Supporting Information

Glycosylation catalysed by a chiral Brønsted acid

Daniel J. Cox,[a] Martin D. Smith,[a] and Antony J. Fairbanks[*,b]

[a] *Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford, OX1 3TA, UK*

[b] *Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch 8140, New Zealand*

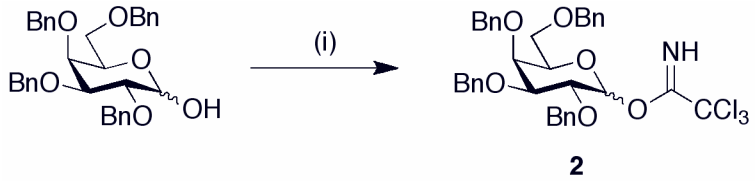
e-mail: antony.fairbanks@canterbury.ac.nz

General Experimental Methods:

Melting points were recorded on a Kofler hot block and are uncorrected. Proton and carbon nuclear magnetic resonance (δ_H, δ_C) spectra were recorded on Bruker DPX 400 (400 MHz) spectrometer. All chemical shifts are quoted on the δ-scale in ppm using residual solvent as an internal standard. Low resolution mass spectra were recorded on a Micromass Platform 1 spectrometer using electospray ionisation in either positive or negative polarity (ES^+ and/or ES^-). High resolution mass spectra were recorded by Mr. Robin Procter on a Walters 2790-Micromass LCT electrospray ionisation mass spectrometry using either electrospray ionisation (NH_3, CI) techniques as stated. M/z values are reported in Daltons and are followed by their percentage abundance in parentheses. Optical rotations were measured on a Perkin-Elmer 241 polarimeter with a path length of 1 dm. Concentrations are given in g / 100 ml. Thin Layer Chromatography (t.l.c.) was carried out on Merck silica gel $60F_{254}$ aluminium-backed plates. Visualisation of the plates was achieved using a u.v. lamp (λ_{max} = 254 or 365 nm), and/or ammonium molybdate (5% in 2M H_2SO_4), or sulphuric acid (5% in EtOH). Flash column chromatography was carried out using Sorbsil C60 40/60 silica.

Preparation of Glycosyl Donors

Glycosyl donor **2** was prepared from commercially available 2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranose as follows:



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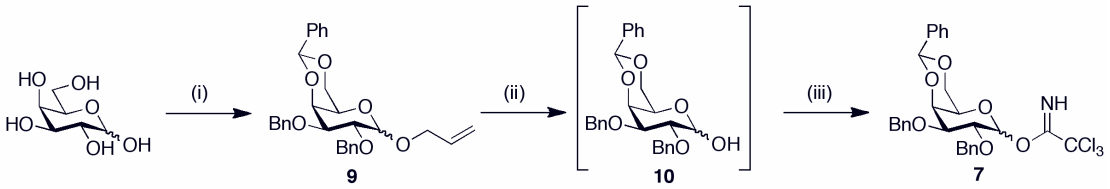
Reagents and Conditions: (i) Cl_3CCN, DBU, CH_2Cl_2, 0 °C, 2h

***O*-(2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranosyl) trichloroacetimidate 2[i,ii]**

2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranose (1.00 g, 1.850 mmol) was dissolved in freshly distilled CH_2Cl_2 (20 ml) and cooled to 0 °C under an argon atmosphere. DBU (0.114 ml, 0.740 mmol) was added followed by trichloroacetonitrile (0.946 ml, 9.248 mmol). After 2 h, t.l.c (petrol:ethyl acetate, 3:1, with 1% added triethylamine) indicated the formation of two products (R_f 0.58 and R_f 0.39) and complete consumption of starting material (R_f 0.16). The reaction was concentrated *in vacuo*

and the resulting residue was purified by flash column chromatography (petrol:ethyl acetate, 5:1, with 1% added triethylamine) to afford *O*-(2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranosyl) trichloroacetimidate **2** (1.10 g, 87%) as a pale yellow oil; (400 MHz, $CDCl_3$) [7.9:1 mixture of α:β anomers observed] 3.49-3.71 (18.8H, m), 3.77 (1H, at, *J* 6.6 Hz), 3.99-4.21 (25.7H, m), 4.27 (7.9H, dd, *J* 10.0 Hz, *J* 3.4 Hz), 4.39-4.50 (17.8H, m), 4.74-5.01 (43.5H, m), 5.78 (1H, d, $J_{1,2}$ 8.1 Hz, H-1β), 6.55 (1H, d, $J_{1,2}$ 3.5 Hz, H-1α), 7.25-7.38 (178H, m), 8.54 (7.9H, br s, NHβ), 8.65 (1H, br s, NHα); δ_C (100 MHz, $CDCl_3$) 60.4, 68.3, 72.2, 72.9, 73.0, 73.5, 74.4, 74.6, 74.8, 75.0, 75.3, 75.9, 77.9, 78.1, 82.2, 91.5, 95.2, 98.7, 127.5, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.2, 128.2, 128.3, 128.3, 128.4, 128.5, 137.8, 138.3, 138.4, 138.5, 138.5, 161.3; *m/z* (ES^+) 604 ($M+Na^+$, 100%).

Glycosyl donor **7** was prepared from commercially available D-galactose as follows:



Reagents and Conditions: (i) $PhCH(OMe)_2$, CSA, DMF, 60 °C, 250 mbar, 1.5 h; then AllBr, NaH, DMF, 0.5 h; then BnBr, NaH, DMF, 3.5 h; (ii) $[Ir(coa)(PPh_2Me)_2]PF_0$, H_2, THF, 16h; then NIS, H_2O, 16 h; (iii) Cl_3CCN, DBU, CH_2Cl_2, 0 °C, 2h

Allyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-galactopyranoside 9[iii]

Benzaldehyde dimethyl acetal (3.19 ml, 21.25 mmol) was added to a solution of D-Galactose (3.19 g, 17.71 mmol) and camphor sulfonic acid (0.041 g, 0.177 mmol) in DMF (50 ml). The resulting solution was heated to 60 °C on a rotary evaporator under a pressure of 250 mbar. After 1.5h, t.l.c (ethyl acetate) indicated the formation of a single product (R_f 0.30) and complete consumption starting material (R_f 0). The crude reaction mixture was diluted with DMF (50 ml) and allyl bromide (2.30 ml, 26.57 mmol). The mixture was cooled to 0 °C and NaH (60% in mineral oil, 0.850 g, 21.25 mmol) was added. After addition was complete, the reaction mixture was stirred for 0.5 h at RT and then diluted with benzyl bromide (8.43 ml, 70.84 mmol). The reaction was again cooled to 0 °C and further NaH (60% in mineral oil, 2.125 g, 53.13 mmol) added. After 3.5 h at RT, t.l.c (petrol:ethyl acetate, 3:1) indicated the formation of two major products (R_f 0.33 and R_f 0.26). Methanol (25 ml) was added portion-wise in order to quench the reaction. The reaction was then concentrated *in*

vacuo. The resulting residue was dissolved in ether (100 ml), washed with water (200 ml), and the aqueous layer extracted with ether (2 x 100 ml). The combined organic extracts were washed with brine (200 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (petrol:ethyl acetate, 3:1) to afford Allyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-galactopyranoside **9** (5.2 g, 60%) as a white solid; δ_H (400 MHz, $CDCl_3$) [4:1 mixture of α:β anomers observed] 3.33 (4H, m), 3.39 (1H, m), 3.45-3.54 (2H, m), 3.57 (4H, dd, *J* 9.6 Hz, *J* 3.8 Hz), 3.70-3.85 (3H, m), 3.90 (4H, dd, *J* 9.6 Hz, *J* 7.9 Hz), 3.94-3.96 (1H, m), 4.00-4.19 (13H, m), 4.22-4.53 (11H, m), 4.63-4.82 (15H, m), 4.88-5.04 (4H, m), 5.15-5.23 (5H, m), 5.29-5.39 (5H, m), 5.50-5.58 (5H, m), 5.91-6.03 (5H, m), 7.21-7.60 (75H, m); δ_C (100 MHz, $CDCl_3$) [major α anomer quoted] 66.4, 69.2, 70.2, 72.1, 74.0, 75.3, 78.5, 79.2, 101.3, 102.7, 117.2, 126.5, 127.5, 127.7, 127.8, 127.9, 128.1, 128.1, 128.3, 128.3, 128.9, 134.3, 135.3, 137.8, 138.5, 138.9; *m/z* (ES^+) 485 ($M+Na^+$, 100%).

_O_-(2,3-di-_O_-benzyl-4,6-_O_-benzylidene-α-D-galactopyranosyl) trichloroacetimidate 7[iv]

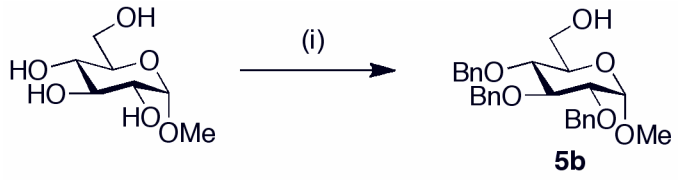
(1,5-Cyclooctadiene)bis(methyl-diphenylphosphine)iridium(I) hexafluorophosphate (0.073 g, 0.086 mmol) was dissolved in freshly distilled THF (10 ml). The reaction mixture was placed under a hydrogen atmosphere, resulting in a colour change from red to colourless. Allyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-galactopyranoside **9** (0.843 g, 1.725 mmol) was then added as a solution in freshly distilled THF (10 ml). After 16h, N-Iodosuccinimide (2.04 g, 8.625 mmol) was added followed by H_2O (5 ml). After 16 h, t.l.c (petrol:ethyl acetate, 1:1) indicated the formation of 2 major products (R_f 0.22 and R_f 0.18) and complete consumption of starting materials (R_f 0.56 and R_f 0.52). The reaction was diluted with CH_2Cl_2 (40 ml) and the organic layer washed with sodium thiosulfate (10% solution, 40 ml). The aqueous layer was extracted with CH_2Cl_2 (2 x 20 ml). The combined organic layers were washed with saturated sodium bicarbonate solution (40 ml), then brine (40 ml), dried ($MgSO_4$), filtered concentrated *in vacuo*. The residue was dried under high vacuum for 2 h, and then the crude mixture of 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-galactopyranoses **10** was dissolved in freshly distilled CH_2Cl_2 (20 ml) and cooled to 0 °C under an argon atmosphere. DBU (0.107 ml, 0.690 mmol) was added followed by trichloroacetonitrile (0.882 ml, 8.625 mmol). After 2 h, t.l.c (petrol:ethyl acetate, 4:1,

with 1% added triethylamine) indicated the formation of two major products (R_f 0.33 and R_f 0.31) and complete consumption of starting material (R_f 0.05). The reaction was concentrated *in vacuo* and the resulting residue was purified by flash column chromatography (petrol:ethyl acetate, 4:1, with 1% added triethylamine) to afford *O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl) trichloroacetimidate **7** (0.590 g, 57%, 2 steps) as a pale yellow oil; δ_H (400 MHz, $CDCl_3$) [10:1 mixture of α:β anomers observed] 3.67-3.70 (1H, m), 3.84 (10H, br s), 3.96-4.14 (23H, m), 4.23-4.31 (32H, m), 4.64-4.94 (44H, m), 5.50 (1H, s, PhCHα), 5.52 (10H, s, PhCHβ), 6.23 (1H, d, $J_{1,2}$ 3.8 Hz, H-1β), 6.65 (10H, d, $J_{1,2}$ 3.4 Hz, H-1α), 7.26-7.43 (143H, m) 7.50-7.55 (22H, m), 8.27 (1H, br s, NHβ), 8.57 (1H, br s, NHα); δ_C (100 MHz, $CDCl_3$) 65.2, 69.0, 72.3, 73.1, 74.5, 74.6, 75.1, 95.5, 101.1, 126.3, 127.4, 127.5, 127.7, 128.1, 128.2, 128.3, 128.3, 129.1, 137.6, 138.2, 138.3, 161.0. 163.6; *m/z* (ES^+) 616 ($M+Na^+$, 100%).

Preparation of Glycosyl Acceptors

Glycosyl acceptors **3** and **5a** are both commercially available.

Glycosyl acceptor **5b** was prepared from commercially available methyl α-D-glucopyranoside as follows:



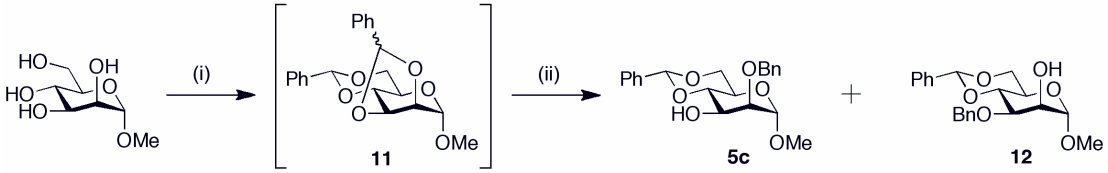
Reagents and Conditions: (i) TIPSCl, Imidazole, DMF, 16 h; then BnBr, NaH, DMF, 16 h; then $TBAF{\cdot}H_2O$, THF, 16 h

Methyl-2,3,4-*O*-benzyl-α-D-glucopyranose 5b[v]

Methyl α-D-glucopyranoside (5.00 g, 25.75 mmol) and imidazole (5.26 g, 77.25 mmol) were dissolved in anhydrous DMF (40 ml) and the reaction mixture cooled to 0 °C. TIPSCl (6.06 ml, 28.33 mmol) was slowly added and then the reaction mixture was allowed to warm to RT. After 16 h the reaction mixture was concentrated *in vacuo* and the resulting residue dissolved in CH_2Cl_2 (100 ml). The organic layer was washed with H_2O (100 ml) and the aqueous layer extracted with CH_2Cl_2 (2 x 100 ml). The combined organic layers were washed with brine (100 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude residue was dried under high vacuum for 2 h and then dissolved in anhydrous DMF (150 ml). The reaction mixture was cooled to 0 °C and NaH (60% in mineral oil, 5.15 g, 128.79 mmol) was added. The mixture was allowed to warm to RT, then BnBr (15.63 ml, 128.79 mmol) was slowly added. After 16 h the reaction was quenched with MeOH and concentrated *in vacuo*. The resulting residue was dissolved in Et_2O (200 ml) and washed with H_2O (200 ml). The aqueous layer was extracted with Et_2O (2 x 100 ml) and the combined organic layers washed with brine (200 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude residue was combined with $TBAF{\cdot}H_2O$ (13.47 g, 51.50 mmol) and dissolved in THF (50 ml). After 16 h, t.l.c (petrol:ethyl acetate, 1:1) indicated the formation of a single major product (R_f 0.45). The reaction was diluted with H_2O (50 ml) and the aqueous layer extracted with CH_2Cl_2 (4 x 50 ml). The combined organic layers were washed with brine (100 ml), dried ($MgSO_4$), filtered and concentrated *in*

vacuo. The resulting residue was purified by flash column chromatography (petrol:ethyl acetate, 1:1) to afford methyl-2,3,4-*O*-benzyl-α-D-glucopyranose **5b** (11.12 g, 93%) as a white crystalline solid; $[\alpha]_D^{18}$ + 26.2 (*c*, 1.0 in $CHCl_3$) [Lit. $[\alpha]_D^{21}$ + 27.5 (*c*, 1.0 in $CHCl_3$)][5]; δ_H (400 MHz, $CDCl_3$) 1.65 (1H, s, OH), 3.33 (3H, s, OMe), 3.45-3.52 (2H, m), 3.60-3.73 (2H, m), 3.73 (1H, dd, *J* 11.6 Hz, *J* 2.0 Hz), 3.98 (1H, at, *J* 9.4 Hz), 4.54 (1H, d, $J_{1,2}$ 3.3 Hz, H-1), 4.60-4.65 (2H, m), 4.76-4.87 (3H, m), 4.97 (1H, d, *J* 10.9 Hz), 7.22-7.34 (15H, m, 15 x Ar-H); δ_C (100 MHz, $CDCl_3$) 55.2, 61.9, 70.7, 73.4, 75.0, 75.8, 80.0, 82.0, 98.2 (C-1), 127.6, 127.9, 128.0, 128.1, 128.1, 128.4, 128.5, 138.1, 138.1, 138.7; *m/z* (ES^+) 487 ($M+Na^+$, 100%).

Glycosyl acceptor **5c** was prepared from commercially available methyl α-D-mannopyranoside as follows:



Reagents and Conditions: (i) $PhCH(OMe)_2$, CSA, DMF, 60 °C, 250 mbar, 5 h; (ii) DIBAL-H, toluene, 2 h

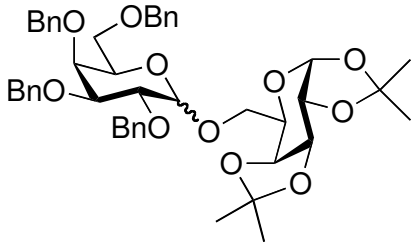
Methyl-2-*O*-benzyl-4,6-di-*O*-benzylidene-α-D-mannopyranoside 5c[vi]

Benzaldehyde dimethylacetal (9.74 ml, 64.89 mmol) was added to a solution of methyl α-D-mannopyranoside (5.04 g, 25.96 mmol) and camphor sulfonic acid (0.060 g, 0.260 mmol) in DMF (75 ml). The resulting solution was heated to 60 °C on a rotary evaporator under a pressure of 250 mbar. After 3 h, TLC (petrol/ethyl acetate, 3:1) indicated complete conversion of starting material (Rf 0.0) to two products (Rf 0.50 and 0.80). Further benzaldehyde dimethyl acetal (4.87 ml, 32.45 mmol) and camphor sulfonic acid (0.030 g, 0.130 mmol) was added to the reaction mixture. After 2 h, TLC (petrol/ethyl acetate, 3:1) indicated the formation of a single product (Rf 0.80). The solvent was removed *in vacuo*, the residue coevaporated with toluene (50 ml), then dissolved in DCM (100 ml), and washed with saturated sodium bicarbonate solution (50 ml) and brine (50 ml). The organic phase was then dried (MgSO4), filtered and concentrated *in vacuo*. The resulting crude mixture of *endo* and *exo*-dibenzylidene derivatives **11** was dissolved in freshly distilled toluene (150 ml) and cooled to -40 °C under an atmosphere of argon. Di-*iso*-butyl aluminium hydride (64.89 ml, 64.89 mmol of a 1 M solution in toluene) was slowly added to the reaction

mixture and then the mixture was allowed to slowly warm to RT. After 2h, t.l.c (petrol:ethyl acetate, 3:1) indicated complete consumption of starting material (R_f 0.80) and formation of two products (R_f 0.40 and R_f 0.30). MeOH was added dropwise to quench the reaction and then the reaction was diluted with CH_2Cl_2 (250 ml). The organic layer was washed with Rochelle's Salt (10% solution, 200 ml), then brine (200 ml), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (petrol:ethyl acetate, 3:1) to afford the undesired compound **12** (R_f 0.30) and the desired methyl-2-*O*-benzyl-4,6-di-*O*-benzylidene-α-D-mannopyranoside **5c** (4.25 g, 44%) as a white crystalline solid (R_f 0.40); m.p 43-45°C; $[\alpha]_D^{18}$ + 1.4 (*c*, 1.0 in $CHCl_3$) [Lit. m.p 44-46°C; $[\alpha]_D^{20}$ + 1.10 (*c*, 1.0 in $CHCl_3$)][6]; δ_H (400 MHz, $CDCl_3$) 2.38 (1H, br s, OH), 3.31 (3H, s, OMe), 3.69-3.80 (3H, m), 3.86 (1H, at, *J* 9.4 Hz), 4.03 (1H, dd, *J* 9.9 Hz, *J* 3.5 Hz), 4.21 (1H, dd, *J* 9.4 Hz, *J* 4.0 Hz), 4.60-4.71 (3H, m), 5.52 (1H, s, PhC<u>H</u>), 7.20-7.50 (10H, m, 10 x Ar-H); δ_C (100 MHz, $CDCl_3$) 55.0, 63.3, 68.7, 68.8, 73.7, 78.5, 79.5, 99.4, 102.1, 126.3, 127.0, 127.8, 128.0, 128.1, 128.3, 128.6, 129.0, 129.1, 129.8, 134.5, 137.4, 137.6; *m/z* (ES^+) 395 ($M+Na^+$, 100%).

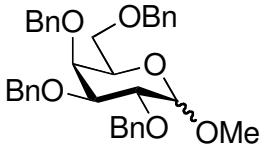
Glycosylation Reactions

2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranosyl-(1→6)-1:2,3:4-Di-*O*-isopropylidene-D-galactopyranoside 4[vii]



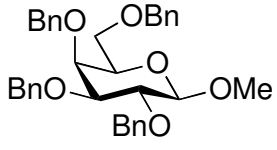
A solution of *O*-(2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranosyl) trichloroacetimidate **2** (50 mg, 0.073 mmol) and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside **3** (38 mg, 0.146 mmol) in freshly distilled toluene (1 mL) were added to a flame-dried round-bottomed flask containing activated 3 Å molecular sieves (100 mg) under argon. The reaction mixture was stirred for 10 min, before the reaction was activated by addition of either TMSOTf (2μl, 0.011 mmol) or (*R*)/(*S*)-**1** (8.5 mg, 0.011 mmol). When t.l.c (petrol:ethyl acetate, 4:1) indicated the complete consumption of starting material (R_f 0.52 and R_f 0.35) and the formation of two products (R_f 0.22 and R_f 0.18) the reaction was quenched by the addition of triethylamine and filtered through Celite®. The mixture was then concentrated *in vacuo* and the resulting residue was purified by flash column chromatography (petrol:ethyl acetate, 3:1) to afford 2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranosyl-(1→6)-1:2,3:4-Di-*O*-isopropylidene-D-galactopyranoside **4** as a pale yellow oil; δ_H (400 MHz, $CDCl_3$) [Data provided for 1:7 mixture of α:β anomers (Table 1, entry 3)] 1.32 (48H, s), 1.45 (24H, s), 1.50 (24H, s), 3.50-3.59 (28H, m), 3.70 (7H, dd, *J* 10.7 Hz, *J* 7.5 Hz), 3.74-3.79 (2H, m), 3.84 (7H, dd, *J* 9.9 Hz, *J* 7.9 Hz), 3.90 (7H, br d, *J* 2.7 Hz), 3.95-3.98 (1H, m), 4.01-4.10 (13H, m), 4.14 (7H, dd, *J* 10.7 Hz, *J* 3.4 Hz), 4.23 (7H, dd, *J* 7.9 Hz, *J* 2.1 Hz), 4.30-4.34 (9H, m), 4.39-4.52 (24H, m), 4.59-4.63 (16H, m), 4.71-4.86 (24H, m), 4.93-4.96 (8H, m), 5.03 (1H, d, $J_{1,2}$ 3.4 Hz, H-1_bα), 5.07 (7H, d, *J* 10.9 Hz), 5.52 (1H, d, $J_{1,2}$ 5.1 Hz, H-1_aα), 5.58 (7H, d, $J_{1,2}$ 4.8 Hz, H-1_aβ), 7.23-7.41 (146H, m), 7.45-7.48 (14H, m); δ_C (100 MHz, $CDCl_3$) 24.4, 25.1, 26.0, 26.0, 67.4, 68.6, 69.6, 70.5, 70.7, 71.5, 73.1, 73.3, 73.5, 74.5, 74.7, 79.1, 81.9, 96.4, 104.7, 108.6, 109.3, 127.3, 127.5, 127.5, 127.8, 127.9, 128.1, 128.3, 128.4, 128.4, 128.6, 137.9, 138.6, 139.0; *m/z* (ES^+) 800 ($M+NH_4^+$, 100%).

Methyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranoside 6a[viii]



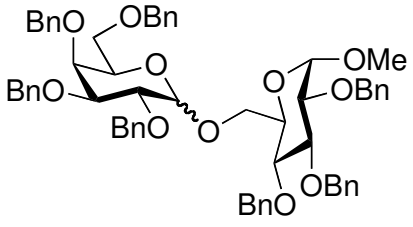
A solution of *O*-(2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranosyl) trichloroacetimidate **2** (50 mg, 0.073 mmol) in freshly distilled toluene (1 mL) was added to a flame-dried round-bottomed flask containing activated 3 Å molecular sieves (100 mg) under argon. Anhydrous MeOH **5a** (6 μl, 0.146 mmol) was added and the reaction mixture was stirred for 10 min, before the reaction was activated by addition of either TMSOTf (2μl, 0.011 mmol) or (*R*)-**1** (8.5 mg, 0.011 mmol). When t.l.c (petrol:ethyl acetate, 4:1) indicated the complete consumption of starting material (R_f 0.52 and R_f 0.35) and the formation of two products (R_f 0.32 and R_f 0.30) the reaction was quenched by the addition of triethylamine and filtered through Celite®. The mixture was then concentrated *in vacuo* and the resulting residue was purified by flash column chromatography (petrol:ethyl acetate, 4:1) to afford methyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranoside **6a** as a pale yellow oil; δ_H (400 MHz, $CDCl_3$) [Data provided for 1:10 mixture of α:β anomers (Table 3, entry 1)] 3.39 (3H, s, $OCH_3\alpha$), 3.51-3.55 (20H, m, H-3β, H-5β), 3.56 (30H, s, $OCH_3\beta$), 3.57-3.63 (22H, m, H-6α, H-6α', H-6β, H-6'β), 3.82 (10H, dd, $J_{1,2}$ 7.5 Hz, $J_{2,3}$ 9.7 Hz, H-2β), 3.91 (10H, br d, *J* 2.4 Hz, H-4β), 3.93-3.99 (3H, m, H-3α, H-4α, H-5α), 4.03-4.07 (1H, m, H-2α), 4.29 (10H, d, $J_{1,2}$ 7.5 Hz, H-1β), 4.39-4.51 (22H, m, 2 x PhC<u>H</u>H'α, 2 x PhC<u>H</u>H'β), 4.58 (1H, d, *J* 11.6 Hz, PhC<u>H</u>H'α), 4.64 (10H, d, *J* 11.6 Hz, PhC<u>H</u>H'β), 4.69-4.78 (33H, m, H-1α, 2 x PhC<u>H</u>H'α, 3 x PhC<u>H</u>H'β), 4.84-4.88 (2H, m, 2 x PhC<u>H</u>H'α), 4.92 (10H, d, *J* 10.9 Hz, PhC<u>H</u>H'β), 4.94-4.97 (11H, m, PhC<u>H</u>H'α, PhC<u>H</u>H'β), 7.25-7.40 (220H, m, 20 x Ar-Hα, 20 x Ar-Hβ); δ_C (100 MHz, $CDCl_3$) 57.0, 68.9, 73.0, 73.4, 73.4, 73.6, 74.5, 75.1, 79.6, 82.1, 105.0, 127.5, 127.5, 127.8, 127.9, 128.1, 128.1, 128.3, 128.4, 128.4, 137.9, 138.5, 138.6, 138.8; *m/z* (ES^+) 572 ($M+NH_4^+$, 100%).

Methyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranoside 6a[8]



A solution of *O*-(2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranosyl) trichloroacetimidate **2** (50 mg, 0.073 mmol) in freshly distilled toluene (1 mL) was added to a flame-dried round-bottomed flask containing activated 3 Å molecular sieves (100 mg) under argon. Anhydrous MeOH **5a** (6 μl, 0.146 mmol) was added and the reaction mixture was stirred for 10 min, before the reaction was activated by the addition of (*S*)-**1** (8.5 mg, 0.011 mmol). When t.l.c (petrol:ethyl acetate, 4:1) indicated the complete consumption of starting material (R_f 0.52 and R_f 0.35) and the formation of a single product (R_f 0.30) the reaction was quenched by the addition of triethylamine and filtered through Celite®. The mixture was then concentrated *in vacuo* and the resulting residue was purified by flash column chromatography (petrol:ethyl acetate, 4:1) to afford methyl 2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranoside **6a** as white crystalline solid; m.p 83-85°C; $[\alpha]_D^{18}$ – 0.9 (*c*, 1.0 in $CHCl_3$) [Lit. m.p 83-85.5°C; $[\alpha]_D^{27}$ – 0.84 (*c*, 0.7 in $CHCl_3$)][8]; δ_H (400 MHz, $CDCl_3$) 3.51-3.55 (2H, m, H-3, H-5), 3.56 (3H, s, OCH_3), 3.58-3.63 (2H, m, H-6, H-6'), 3.82 (1H, dd, $J_{1,2}$ 7.5 Hz, $J_{2,3}$ 9.7 Hz, H-2), 3.91 (1H, br d, *J* 2.4 Hz, H-4), 4.29 (1H, d, $J_{1,2}$ 7.5 Hz, H-1), 4.45 (2H, ABq, *J* 12.0 Hz, PhC$\underline{H}_2$), 4.64 (1H, d, *J* 11.6 Hz, PhC$\underline{H}$H'), 4.71-4.78 (3H, m, 3 x PhC$\underline{H}$H'), 4.92 (1H, d, *J* 10.9 Hz, PhC$\underline{H}$H'), 4.96 (1H, d, *J* 11.6 Hz, PhC$\underline{H}$H'), 7.25-7.40 (20H, m, 20 x Ar-H); δ_C (100 MHz, $CDCl_3$) 57.0, 68.9, 73.0, 73.4, 73.4, 73.6, 74.5, 75.1, 79.6, 82.1, 105.0, 127.5, 127.5, 127.8, 127.9, 128.1, 128.1, 128.3, 128.4, 128.4, 137.9, 138.5, 138.6, 138.8; *m/z* (ES^+) 572 ($M+NH_4^+$, 100%).

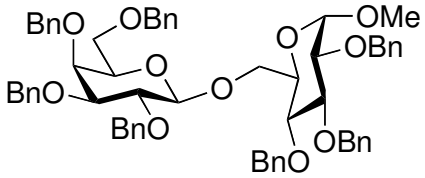
2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranosyl-(1→6)-methyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside 6b[ix]



A solution of *O*-(2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranosyl) trichloroacetimidate **2** (50 mg, 0.073 mmol) and methyl-2,3,4-*O*-benzyl-α-D-glucopyranose **5b** (68 mg, 0.146 mmol) in freshly distilled toluene (1 mL) were added

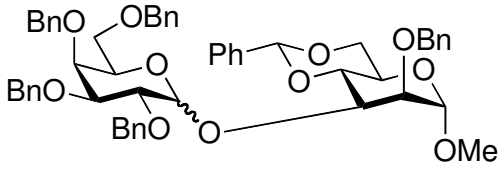
to a flame-dried round-bottomed flask containing activated 3 Å molecular sieves (100 mg) under argon. The reaction mixture was stirred for 10 min, before the reaction was activated by addition of either TMSOTf (2μl, 0.011 mmol) or (*R*)-**1** (8.5 mg, 0.011 mmol). When t.l.c (petrol:ethyl acetate, 4:1) indicated the complete consumption of starting material (R_f 0.52 and R_f 0.35) and the formation of two products (R_f 0.34 and R_f 0.31) the reaction was quenched by the addition of triethylamine and filtered through Celite®. The mixture was then concentrated *in vacuo* and the resulting residue was purified by flash column chromatography (petrol:ethyl acetate, 4:1) to afford 2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranosyl-(1→6)-methyl-2,3,4-tri-*O*-benzyl- α-D-glucopyranoside **6b** as a pale yellow oil; δ_H (400 MHz, C_6D_6) [Data provided for 1:1.2 mixture of α:β anomers (Table 3, entry 4)] 3.12 (3H, s, OMeα), 3.14 (3.6H, s, OMeβ), 3.39 (1.2H, dd, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 2.9 Hz, H-3_bβ), 3.43 (1.2H, m, H-3_aβ), 3.50 (1H, dd, $J_{1,2}$ 3.4 Hz, $J_{2,3}$ 9.6 Hz, H-2_aα), 3.61-3.66 (2.4H, m, H-2_aβ, H-6_bβ), 3.73-3.87 (7.8H, m, H-6_aα, H-6_bα, H-6'$_b$α, H-4_aβ, H-4_bβ, H-6_aβ, H-6'$_b$β), 3.88-3.94 (2H, m, H-4_aα, H-5_aα), 3.96-4.08 (3.2H, m, H-4_bα, H-6'$_a$α, H-5_aβ), 4.11 (1H, dd, $J_{2,3}$ 10.2 Hz, $J_{3,4}$ 2.7 Hz, H-3_bα), 4.16 (1.2H, dd, $J_{1,2}$ 7.5 Hz, $J_{2,3}$ 9.7 Hz, H-2_bβ), 4.21-4.32 (8.6H, m, H-2_bα, H-3_aα, H-5_bα, PhC$\underline{H}_2$α, H-5_bβ, PhC$\underline{H}_2$β), 4.34-4.38 (3.2H, m, PhC$\underline{H}_2$α, H-6'$_a$β), 4.44 (1.2H, d, $J_{1,2}$ 7.5 Hz, H-1_bβ), 4.46-5.13 (26.6H, m, H-1_aα, 10 x PhC$\underline{H}$H'α, H-1_aβ, 12 x PhC$\underline{H}$H'β), 5.29 (1H, d, $J_{1,2}$ 3.4 Hz, H-1_bα), 7.04-7.20 (47.4H, m, 21 x Ar-Hα, 22 x Ar-Hβ), 7.24-7.45 (29.6H, m, 14 x Ar-Hα, 13 x Ar-Hβ); δ_C (100 MHz, C_6D_6) 54.9, 55.0, 68.7, 69.0, 70.0, 70.7, 71.3, 72.7, 72.8, 73.0, 73.5, 73.7, 74.7, 74.8, 75.1, 75.2, 75.3, 75.5, 76.2, 78.3, 78.6, 78.6, 79.9, 81.1, 81.2, 82.3, 82.4, 82.7, 98.2, 98.4, 104.6, 127.4, 127.6, 127.7, 127.8, 128.0, 128.1, 128.2, 128.2, 128.4, 128.5, 128.5, 128.6, 128.6, 138.7, 139.2, 139.2, 139.5, 139.7, 139.8; *m/z* (ES^+) 1004 ($M+NH_4^+$, 100%).

2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranosyl-(1→6)-methyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside 6b[9]



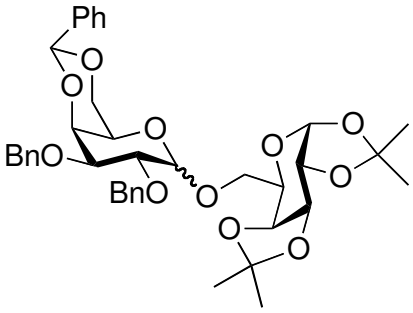
A solution of *O*-(2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranosyl) trichloroacetimidate **2** (50 mg, 0.073 mmol) and methyl-2,3,4-*O*-benzyl-α-D-glucopyranose **5b** (68 mg, 0.146 mmol) in freshly distilled toluene (1 mL) were added to a flame-dried round-bottomed flask containing activated 3 Å molecular sieves (100 mg) under argon. The reaction mixture was stirred for 10 min, before the reaction was activated by addition of (*S*)-**1** (8.5 mg, 0.011 mmol). When t.l.c (petrol:ethyl acetate, 4:1) indicated the complete consumption of starting material (R_f 0.52 and R_f 0.35) and the formation of a single major product (R_f 0.31) the reaction was quenched by the addition of triethylamine and filtered through Celite®. The mixture was then concentrated *in vacuo* and the resulting residue was purified by flash column chromatography (petrol:ethyl acetate, 4:1) to afford 2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranosyl-(1→6)-methyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **6b** as a white crystalline solid; m.p 125-127°C; $[\alpha]_D^{18}$ + 11.4 (*c*, 1.0 in $CHCl_3$) [Lit. m.p 126-128°C; $[\alpha]_D^{21}$ + 12.0 (*c*, 1.0 in $CHCl_3$)][9]; δ_H (400 MHz, C_6D_6) [1:70 mixture α:β anomers observed, major β anomer quoted] 3.14 (3H, s, OMe), 3.39 (1H, dd, $J_{2,3}$ 9.7 Hz, $J_{3,4}$ 2.9 Hz, H-3_b), 3.43 (1H, m, H-3_a), 3.61-3.66 (2H, m, H-2_a, H-6_b), 3.74-3.80 (2H, m, H-4_a, H-$6'_b$), 3.82-3.86 (2H, m, H-4_b, H-6_a), 4.03-4.08 (1H, m, H-5_a), 4.16 (1H, dd, $J_{1,2}$ 7.5 Hz, $J_{2,3}$ 9.7 Hz, H-2_b), 4.24-4.32 (3H, m, H-5_b, PhC$\underline{H}_2$), 4.38 (1H, dd, $J_{6,6'}$ 10.8 Hz, $J_{5,6}$ 1.5 Hz, H-$6'_a$), 4.44 (1H, d, $J_{1,2}$ 7.5 Hz, H-1_b), 4.46 (1H, d, *J* 12.0 Hz, PhC$\underline{H}$H'), 4.52 (2H, at, *J* 12.0 Hz, PhC$\underline{H}_2$), 4.61 (1H, d, *J* 12.0 Hz, PhC$\underline{H}$H'), 4.61 (1H, d, *J* 11.3 Hz, PhC$\underline{H}$H'), 4.67-4.70 (2H, m, H-1_a, PhC$\underline{H}$H'), 4.79 (2H, m, PhC$\underline{H}_2$), 4.92 (1H, d, *J* 12.0 Hz, PhC$\underline{H}$H'), 5.01-5.10 (3H, m, $PhCH_2$, PhC$\underline{H}$H'), 7.05-7.19 (22H, m, 22 x Ar-H), 7.24-7.45 (13H, m, 13 x Ar-H); δ_C (100 MHz, C_6D_6) 55.0, 68.8, 69.0, 70.7, 72.7, 73.0, 73.5, 73.7, 74.7, 74.8, 75.2, 75.3, 75.5, 78.6, 79.9, 81.2, 82.3, 82.7, 98.2, 104.7, 127.4, 127.6, 127.7, 127.8, 127.9, 127.9, 128.0, 128.1, 128.2, 128.2, 128.4, 128.5, 128.5, 128.6, 128.6, 138.7, 139.2, 139.2, 139.5, 139.7, 139.8; *m/z* (ES^+) 1004 ($M+NH_4^+$, 100%).

2,3,4,6-Tetra-*O*-benzyl-α/β-D-glucopyranosyl-(1→2)-methyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside 6c



A solution of *O*-(2,3,4,6-Tetra-*O*-benzyl-α/β-D-galactopyranosyl) trichloroacetimidate **2** (50 mg, 0.073 mmol) and methyl-2-*O*-benzyl-4,6-di-*O*-benzylidene-α-D-mannopyranoside **5c** (54 mg, 0.146 mmol) in freshly distilled toluene (1 mL) were added to a flame-dried round-bottomed flask containing activated 3 Å molecular sieves (100 mg) under argon. The reaction mixture was stirred for 10 min, before the reaction was activated by addition of either TMSOTf (2μl, 0.011 mmol) or (*R*)/(*S*)-**1** (8.5 mg, 0.011 mmol). When t.l.c (toluene:ethyl acetate, 4:1) indicated the complete consumption of starting material (R_f 0.72 and R_f 0.65) and the formation of two products (R_f 0.50 and R_f 0.46) the reaction was quenched by the addition of triethylamine and filtered through Celite®. The mixture was then concentrated *in vacuo* and the resulting residue was purified by flash column chromatography (toluene:ethyl acetate, 12:1) to afford 2,3,4,6-Tetra-*O*-benzyl-α/β-D-glucopyranosyl-(1→2)-methyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside **6c** as a pale yellow oil; δ_H (400 MHz, $CDCl_3$) [Data provided for 1:6 mixture of α:β anomers (Table 3, entry 8] 3.31 (18H, s, $OCH_3\beta$), 3.32 (3H, s, $OCH_3\alpha$), 3.38 (6H, dd, *J* 8.6 Hz, *J* 5.1 Hz), 3.42-3.49 (8H, m), 3.52 (6H, dd, *J* 9.6 Hz, *J* 2.8 Hz), 3.55-3.59 (1H, m), 3.69 (6H, at, *J* 8.3 Hz), 3.73-3.90 (29H, m), 3.95 (6H, br d, *J* 2.5 Hz), 4.00 (1H, dd, *J* 10.0 Hz, *J* 3.7 Hz), 4.22-4.38 (32H, m), 4.51 (1H, d, *J* 12.1 Hz, PhC<u>H</u>H'α), 4.56 (6H, d, $J_{1,2}$ 7.8 Hz, H-$1_b\beta$), 4.59-4.87 (59H, m), 4.95 (6H, d, *J* 11.6 Hz, PhC<u>H</u>H'β), 5.44 (1H, s, PhC<u>H</u>α), 5.54 (1H, d, $J_{1,2}$ 3.8 Hz, H-$1_b\alpha$), 5.61 (6H, s, PhC<u>H</u>β), 7.15-7.39 (196H, m), 7.49-7.51 (14H, m); δ_C (100 MHz, $CDCl_3$) [major β anomer quoted] 54.8 ($O\underline{C}H_3$), 64.2, 68.2, 68.8, 72.4, 73.2, 73.5, 74.5, 74.9, 76.7, 78.2, 79.6, 82.8, 100.3 (C-1_a), 101.4 (Ph<u>C</u>H), 103.6 (C-1_b), 125.3, 126.2, 126.3, 127.2, 127.2, 127.3, 127.5, 127.5, 127.8, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.7, 129.0 (17 x Ar<u>C</u>H), 137.8, 137.9, 139.0 (3 x Ar<u>C</u>); *m/z* (ES^+) 917 ($M+Na^+$, 100%). (HRMS (ES^+) Calcd. for $C_{55}H_{58}O_{11}Na$ (MNa^+) 917.3877. Found 917.3872).

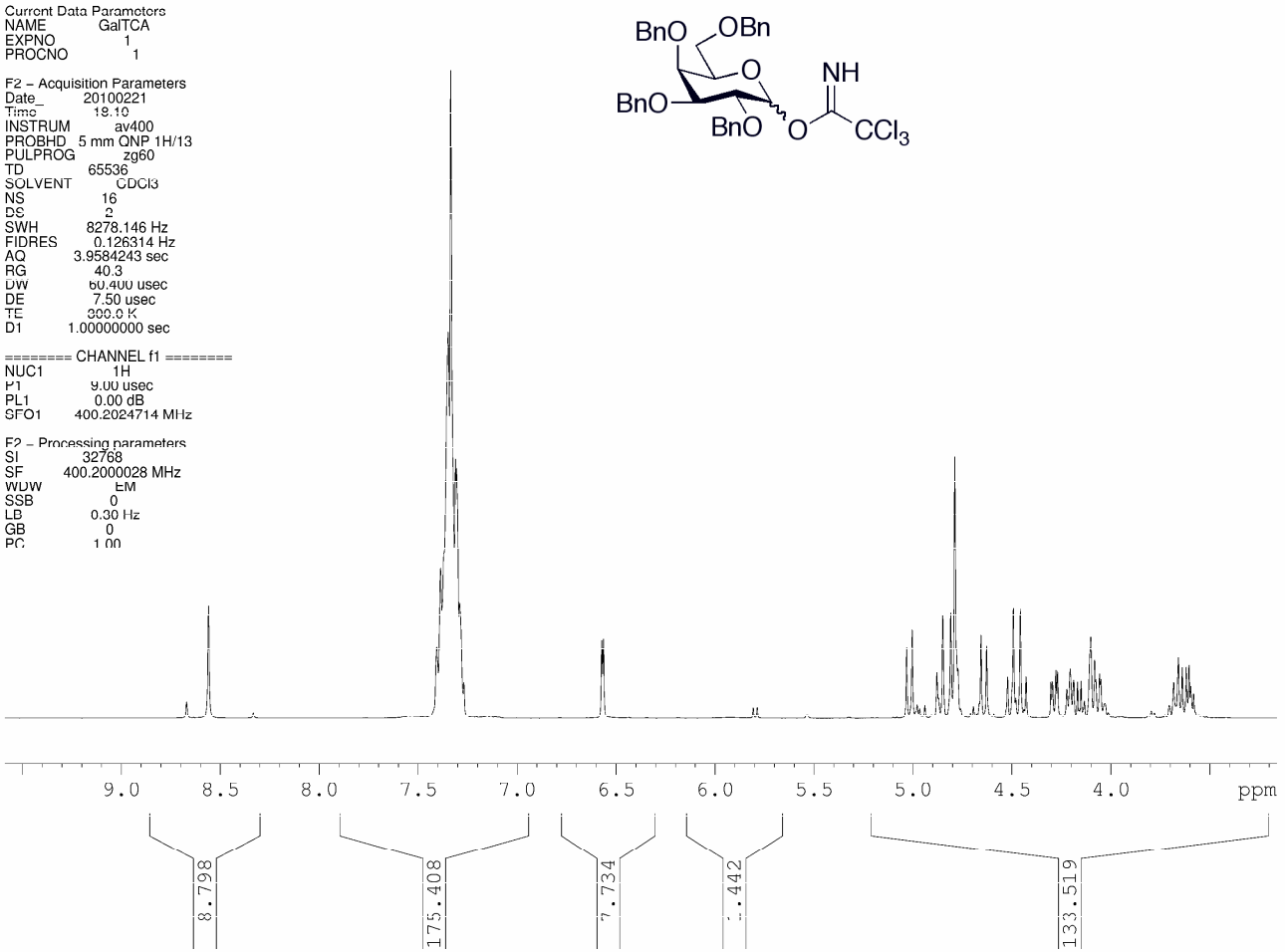
2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-galactopyranosyl-(1→6)-1:2,3:4-Di-*O*-isopropylidene-D-galactopyranoside 8



A solution of *O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-galactopyranosyl) trichloroacetimidate **7** (43 mg, 0.073 mmol) and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside **3** (38 mg, 0.146 mmol) in freshly distilled toluene (1 mL) were added to a flame-dried round-bottomed flask containing activated 3 Å molecular sieves (100 mg) under argon. The reaction mixture was stirred for 10 min, before the reaction was activated by addition of either TMSOTf (2μl, 0.011 mmol) or (*R*)/(*S*)-**1** (8.5 mg, 0.011 mmol). When t.l.c (petrol:ethyl acetate, 4:1) indicated the complete consumption of starting material (R_f 0.52 and R_f 0.35) and the formation of two products (R_f 0.31 and R_f 0.27) the reaction was quenched by the addition of triethylamine and filtered through Celite®. The mixture was then concentrated *in vacuo* and the resulting residue was purified by flash column chromatography (petrol:ethyl acetate, 4:1) to afford 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α/β-D-galactopyranosyl-(1→6)-1:2,3:4-Di-*O*-isopropylidene-D-galactopyranoside **8** as a pale yellow oil; δ_H (400 MHz, $CDCl_3$) [Data provided for 1:3.4 mixture of α:β anomers (Table 4, entry 3)] 1.33 (26.4H, s), 1.46 (13.2H, s), 1.51 (13.2H, s), 3.03 (3.4H, br s), 3.57 (3.4H, dd, *J* 9.5 Hz, *J* 3.7 Hz), 3.73 (3.4H, dd, *J* 10.6 Hz, *J* 7.3 Hz), 3.77-3.79 (3.4H, m), 3.87 (3.4H, dd, *J* 9.5 Hz, *J* 7.8 Hz), 3.99-4.05 (5.4H, m), 4.07 (1H, d, *J* 3.5 Hz), 4.09-4.13 (6.4H, m), 4.17-4.34 (18.6H, m), 4.45 (3.4H, d, $J_{1,2}$ 7.8 Hz, H-1_bβ), 4.57-4.61 (4.4H, m), 4.71-4.85 (15.2H, m), 5.08 (4.4H, m), 5.49-5.52 (5.4H, m, H-1_aα, PhC<u>H</u>α, PhC<u>H</u>β), 5.59 (3.4H, d, $J_{1,2}$ 5.1 Hz, H-1_aβ), 7.25-7.42 (48.4H, m), 7.47-7.57 (17.6H, m); δ_C (100 MHz, $CDCl_3$) 24.4, 25.0, 26.0, 26.1 (4 x <u>C</u>H_3), 66.4, 67.3, 69.2, 69.6, 70.5, 70.8, 72.1, 74.2, 75.0, 75.5, 78.2, 78.8, 96.4 (C-1_aβ), 101.2 (C-1_bα), 104.3, 104.4 (Ph<u>C</u>Hα/β), 108.6 (C-1_aα), 109.3 (C-1_bβ), 126.4, 126.5, 127.4, 127.6, 127.8, 128.1, 128.1, 128.3, 128.3, 128.5, 128.9, 129.0 (12 x

Ar<u>C</u>H), 137.8, 138.5, 139.0 (3 x Ar<u>C</u>); *m/z* (ES^+) 708 ($M+NH_4^+$, 100%). (HRMS (ES^+) Calcd. for $C_{39}H_{46}O_{11}Na$ (MNa^+) 713.2932. Found 713.2925).

Compound 2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DE 7.50 usec
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GB 0
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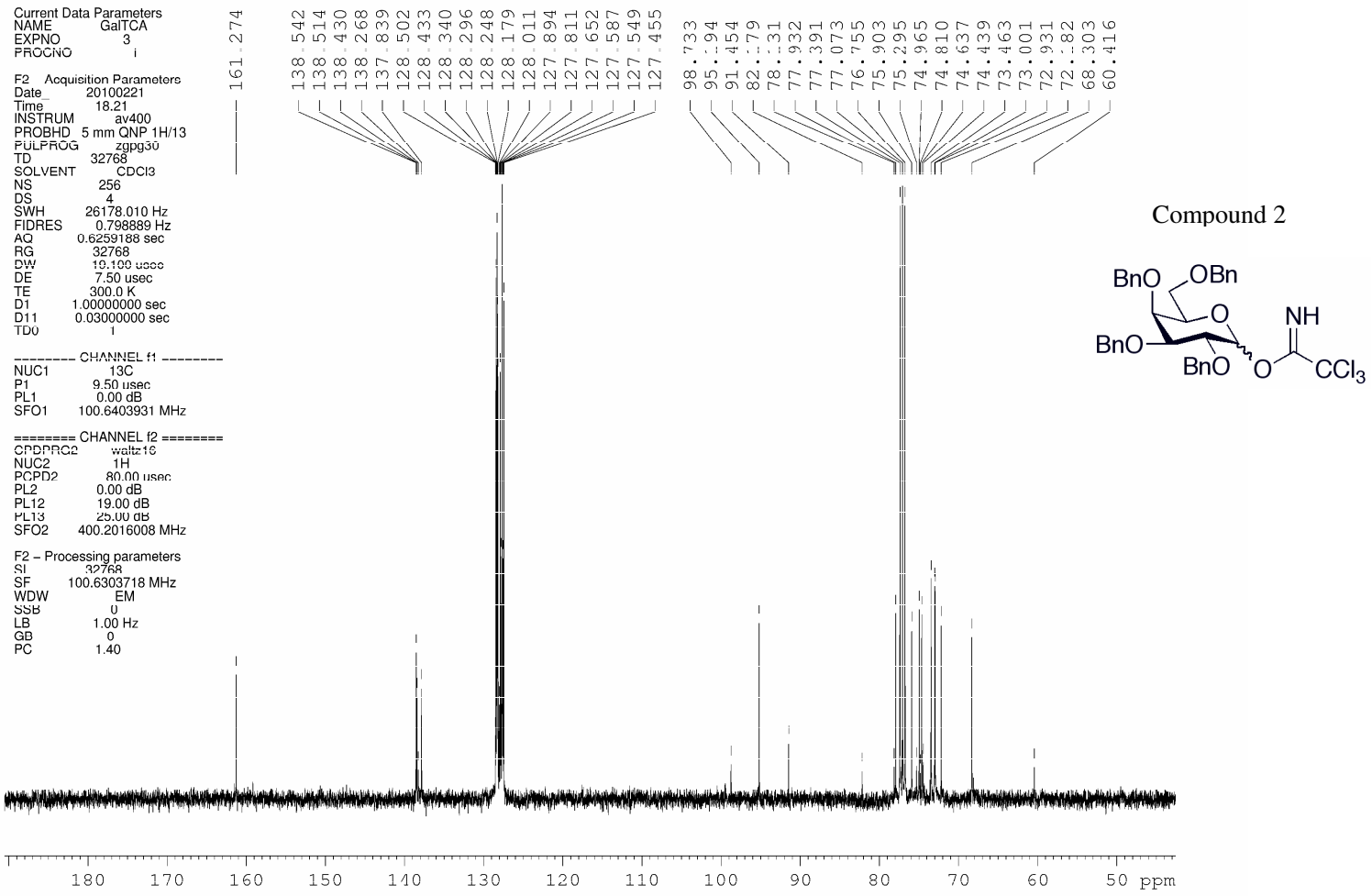
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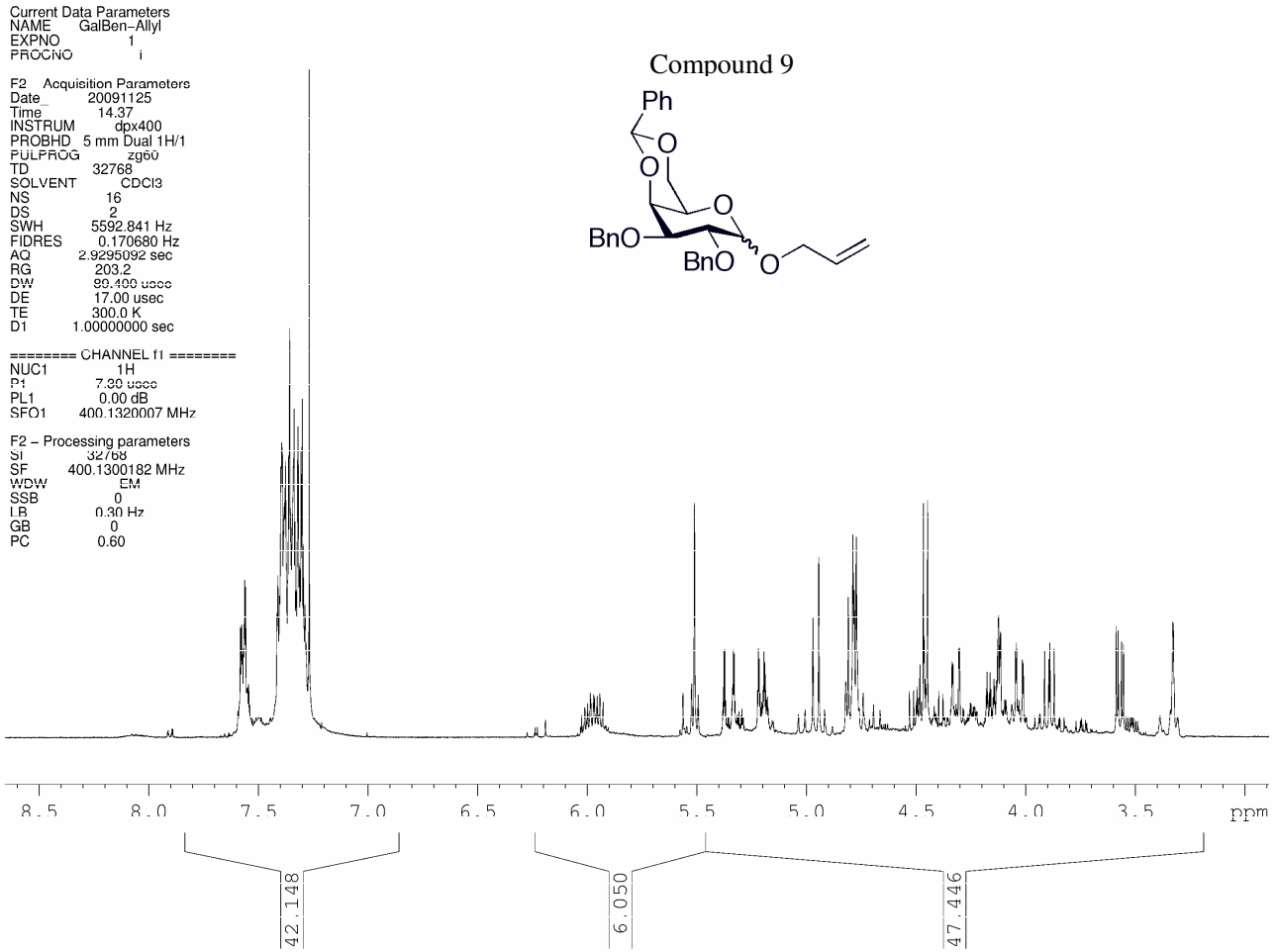
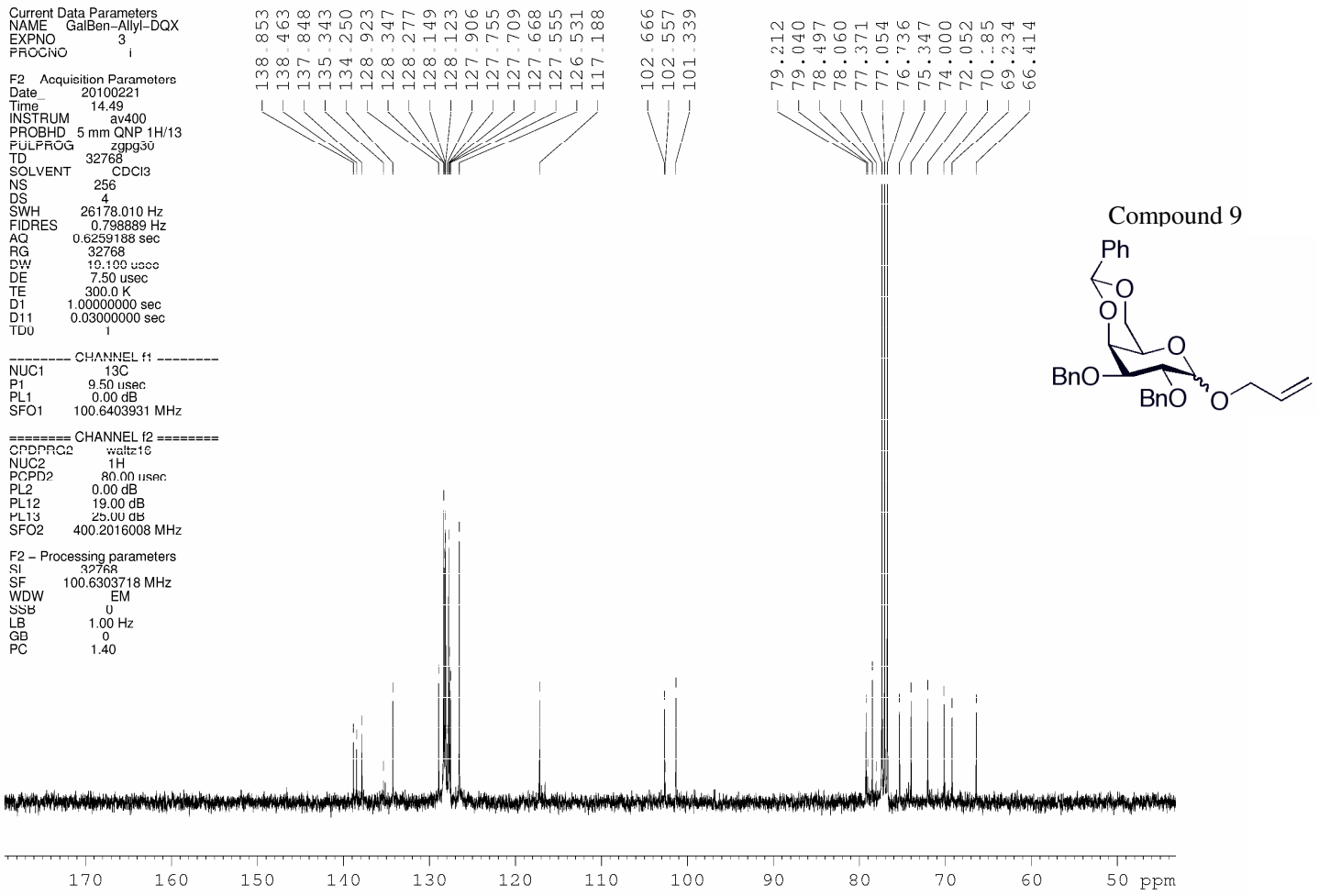
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 256
DS 4
SWH 26178.010 Hz
FIDRES 0.798889 Hz
AQ 0.6259188 sec
RG 32768
DW 19.100 usec
DE 7.50 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 9.50 usec
PL1 0.00 dB
SFO1 100.6403931 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 19.00 dB
PL13 25.00 dB
SFO2 400.2016008 MHz
F2 – Processing parameters
SI 32768
SF 100.6303718 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
161.274
138.542
138.514
138.430
138.268
137.839
128.502
128.433
128.340
128.296
128.248
128.179
128.011
127.894
127.811
127.652
127.587
127.549
127.455
98.733
95.194
91.454
82.479
78.331
77.932
77.391
77.073
76.755
75.903
75.295
74.965
74.810
74.637
74.439
73.463
73.001
72.931
72.182
68.303
60.416
180
170
160
150
140
130
120
110
100
90
80
70
60
50 ppm

Compound 2

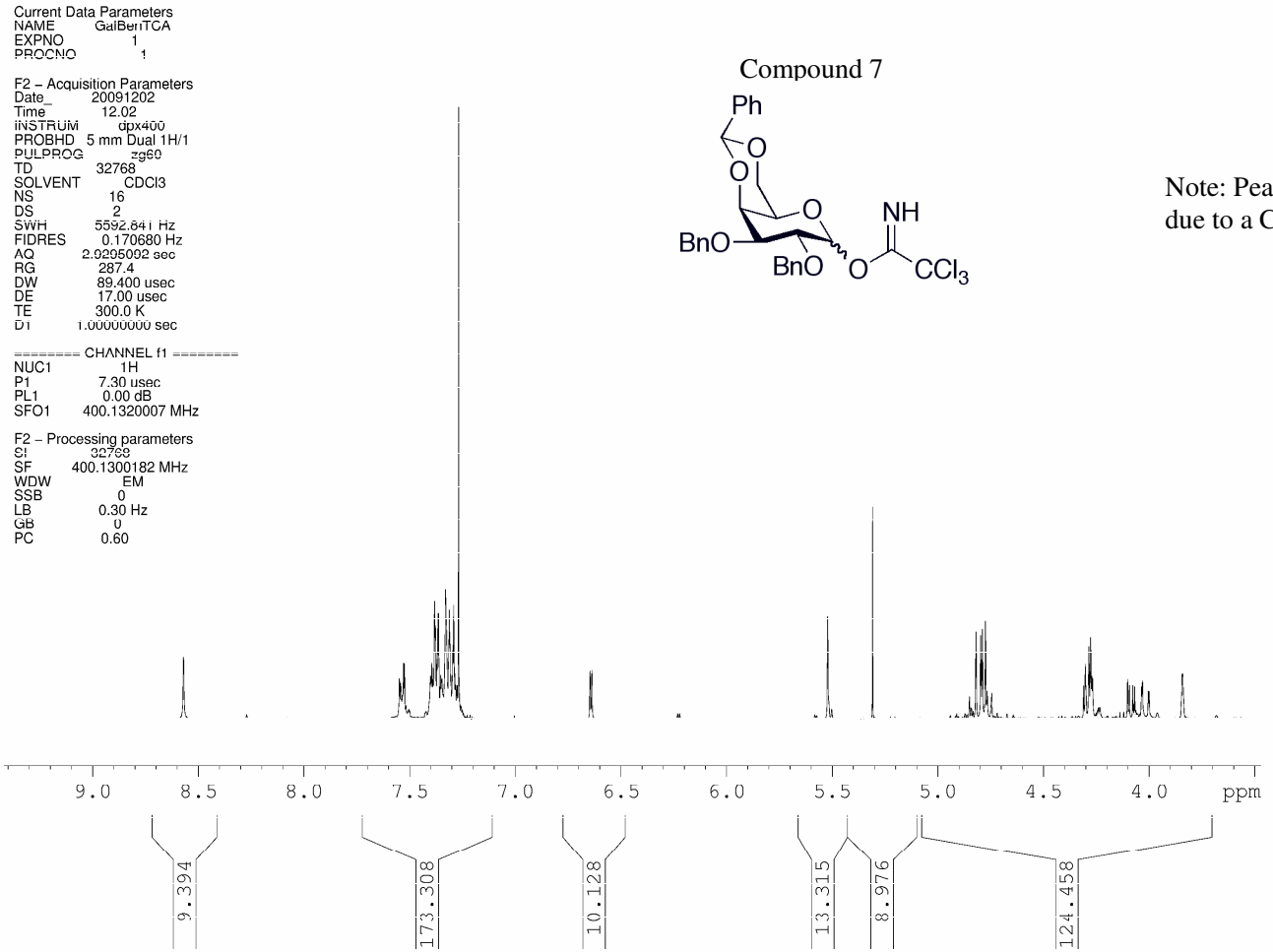
BnO
OBn
O
NH
BnO
BnO
O
CCl3


Current Data Parameters
NAME GalBen-Allyl
EXPNO 1
PROCNO 1
F2 Acquisition Parameters
Date_ 20091125
Time 14.37
INSTRUM dpx400
PROBHD 5 mm Dual 1H/1
PULPROG zg60
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 5592.841 Hz
FIDRES 0.170680 Hz
AQ 2.9295092 sec
RG 203.2
DW 89.400 usec
DE 17.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.30 usec
PL1 0.00 dB
SFO1 400.1320007 MHz
F2 – Processing parameters
SI 32768
SF 400.1300182 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.60
Compound 9
Ph
O
O
O
BnO
BnO
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
42.148
6.050
47.446

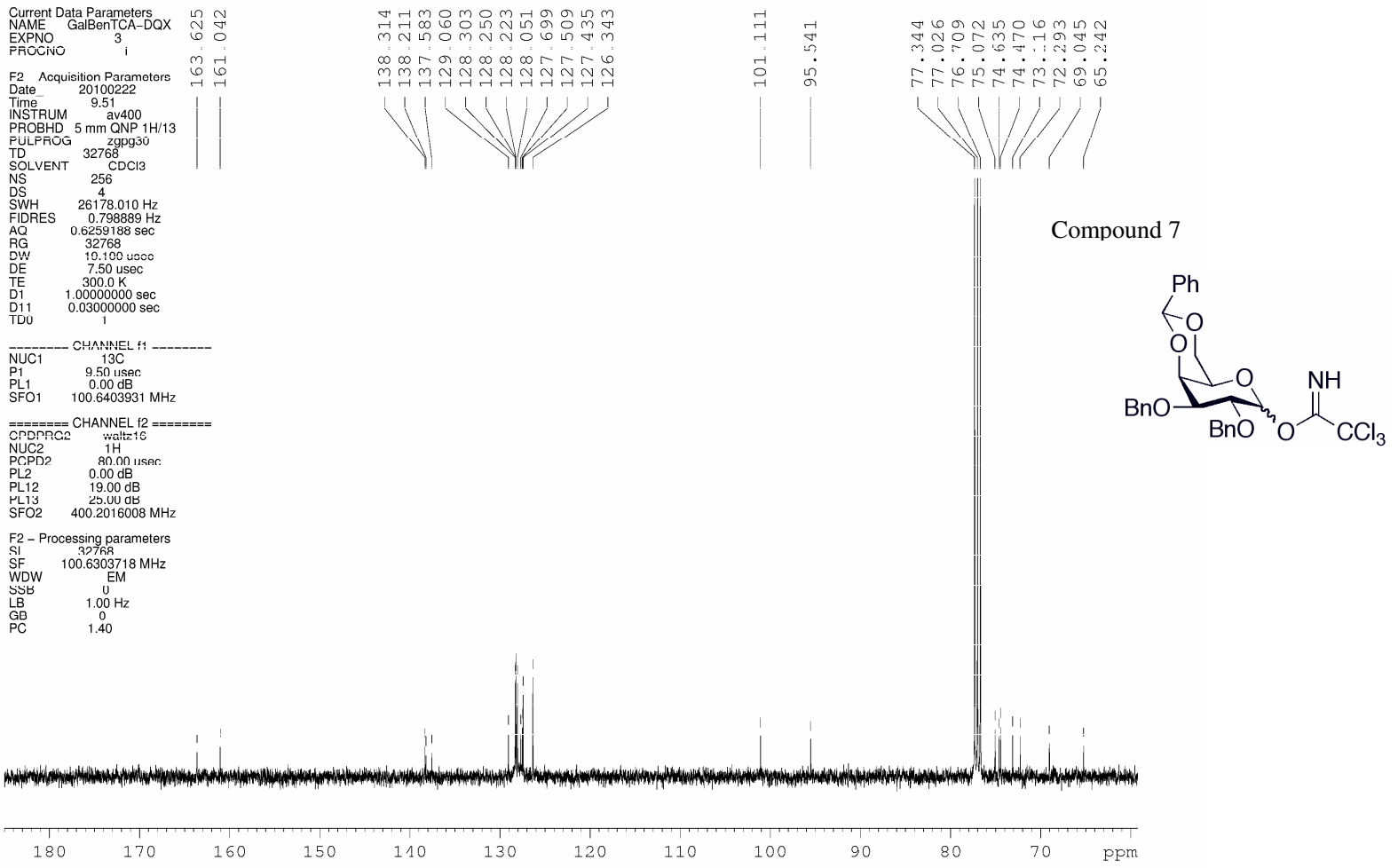

Current Data Parameters
NAME GalBen-Allyl-DQX
EXPNO 3
PROCNO 1
F2 Acquisition Parameters
Date 20100221
Time 14.49
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 256
DS 4
SWH 26178.010 Hz
FIDRES 0.798889 Hz
AQ 0.6259188 sec
RG 32768
DW 19.100 usec
DE 7.50 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
-------- CHANNEL f1 --------
NUC1 13C
P1 9.50 usec
PL1 0.00 dB
SFO1 100.6403931 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 19.00 dB
PL13 25.00 dB
SFO2 400.2016008 MHz
F2 - Processing parameters
SI 32768
SF 100.6303718 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
138.853
138.463
137.848
135.343
134.250
128.923
128.347
128.277
128.149
128.123
127.906
127.755
127.709
127.668
127.555
126.531
117.188
102.666
102.557
101.339
79.212
79.040
78.497
78.060
77.371
77.054
76.736
75.347
74.000
72.052
70.185
69.234
66.414
170
160
150
140
130
120
110
100
90
80
70
60
50 ppm

Compound 9

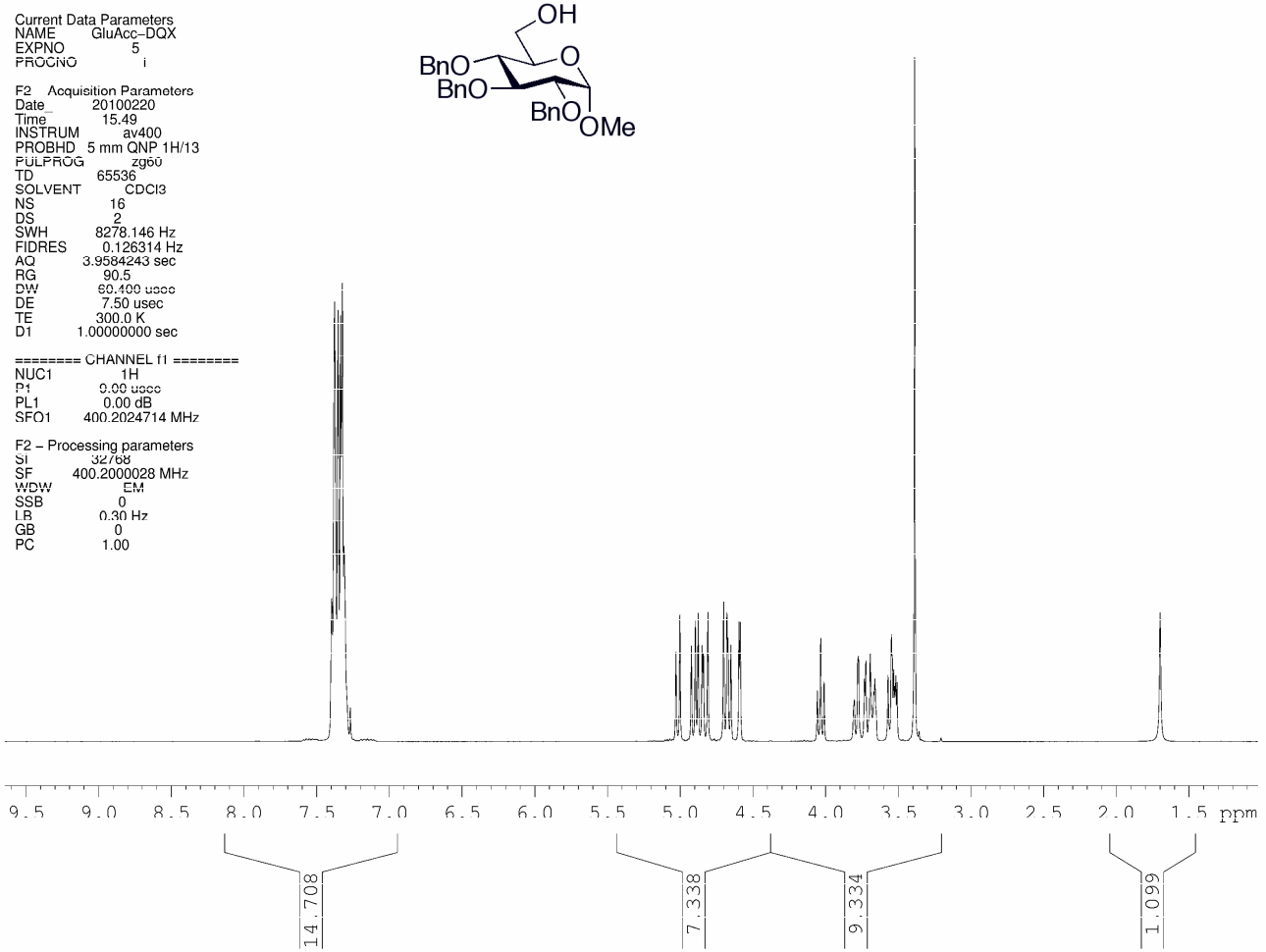
Ph
O
O
O
BnO
BnO
O

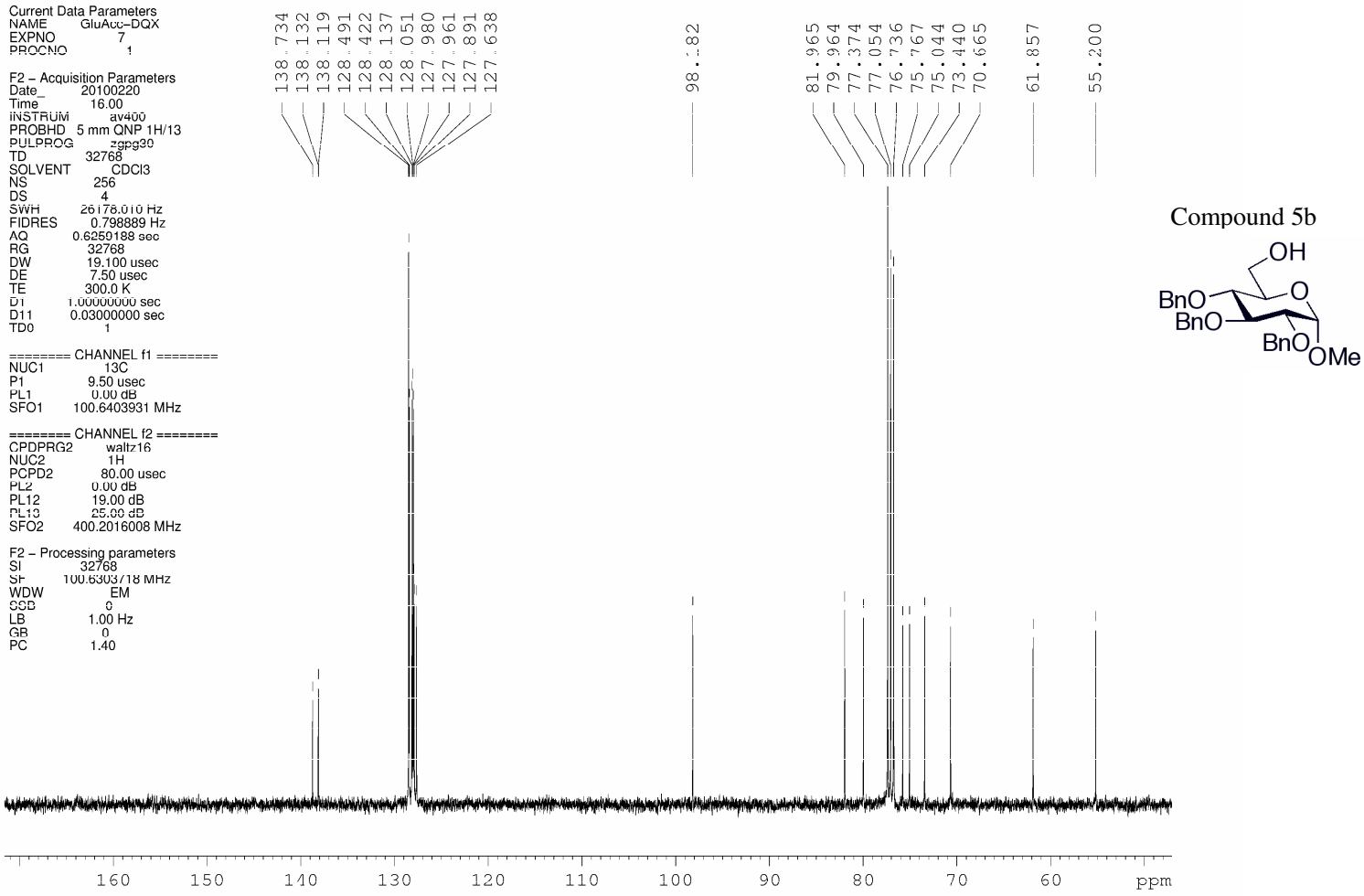


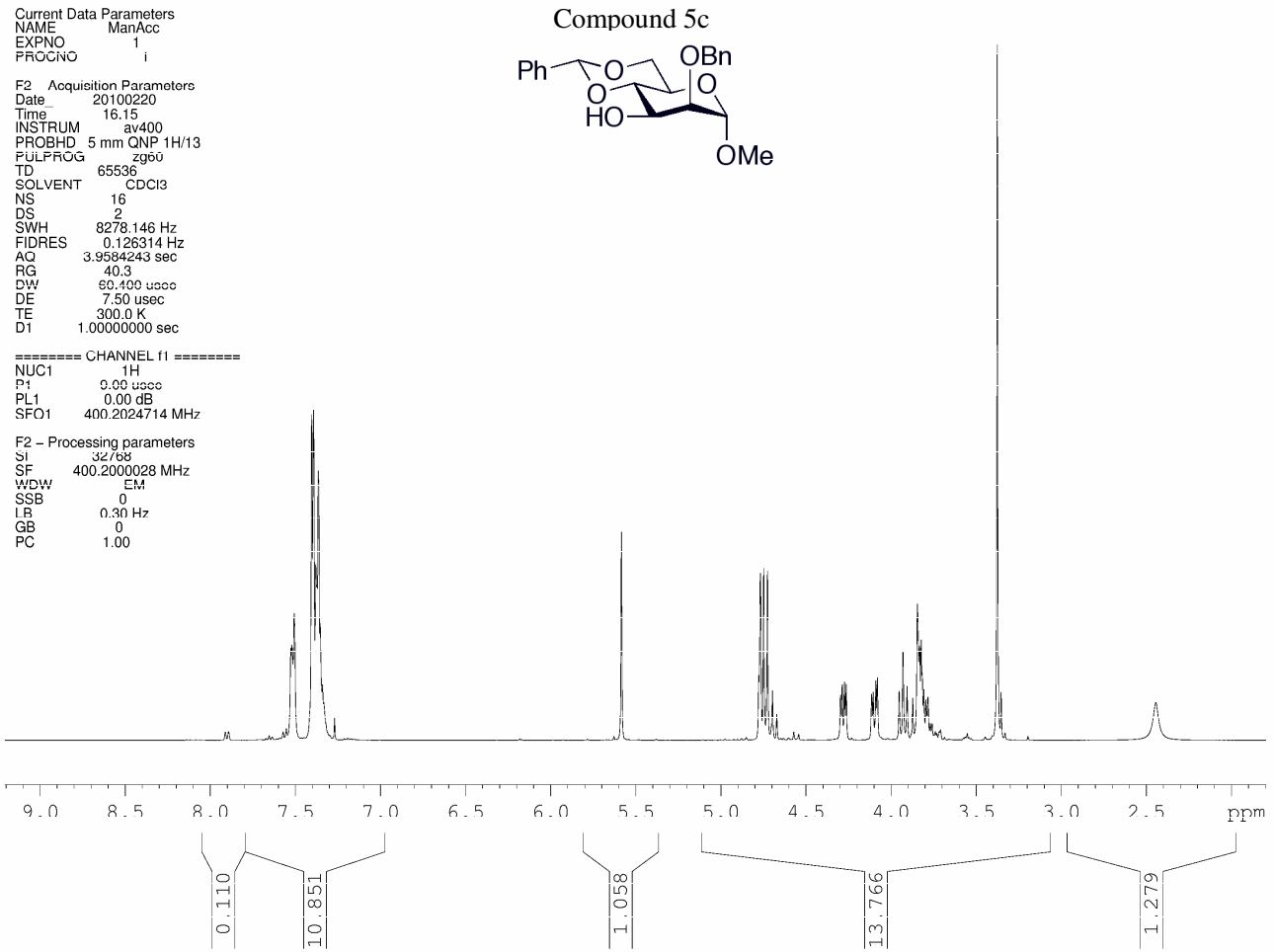
Note: Peak at 5.3 ppm is due to a CH_2Cl_2 impurity

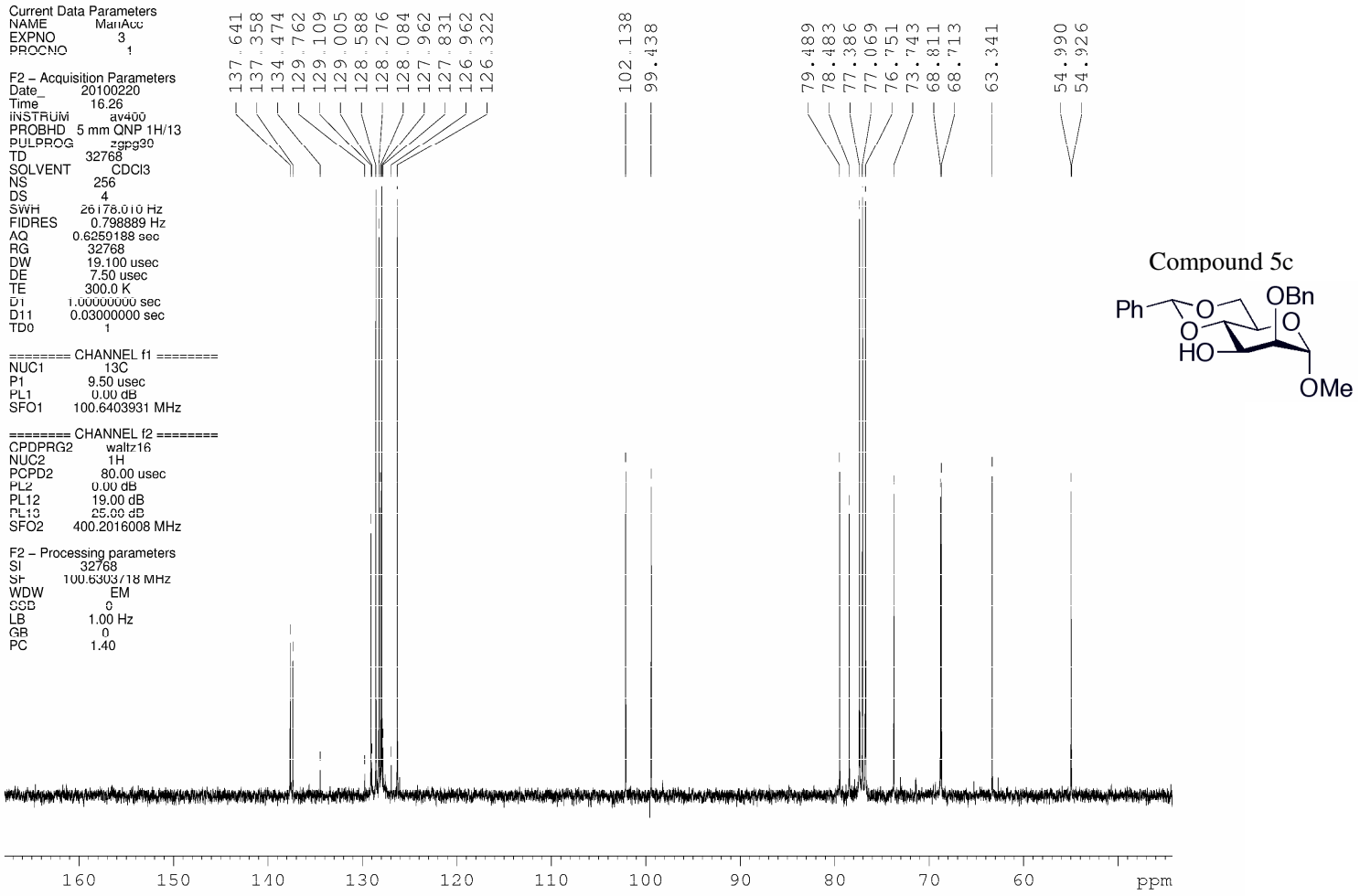

Current Data Parameters
NAME GalBenTCA-DQX
EXPNO 3
PROCNO 1
F2 Acquisition Parameters
Date_ 20100222
Time 9.51
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 256
DS 4
SWH 26178.010 Hz
FIDRES 0.798889 Hz
AQ 0.6259188 sec
RG 32768
DW 19.100 usec
DE 7.50 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 9.50 usec
PL1 0.00 dB
SFO1 100.6403931 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 19.00 dB
PL13 25.00 dB
SFO2 400.2016008 MHz
F2 – Processing parameters
SI 32768
SF 100.6303718 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
163.625
161.042
138.314
138.211
137.583
129.060
128.303
128.250
128.223
128.051
127.699
127.509
127.435
126.343
101.111
95.541
77.344
77.026
76.709
75.072
74.635
74.470
73.116
72.293
69.045
65.242
Compound 7
Ph
O
O
O
BnO
BnO
O
NH
CCl3
180
170
160
150
140
130
120
110
100
90
80
70
ppm

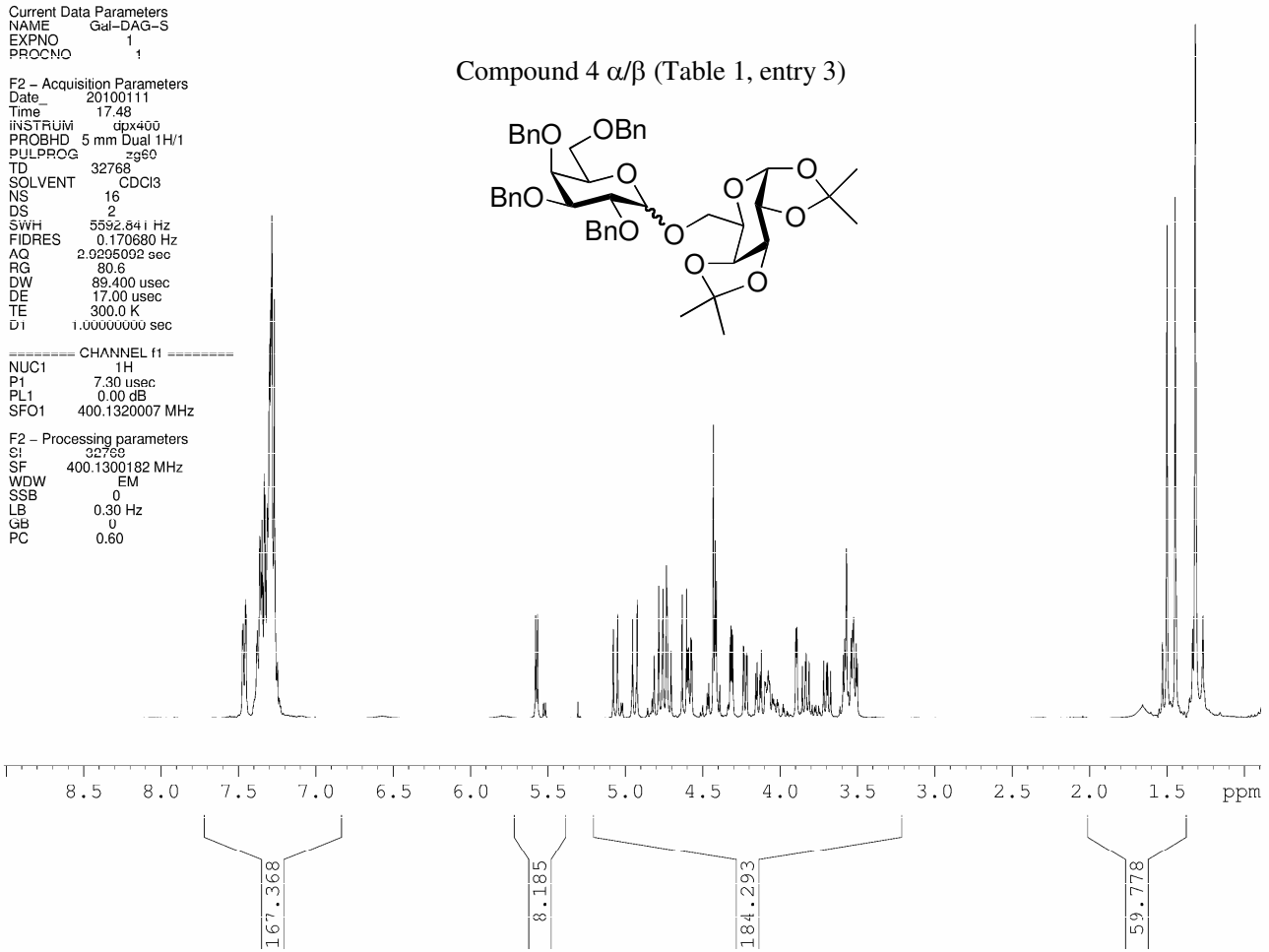
Compound 5b

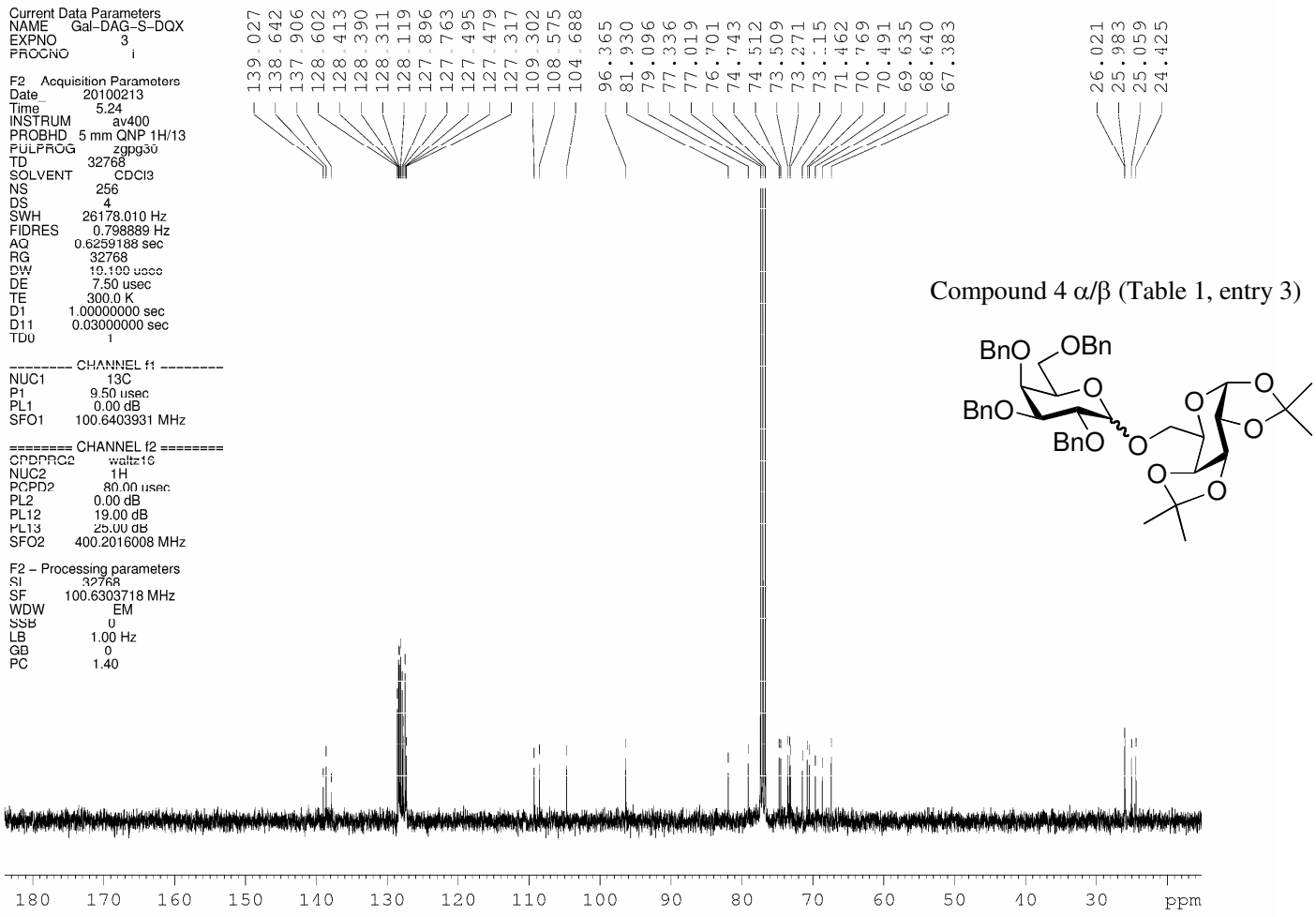

Current Data Parameters
NAME GluAcc-DQX
EXPNO 5
PROCNO 1
F2 Acquisition Parameters
Date 20100220
Time 15.49
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg60
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 90.5
DW 60.400 usec
DE 7.50 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 400.2024714 MHz
F2 - Processing parameters
SI 32768
SF 400.2000028 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
OH
O
BnO
BnO
BnO
OMe
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
14.708
7.338
9.334
1.099


Current Data Parameters
NAME GluAcc-DQX
EXPNO 7
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100220
Time 16.00
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 256
DS 4
SWH 26178.010 Hz
FIDRES 0.798889 Hz
AQ 0.6259188 sec
RG 32768
DW 19.100 usec
DE 7.50 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 0.00 dB
SFO1 100.6403931 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 19.00 dB
PL13 25.00 dB
SFO2 400.2016008 MHz
F2 – Processing parameters
SI 32768
SF 100.6303718 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
138.734
138.132
138.119
128.491
128.422
128.137
128.051
127.980
127.961
127.891
127.638
98.182
81.965
79.964
77.374
77.054
76.736
75.767
75.044
73.440
70.665
61.857
55.200
Compound 5b
OH
BnO
BnO
O
BnO
OMe
160
150
140
130
120
110
100
90
80
70
60
ppm


Current Data Parameters
NAME ManAcc
EXPNO 1
PROCNO i
F2 Acquisition Parameters
Date 20100220
Time 16.15
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg60
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 40.3
DW 60.400 usec
DE 7.50 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 400.2024714 MHz
F2 – Processing parameters
SI 32768
SF 400.2000028 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Compound 5c
Ph
O
OBn
O
HO
O
OMe
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
0.110
10.851
1.058
13.766
1.279

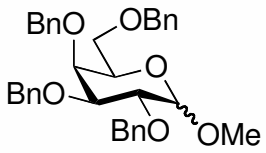

Current Data Parameters
NAME MariAcc
EXPNO 3
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100220
Time 16.26
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 256
DS 4
SWH 26178.010 Hz
FIDRES 0.798889 Hz
AQ 0.6259188 sec
RG 32768
DW 19.100 usec
DE 7.50 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.50 usec
PL1 0.00 dB
SFO1 100.6403931 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 19.00 dB
PL13 25.00 dB
SFO2 400.2016008 MHz
F2 – Processing parameters
SI 32768
SF 100.6303718 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
137.641
137.358
134.474
129.762
129.109
129.005
128.588
128.276
128.084
127.962
127.831
126.962
126.322
102.138
99.438
79.489
78.483
77.386
77.069
76.751
73.743
68.811
68.713
63.341
54.990
54.926
Compound 5c
Ph
O
OBn
O
O
HO
OMe
160
150
140
130
120
110
100
90
80
70
60
ppm

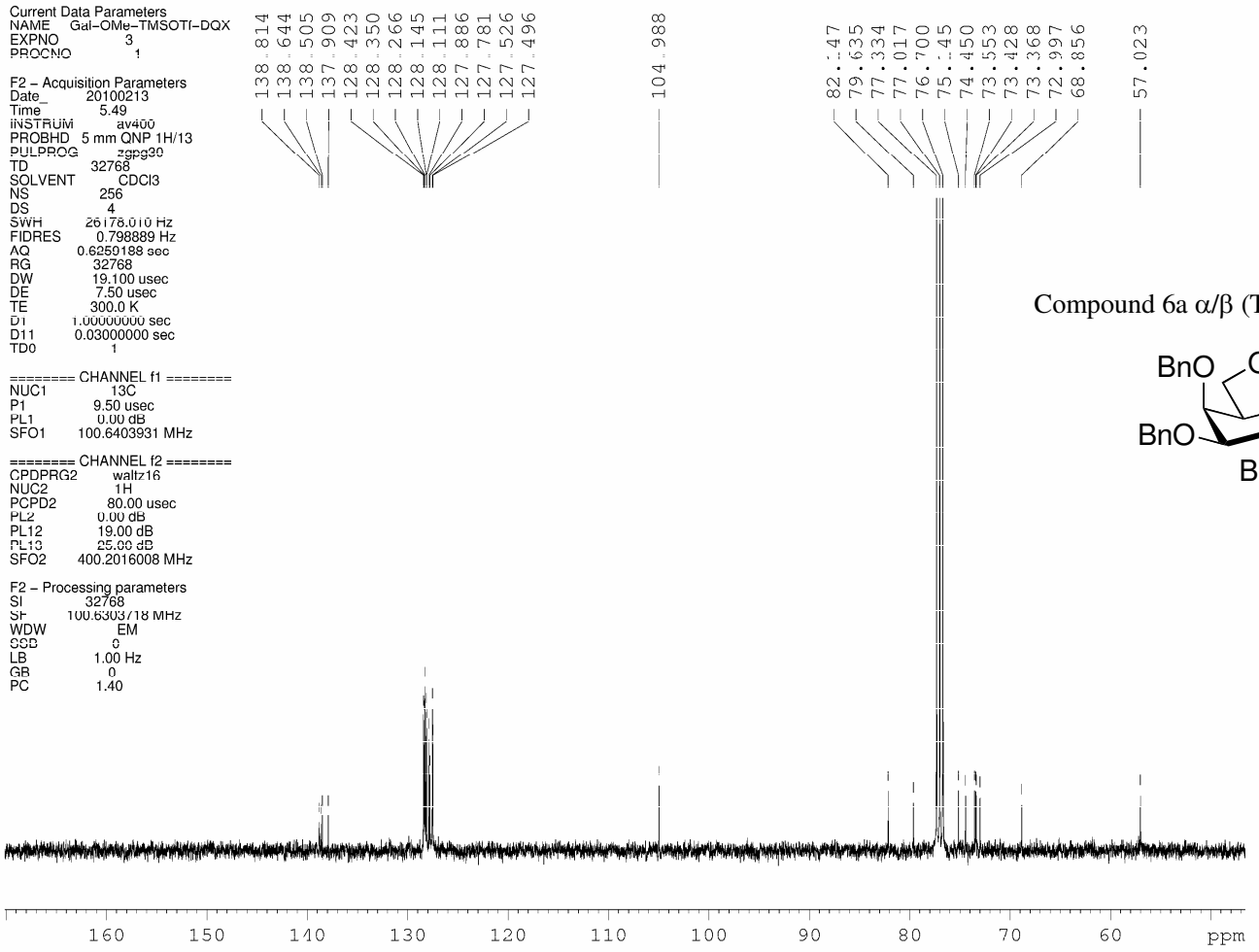

Current Data Parameters
NAME Gal-DAG-S
EXPNO 1
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100111
Time 17.48
INSTRUM dpx400
PROBHD 5 mm Dual 1H/1
PULPROG zg60
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 5592.841 Hz
FIDRES 0.170680 Hz
AQ 2.9295092 sec
RG 80.6
DW 89.400 usec
DE 17.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.30 usec
PL1 0.00 dB
SFO1 400.1320007 MHz
F2 – Processing parameters
SI 32768
SF 400.1300182 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.60
Compound 4 α/β (Table 1, entry 3)
BnO
OBn
BnO
BnO
O
O
O
O
O
O
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
167.368
8.185
184.293
59.778



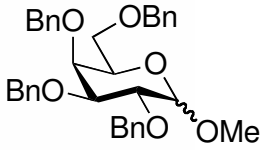
Compound 4 α/β (Table 1, entry 3)

Compound 6a α/β (Table 3, entry 1)

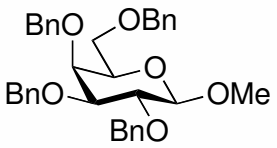


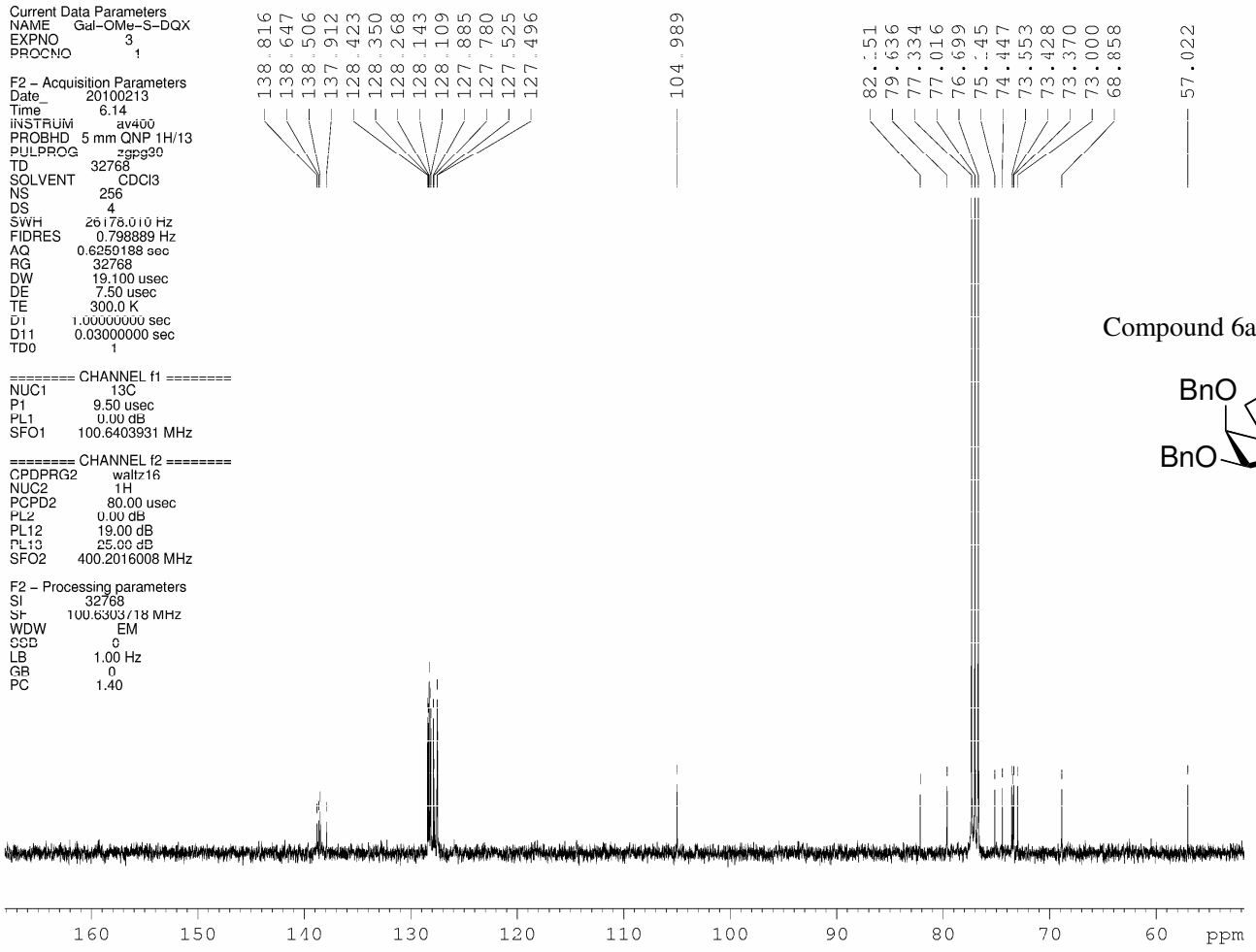


Compound 6a α/β (Table 3, entry 1)

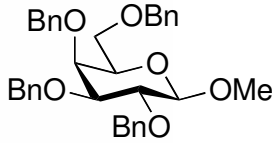


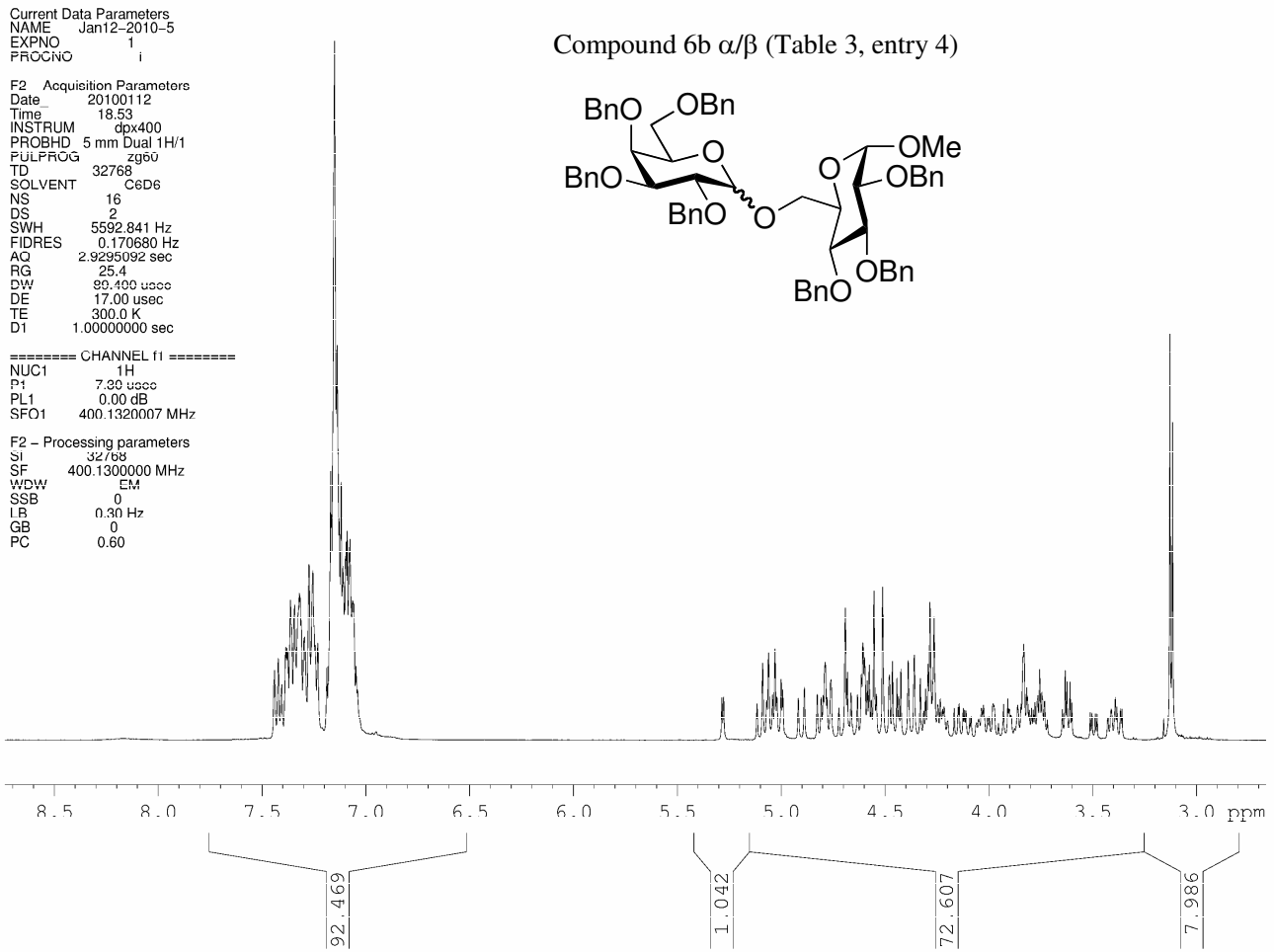
Compound 6a β (Table 3, entry 3)

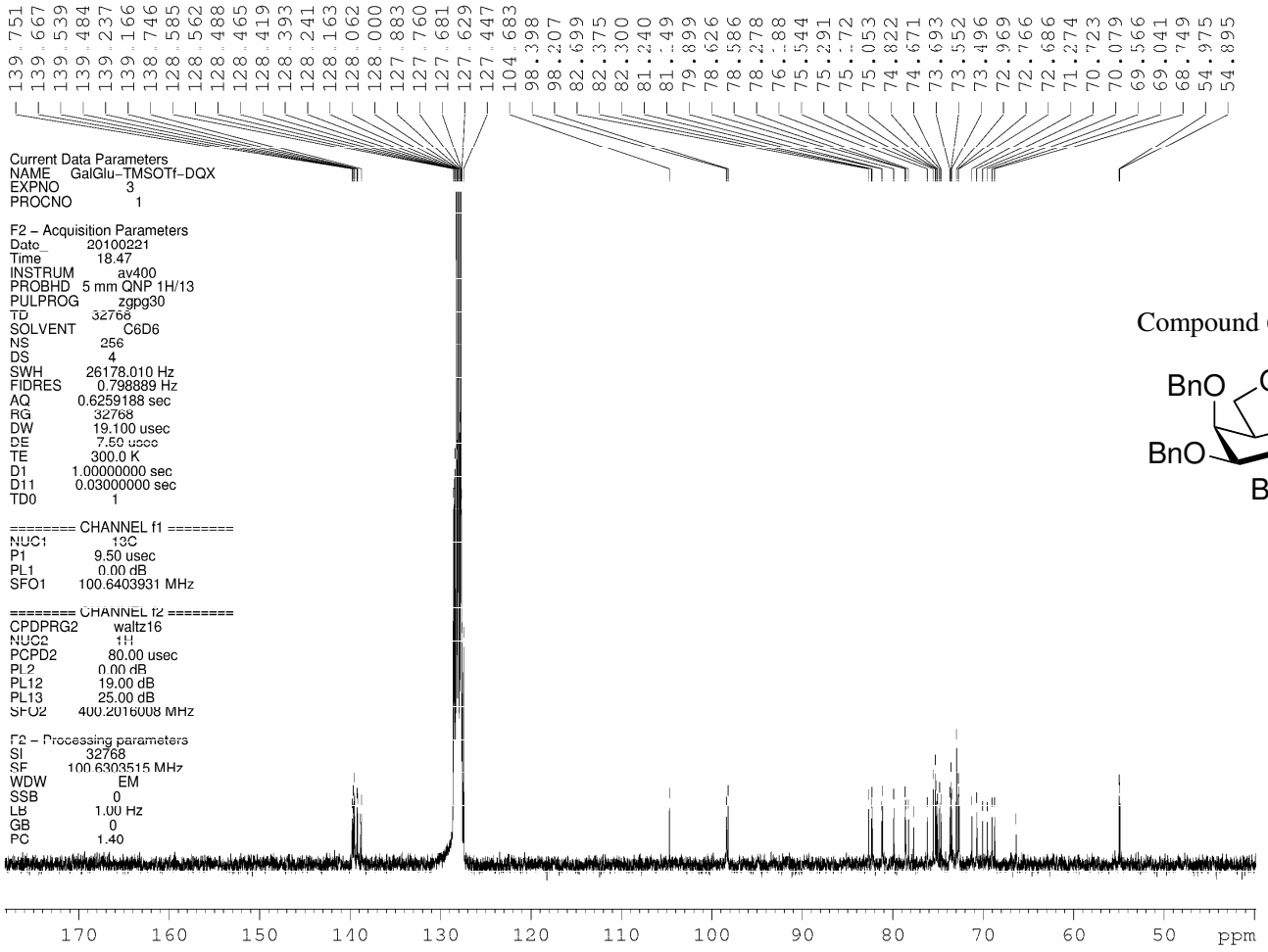




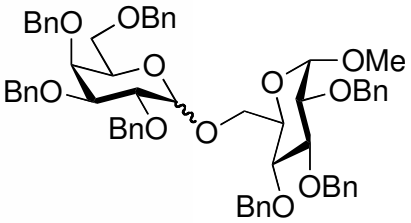
Compound 6a β (Table 3, entry 3)



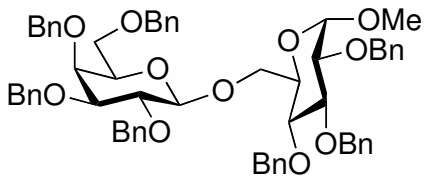

Current Data Parameters
NAME Jan12-2010-5
EXPNO 1
PROCNO 1
F2 Acquisition Parameters
Date 20100112
Time 18.53
INSTRUM dpx400
PROBHD 5 mm Dual 1H/1
PULPROG zg60
TD 32768
SOLVENT C6D6
NS 16
DS 2
SWH 5592.841 Hz
FIDRES 0.170680 Hz
AQ 2.9295092 sec
RG 25.4
DW 89.400 usec
DE 17.00 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 7.30 usec
PL1 0.00 dB
SFO1 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 0.60
Compound 6b α/β (Table 3, entry 4)
BnO
OBn
O
BnO
BnO
O
O
OMe
OBn
BnO
OBn
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
ppm
92.469
1.042
72.607
7.986

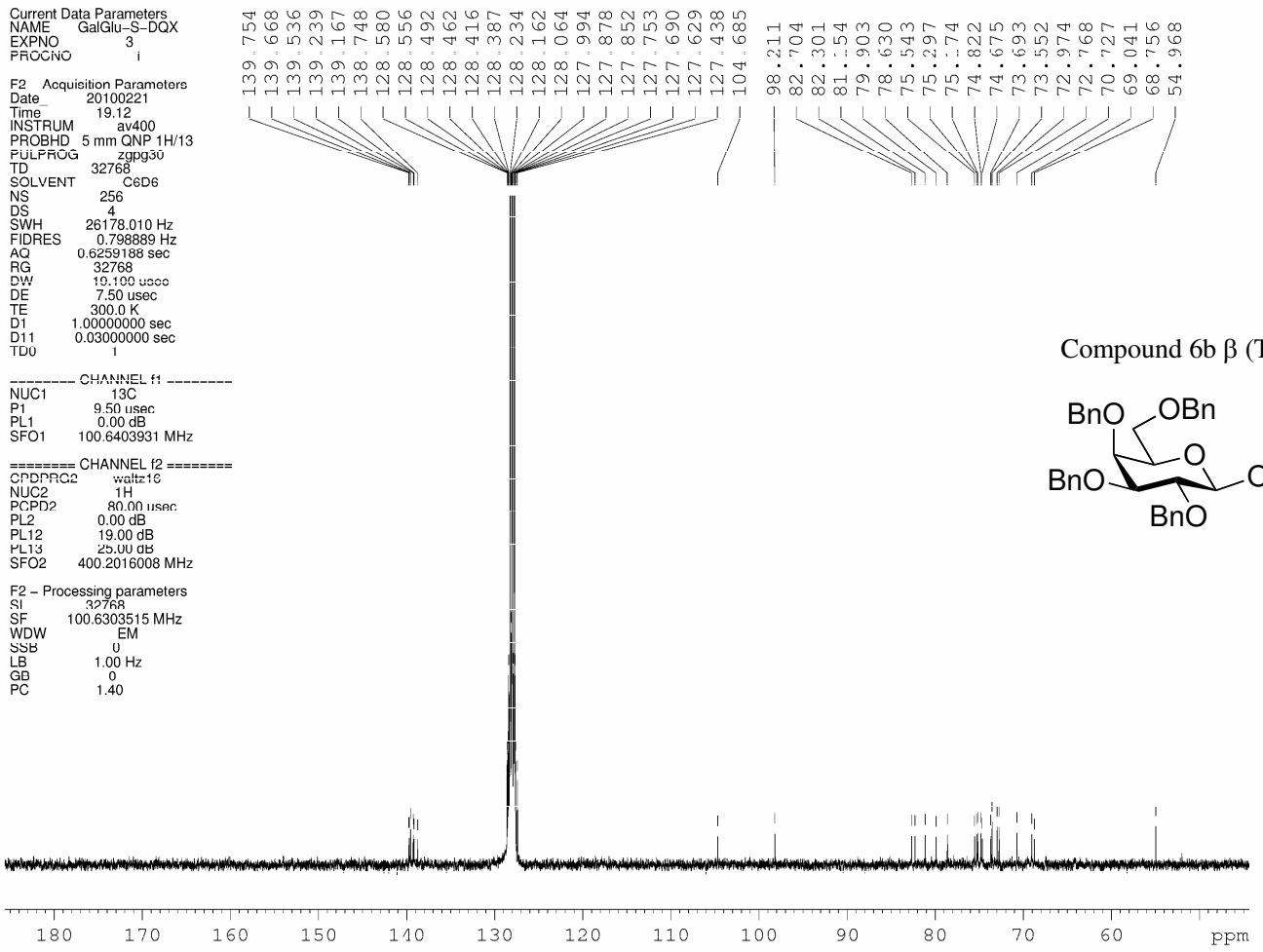


Compound 6b α/β (Table 3, entry 4)

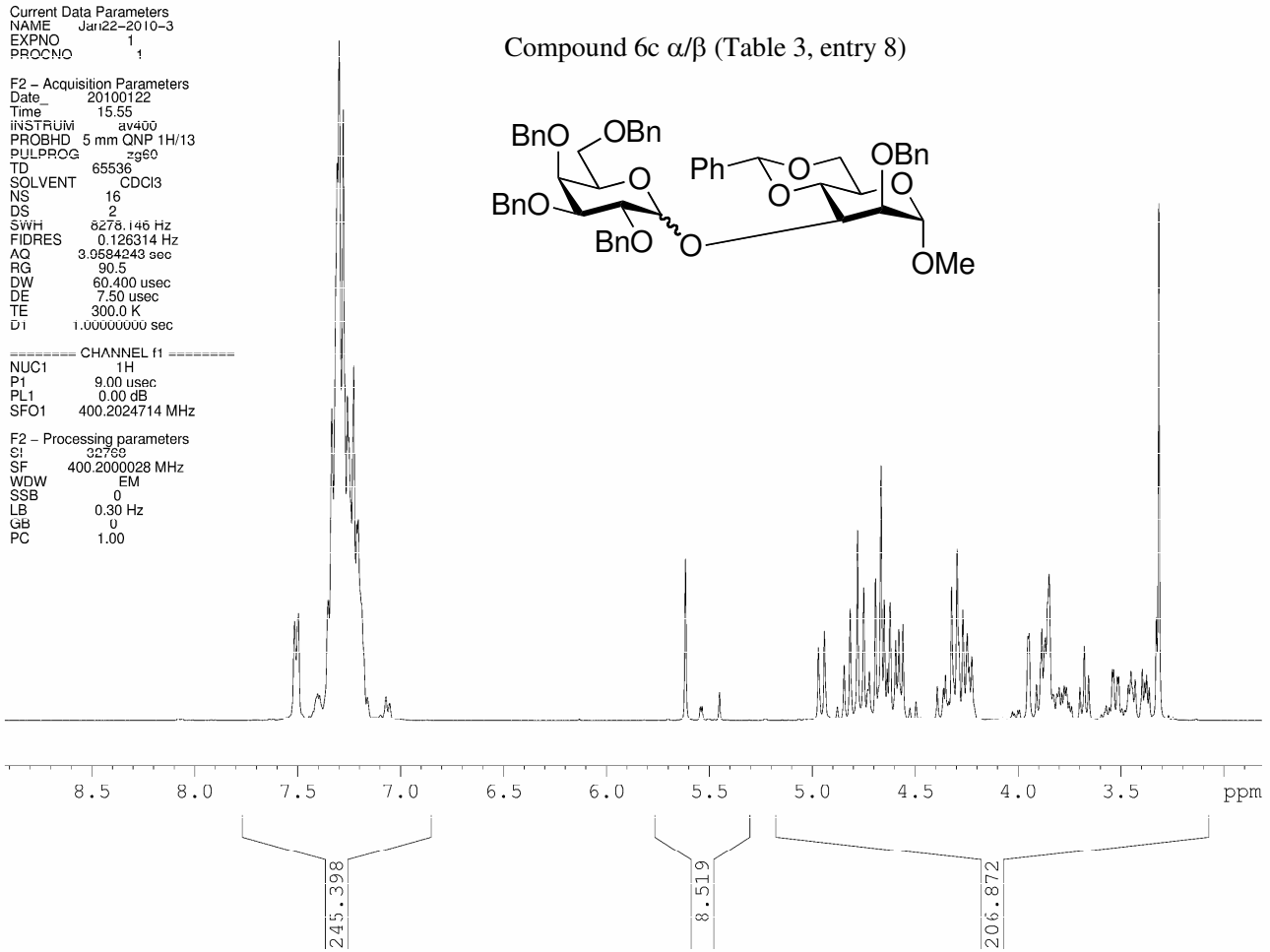


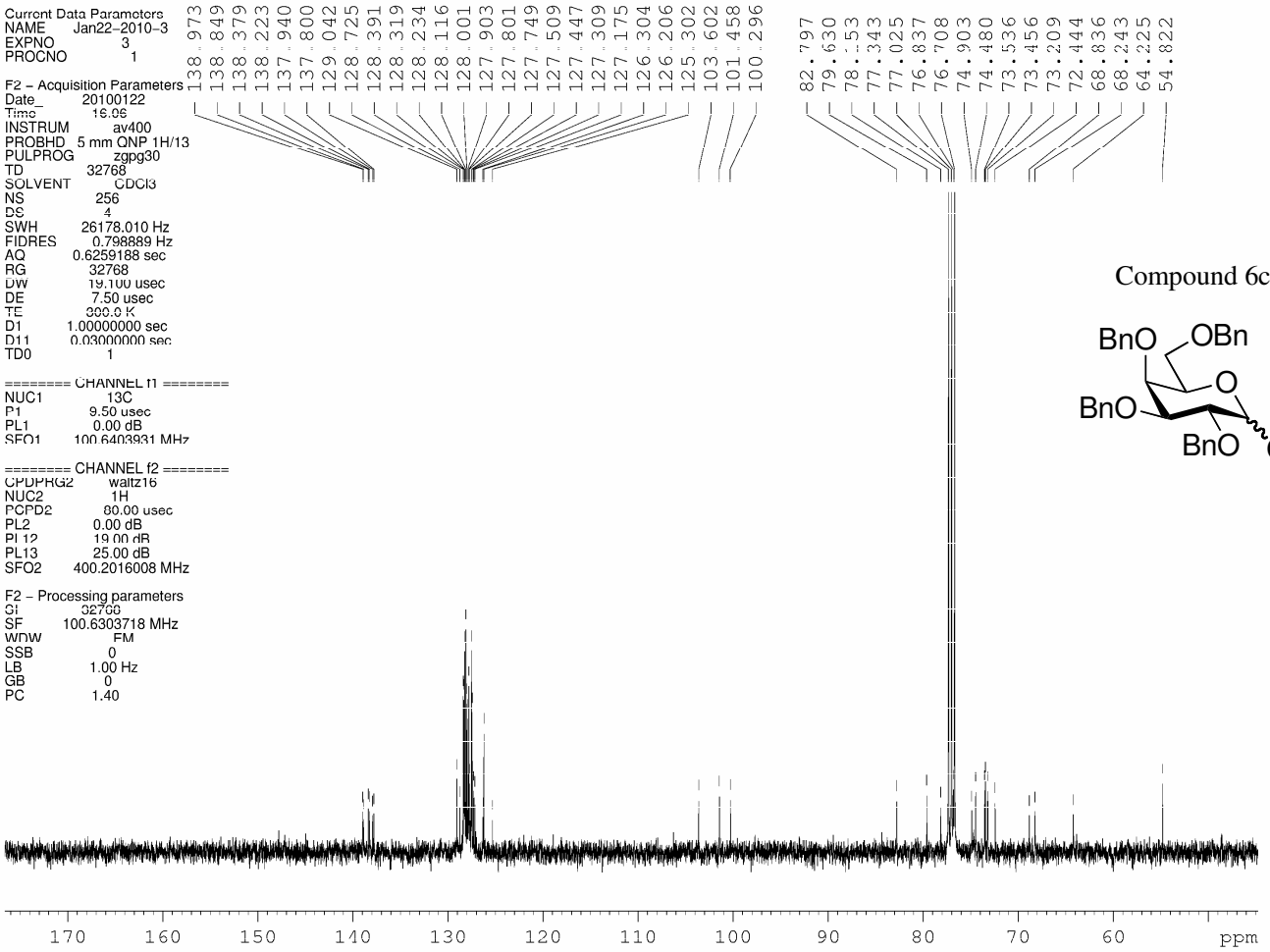
Compound 6b β (Table 3, entry 6)



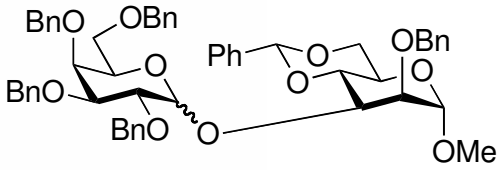


Compound 6b β (Table 3, entry 6)

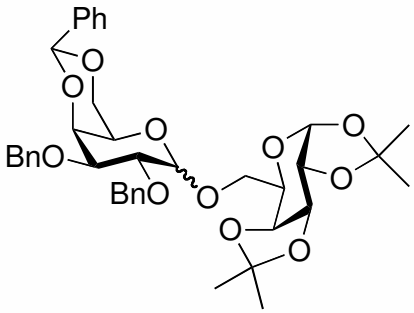

Current Data Parameters
NAME Jan22-2010-3
EXPNO 1
PROCNO 1
F2 – Acquisition Parameters
Date_ 20100122
Time 15.55
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg60
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 90.5
DW 60.400 usec
DE 7.50 usec
TE 300.0 K
D1 1.00000000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 400.2024714 MHz
F2 – Processing parameters
SI 32768
SF 400.2000028 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Compound 6c α/β (Table 3, entry 8)
BnO
OBn
BnO
O
BnO
O
Ph
O
O
OBn
O
OMe
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
245.398
8.519
206.872



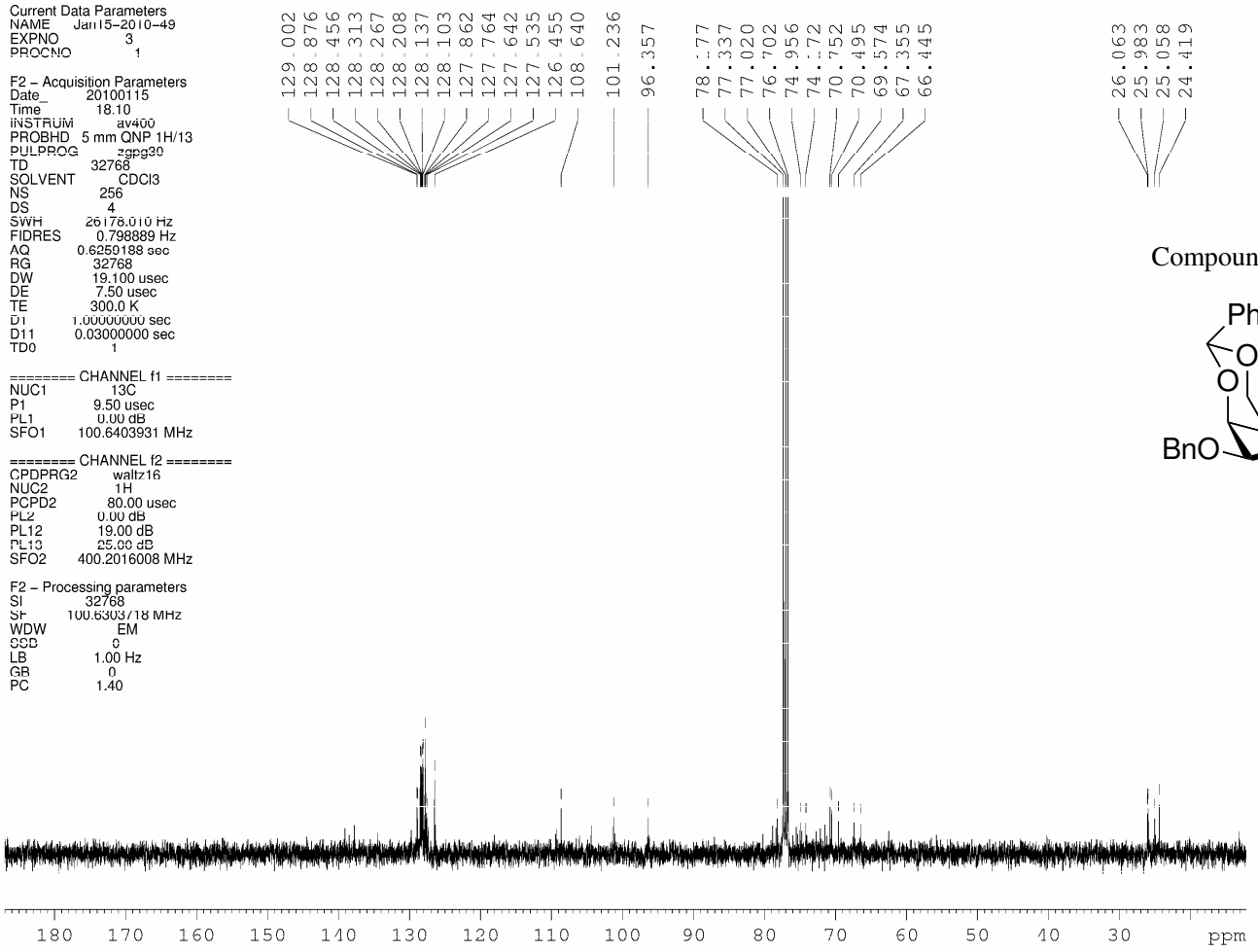
Compound 6c α/β (Table 3, entry 8)



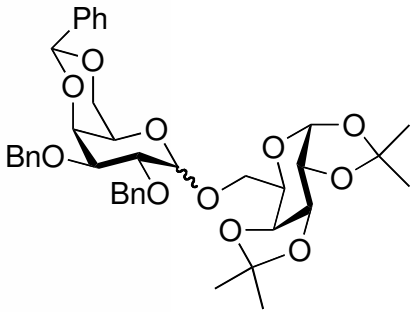
Compound 8 α/β (Table 4, entry 3)



Note: Peak at 5.3 ppm is due to a CH_2Cl_2 impurity



Compound 8 α/β (Table 4, entry 3)



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