000.00 usec
P19                      600.00 usec

F1 - Acquisition parameters
ND0                            2
TD                           128
SFO1                100.6203 MHz
FIDRES              130.208328 Hz
SW                     165.639 ppm
FnMODE          Echo-Antiecho

F2 - Processing parameters
SI                          1024
SF                  400.1300000 MHz
WDW                        QSINE
SSB                            2
LB                          0.00 Hz
GB                             0
PC                          1.40

F1 - Processing parameters
SI                          1024
MC2              echo-antiecho
SF                  100.6127690 MHz
WDW                        QSINE
SSB                            2
LB                          0.00 Hz
GB                             0
```

^{1}H Chemical shifts (ppm), *J* (Hz) and multiplicity of 1,4-anhydrohexopyranoses

Structure	NMR Solvent	1H	2H	3H	4H	5H	6H	6'H	others	$[\alpha]_D$	Ref.
	500 D2O	5.46 br. d $J_{1,2}$ 2.5	3.82 ddd $J_{2,3}$ 1.8	4.45, 3.64 br. d J ~ 1.8	br. d $J_{4,5}$ 0 $^4J_{2,4}$ 1.5	3.7 br. t J 5.6	3.4 dd $J_{6,6'}$ 11.9 $J_{5,6}$ 6	3.46 dd $J_{5,6'}$ 5.3		87 (c 0.85, water)	our data
	400 D_2O/CD_3OD 6 to 1	5.42 br. s	3.84 d $J_{2,3}$ 2.5	4.6 dd $J_{3,4}$ 3.4	4.7 dd $J_{4,5}$ 1.2	4.05-4.15 m (3H)					1
	500 $CDCl_3$	5.48 br. d $J_{1,2}$ 2.3	3.83 ddd $J_{2,3}$ 2.3	3.54, 4.59 br. d J ~ 1.2	br. d $J_{4,5}$ 0 $^4J_{2,4}$ 1.5	3.82 dd $J_{5,6}$ 8.5 $J_{5,6'}$ 5	3.34 dd $J_{6,6'}$ 9.4	3.43 dd	4.5-4.58 m 6H (CH2-Bn)	57.4 (c 1.12, $CDCl_3$)	our data
	400 $CDCl_3$	5.46 d $J_{1,2}$ 2.29	3.84 d $J_{2,3}$ 1.22	3.55 d $J_{3,4}$ 0	4.59 d $J_{4,5}$ 1.52	3.82 q $J_{5,6}$ 7.93	3.35 q $J_{6,6'}$ 9.46	3.43 q	4.46-4.62 6H (CH2-Bn)	57.6 (c 1.0, $CDCl_3$)	3
	400 $CDCl_3$	5.47 d $J_{1,2}$ 2.5	3.85 br s	3.55 d	4.59 d	3.82 m	3.35 q	3.43 q	4.46-4.62 m 6H (CH2-Bn)	57 (c 1.0, $CDCl_3$)	2
	250 $CDCl_3$	5.47 d $J_{1,2}$ 2.4	3.75-3.86 m*	4.367-4.62 m**	3.53 d $J_{3,4}$ 1.2	3.75-3.86 m*	3.4 dd (2H)		4.37-4.62 m** 6H (CH2-Bn)		13

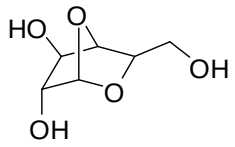
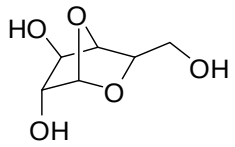
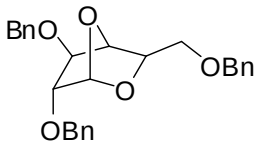
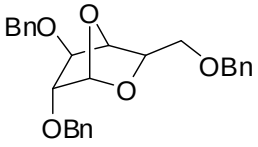
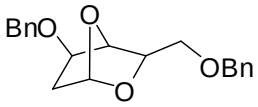
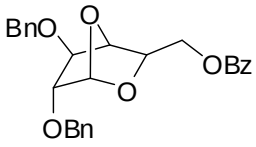
Structure	NMR Solvent	1H	2H	3H	4H	5H	6H	6'H	others	$[\alpha]_D$	Ref.
	300 $CDCl_3$ no asignment	5.95 d $J_{1,2}$ 2.4	5.12 m	4.82 d J 1.5	5.17 d J 1.5	4.09 dd $J_{5,6}$ 7.2 $J_{5,6'}$ 5.7	3.42 dd $J_{6,6'}$ 9.6	3.48 dd	4.5-4.58 m 4H (CH2-Bn)	159 (c 1.8, $CDCl_3$)	4
	100 C_5D_5N	6.27 d $J_{1,2}$ 2.4	5.42 m $J_{2,3}$ 1.5	5.53 d $J_{3,4}$ 0	4.93 d $J_{4,5}$ 0 $^4J_{2,4}$ 1.5	4.5 s (3H)				117 (c 1, $CDCl_3$)	5
	100 C_5D_5N	6 d $J_{1,2}$ 2.5	5.22 m $J_{2,3}$ 1.5	5.27 d $J_{3,4}$ 0	4.93 d $J_{4,5}$ 0 $^4J_{2,4}$ 1.5	4.1 m (3H)				214 (c 1, $CDCl_3$)	5
	100 C_6D_6	5.59 d $J_{1,2}$ 2.4	4.63 m $J_{2,3}$ 1.4	4.66 d $J_{3,4}$ 0	4.38 d $^4J_{2,4}$ 1.4	3.7 t $J_{5,6}$ 5.6 $J_{5,6'}$ 5.6	3.82 q $J_{6,6'}$ 10.3	4 q	1.64		6
	? C_5D_5N	4 d $J_{1,2}$ 2.5	4.78 quintet $J_{2,3}$ 1.5	4.73 d	5.09 d $^4J_{2,4}$ 1.4	5.9 m (3H)					7
	100 C_5D_5N	5.97 d $J_{1,2}$ 2.5	5.22 m	4.83 $J_{4,5}$ 0 1.5 (2H)	d $^4J_{2,4}$	4.03 t $J_{5,6}$ 5.5 $J_{5,6'}$ 5.5	3.64 d (2H)			235 (c 1, $CDCl_3$)	5

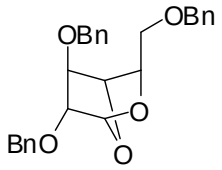
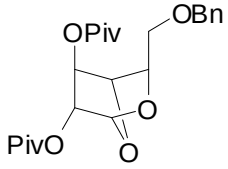
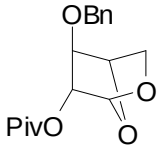
Structure	NMR Solvent	1H	2H	3H	4H	5H	6H	6'H	others	$[\alpha]_D$	Ref.
	100 C_5D_5N	6.03 d $J_{1,2}$ 2.5	5.21 m $J_{2,3}$ 1.5	5.28 d $J_{3,4}$ 0	4.84 d $J_{4,5}$ 0 $^4J_{2,4}$ 1.5	4.1 t $J_{5,6}$ 6 $J_{5,6'}$ 6	3.24 d (2H)			239 (c 1, $CDCl_3$)	5
	400 $CDCl_3$	5.67 d $J_{1,2}$ 2.5 $J_{1,2'}$ 0.5	2.17/1.78 dd/ddd $J_{2,2'}$ 13.2	3.84 dd $J_{2',3}$ 6.6 $J_{2,3}$ 2	4.69 br. s $^4J_{2,4}$ 1.4	3.57 dd $J_{5,6}$ 7.6 $J_{5,6'}$ 5.6	3.37 dd $J_{6,6'}$ 9.2	3.32 dd	4.54-4.51 4H (CH2-Bn)	33 (c 1.05, $CDCl_3$)	8
	400 $CDCl_3$	5.79 br d $J_{1,2}$ 2.6 $J_{1,2'}$ 0.5	1.95/2.44 dddd/ddd $J_{2,2'}$ 13.6	5.15 dd $J_{2',3}$ 7 $J_{2,3}$ 2.2	4.79 s $^4J_{2,4}$ 1.4	3.83 dd $J_{5,6}$ 6.8 $J_{5,6'}$ 5.7	3.95 dd $J_{6,6'}$ 11.2	4.05 dd	1.23 3xCH3 7.44-8.04	34 (c 1.18, $CDCl_3$)	9
	400 $CDCl_3$	5.36 s $J_{1,2}$ 0	3.61 d $J_{2,3}$ 2.1	3.91 s $J_{3,4}$ 5	4.55 q $J_{4,5}$ 3.9 $J_{4,6}$ 7.6 $J_{4,6'}$ 4.3	4.04 quintet $J_{5,6}$ 7.63 $J_{5,6'}$ 4.27	3.75 q $J_{6,6'}$ 10.5	3.8 q	3.34-4.51	-9.7 (c 1.0, $CDCl_3$)	3
	200 $CDCl_3$	5.44 s								-10.5 (c 1.18, $CDCl_3$)	10

Structure	NMR Solvent	1H	2H	3H	4H	5H	6H	6'H	others	$[\alpha]_D$	Ref.
	300 $CDCl_3$	5.46 s $J_{1,2}$ 0	4.74 d $J_{2,3}$ 2.5	4.93 m $J_{3,4}$ 5	4.81 dd $J_{4,5}$ 3	4.19 m $J_{5,6}$ 3.5 $J_{5,6'}$ 8	3.7 dd $J_{6,6'}$ 11	3.82 dd	4.54, 4.65	-9.5 (c 1.0, $CDCl_3$)	11
	300 $CDCl_3$ 1,4-anhydropentopyranose	5.4 d $J_{1,4}$ 0.9	4.7 d $J_{2,3}$ 1.6	3.85 m $J_{3,4}$ 4.9	4.54 m $J_{4,5endo}$ 0	5endo 4.18 d $J_{5endo/exo}$ 6.6	5exo 3.44 m $J_{4,5exo}$ 2.4	x	4.50, 4.71 1.2	-36.3 (c 1.0, $CDCl_3$)	12

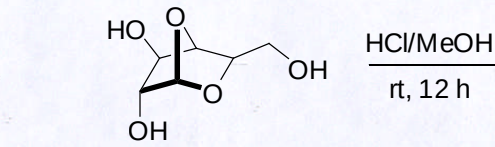
1. A. Caravano, P. Sinay and S. P. Vincent, *Bioorg. Med. Chem. Lett.* , 2006, 16, 1123-1125.
2. P. M. Aberg and B. Ernst, *Acta. Chem. Scand.* , 1994, 48, 228-233.
3. T. Uryu, C. Yamaguchi, K. Morikawa, K. Terui, T. Kanai and K. Matsuzaki, *Macromolecules* , 1985, 18, 599-605.
4. T. Nokami, D. B. Werz and P. H. Seeberger, *Helv. Chim. Acta* , 2005, 88, 2823-2831.
5. C. Bullock, L. Hough and A. C. Richardson, *Carbohydr. Res.* , 1990, 197, 131-138.
6. P. Koll, *Chem. Ber.* , 1973, 106, 3559-3564.
7. C. Bullock, L. Hough and A. C. Richardson, *Chem. Commun.* , 1971, 1276-1277.
8. V. Jaouen, A. Jegou, L. Lemee and A. Veyrieres, *Tetrahedron* , 1999, 55, 9245-9260.
9. V. Jaouen, A. Jegou and A. Veyrieres, *Synlett.* , 1996, 12, 1218-1220.
10. T. Sato, H. Nakamura and Y. Ohno, *Carbohydr. Res.* , 1990, 199, 31-35.
11. H. Kamitakahara and F. Nakatsubo, *Macromolecules* , 1996, 29, 1119-1122.
12. M. Hori and F. Nakatsubo, *Carbohydr. Res.* , 1998, 309, 281-286.
13. L. K. Shi-Shun, J. M. Mallet, M. Moreau and P. Sinay, *Tetrahedron* , 1999, 55, 14043-14068.

^{13}C chemical shifts (ppm) of 1,4-anhydrohexopyranoses

Structure	NMR Solvent	C1	C2	C3	C4	C5	C6	others	Ref.
	125 D_2O	99.6	81.2	83.9, 76.5		75.4	61.7		our data
	100 D_2O/CD_3OD 6 to 1	107.4	81	82.1 d	79.6	81.3	61.7		1
	125 $CDCl_3$	98.7	87.3	82.9, 81.4		74.3	69.9	71.2, 72.4, 73.6 3 (CH2-Bn)	our data
	100 CDCl3	98.7	74.2, 81.3, 82.8, 87.2				69.8	71.1, 72.3, 73.5 3 (CH2-Bn)	2
	100 $CDCl_3$	99.97	41.91	79.93, 77.45, 73.32			73.51	70.96, 70.12 2 (CH2-Bn)	8
	75 $CDCl_3$ no asignment	98.4	81.6, 81.3, 77.2				69.6	73.6 , 74.4 2 (CH2-Bn)	4

Structure	NMR Solvent	C1	C2	C3	C4	C5	C6	others	Ref.
	50 $CDCl_3$ * not assigned	103.1	86.4, 84.8		78.3	76.05*	69.3	73.21, 73.17, 71.7 3 (CH2-Bn)	5
	75 $CDCl_3$	103.3							11
	75 $CDCl_3$	102.2	82.2, 78.5, 75.8, 72.6, 62.8						12

1. A. Caravano, P. Sinay and S. P. Vincent, *Bioorg. Med. Chem. Lett.* , 2006, 16, 1123-1125.
2. P. M. Aberg and B. Ernst, *Acta. Chem. Scand.* , 1994, 48, 228-233.
4. T. Nokami, D. B. Werz and P. H. Seeberger, *Helv. Chim. Acta* , 2005, 88, 2823-2831.
5. C. Bullock, L. Hough and A. C. Richardson, *Carbohydr. Res.* , 1990, 197, 131-138.
8. V. Jaouen, A. Jegou, L. Lemee and A. Veyrieres, *Tetrahedron* , 1999, 55, 9245-9260.
11. H. Kamitakahara and F. Nakatsubo, *Macromolecules* , 1996, 29, 1119-1122.
12. M. Hori and F. Nakatsubo, *Carbohydr. Res.* , 1998, 309, 281-286.



ppm 5.126 5.117 5.029 4.887 4.874 4.847 4.800 4.700 4.602 4.510 4.471 4.463 4.452 4.432 4.330 4.322 4.311 4.172 4.110 4.102 4.019 3.986 3.931 3.890 3.846 3.840 3.790 3.782 3.767 3.751 3.731 3.723 3.705 3.698 3.677 3.668 3.631 3.616 3.611 3.606 3.598 3.579 3.571 3.562 3.549 3.523 3.490 3.213

α-Gal*p*
d
J 3.6

β-Gal*p*
d
J 7.6

***O*-Me Galactosides**

ppm 5.0 4.5 4.0 3.5

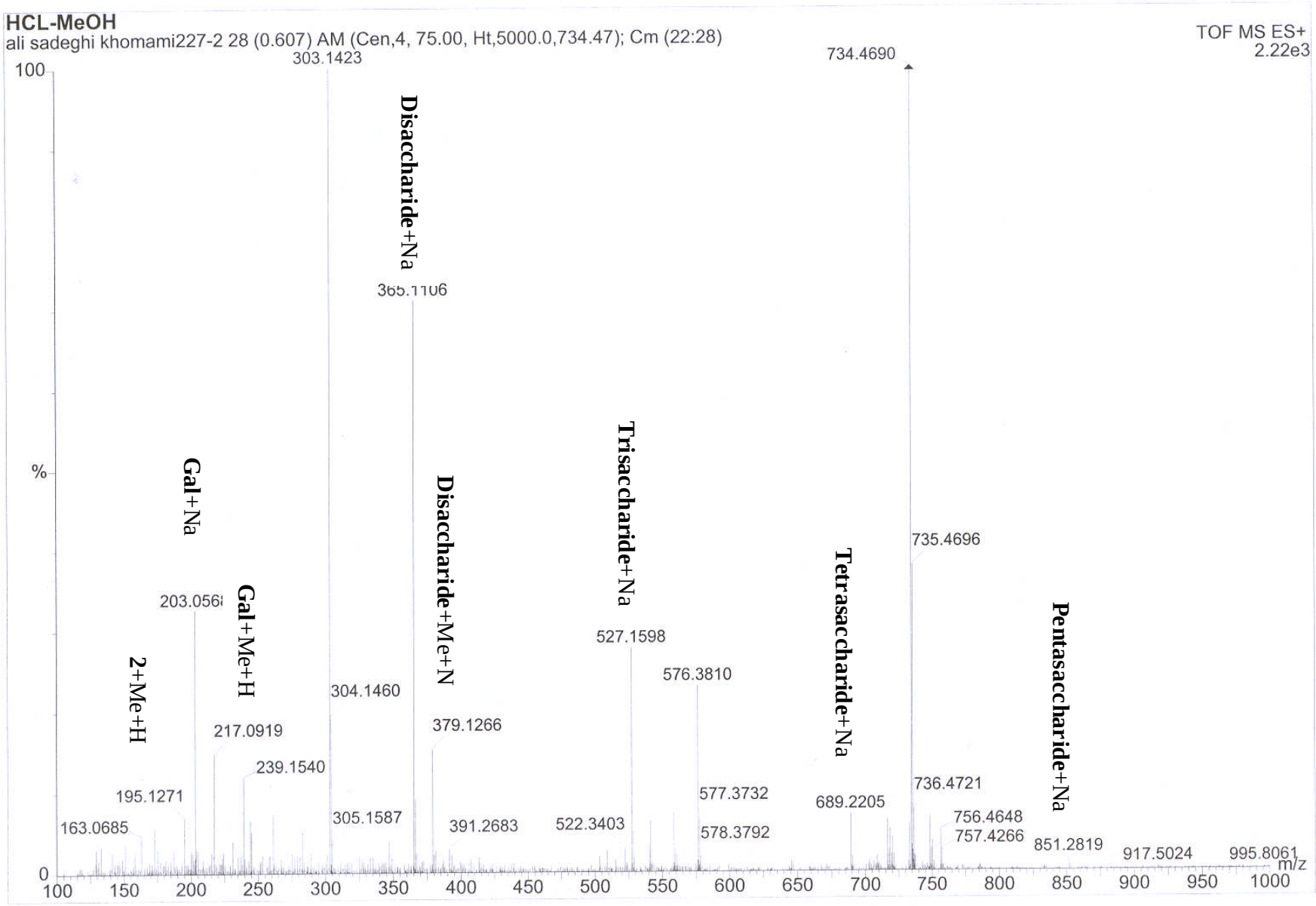
```
Current Data Parameters
NAME                  ASK4-H+
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_               20040528
Time                   13.58
INSTRUM                spect
PROBHD   5 mm QNP 1H/13
PULPROG                 zg30
TD                     65536
SOLVENT                  D2O
NS                        32
DS                         2
SWH                 8278.146 Hz
FIDRES              0.126314 Hz
AQ                  3.9584243 sec
RG                       256
DW                    60.400 usec
DE                     6.00 usec
TE                    294.1 K
D1                  1.00000000 sec
MCREST              0.00000000 sec
MCWRK               0.01500000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                    10.50 usec
PL1                    0.00 dB
SFO1               400.1324710 MHz

F2 - Processing parameters
SI                       32768
SF                 400.1300010 MHz
WDW                         EM
SSB                          0
LB                     0.30 Hz
GB                           0
PC                      1.00

1D NMR plot parameters
CX                     20.00 cm
CY                      0.00 cm
F1P                    5.266 ppm
F1                   2106.90 Hz
F2P                    3.104 ppm
F2                   1241.99 Hz
PPMCM                0.10808 ppm/cm
HZCM                43.24565 Hz/cm
```

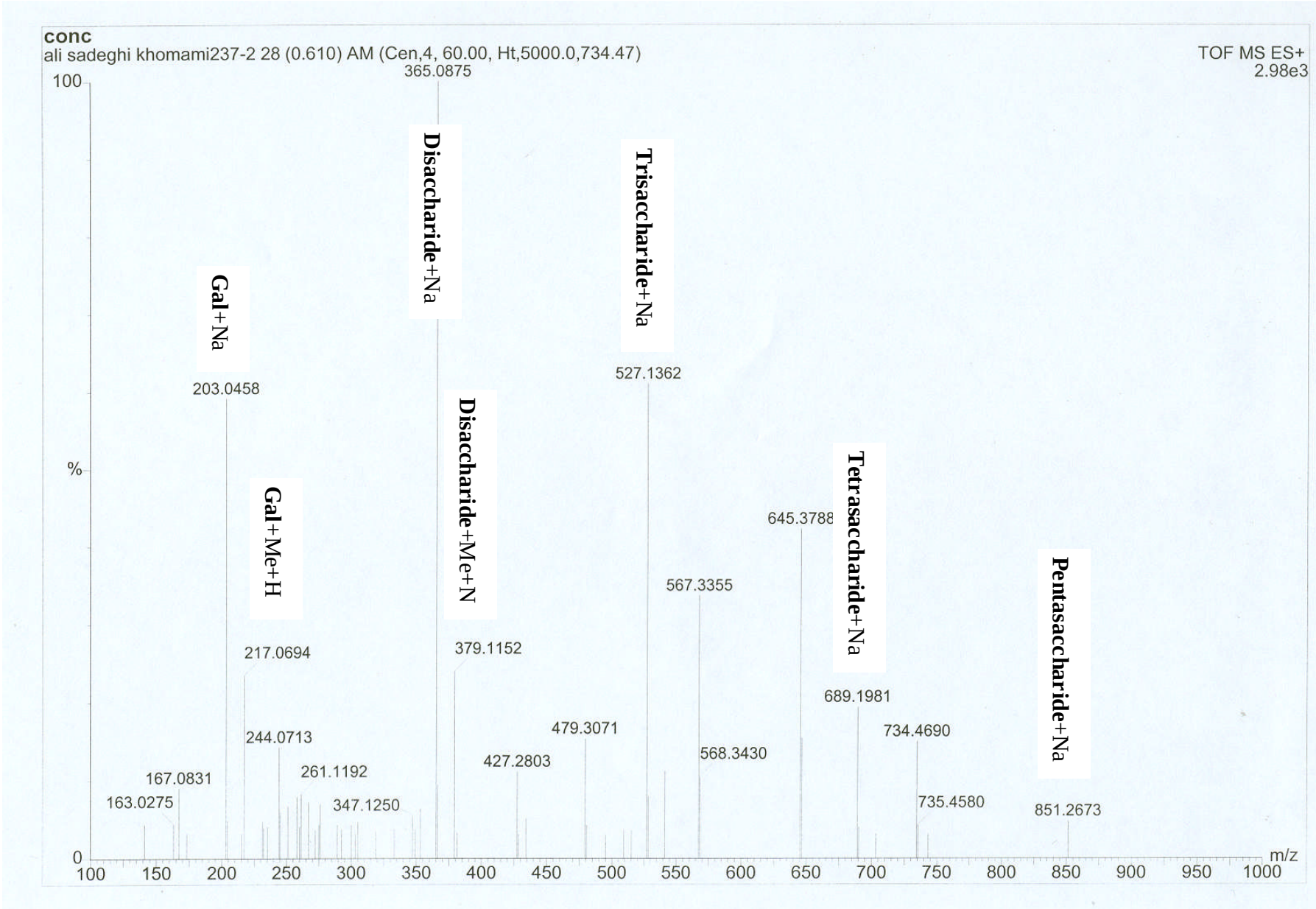
Selected chemical shifts, *J* (Hz) and multiplicity in D2O (^{1}H-NMR, 500 MHz) for galactose configurations and derivatives

D-Galactose	**1-δ_H**	**Multiplicity**	***J* (Hz)**		
α-Gal*p*	5.11	d	3.6		
β-Gal*p*	4.43	d	7.6		
α-Gal*f*	5.13	d	4.8		
β-Gal*f*	5.06	d	3.6		
***O*-Met-D-galactoside**	**1-δ_H**	**Multiplicity**	***J* (Hz)**	***O*Me-δ_H**	**Multiplicity**
α-Gal*p*	4.75	d	2.9	3.30	s
β-Gal*p*	4.23	d	7.9	3.49	s
α-Gal*f*	4.88	d	3.8	3.44	s
β-Gal*f*	4.05	d	1.8	3.43	s

ESI$^{(+)}$ analysis of acidic ring opening of **2**:

Up to pentasaccharides were detected, indicating that oligomerisation was catalysed by HCl. A control sample (galactose) produced only up to disaccharide under the same conditions in ESI analysis.


HCL-MeOH
ali sadeghi khomami227-2 28 (0.607) AM (Cen,4, 75.00, Ht,5000.0,734.47); Cm (22:28)
TOF MS ES+
2.22e3
100
%
0
303.1423
734.4690
Disaccharide+Na
365.1106
Gal+Na
203.0568
Gal+Me+H
2+Me+H
Disaccharide+Me+N
Trisaccharide+Na
Tetrasaccharide+Na
Pentasaccharide+Na
735.4696
527.1598
576.3810
304.1460
379.1266
217.0919
239.1540
195.1271
163.0685
305.1587
391.2683
522.3403
577.3732
578.3792
689.2205
736.4721
756.4648
757.4266
851.2819
917.5024
995.8061
m/z
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000


conc
ali sadeghi khomami237-2 28 (0.610) AM (Cen,4, 60.00, Ht,5000.0,734.47)
TOF MS ES+
2.98e3
100
%
0
m/z
365.0875
Disaccharide+Na
Trisaccharide+Na
527.1362
Gal+Na
203.0458
Disaccharide+Me+N
379.1152
Gal+Me+H
217.0694
Tetrasaccharide+Na
645.3788
567.3355
689.1981
Pentasaccharide+Na
734.4690
479.3071
244.0713
568.3430
427.2803
261.1192
167.0831
163.0275
347.1250
735.4580
851.2673
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000