Supporting Information for

β-Selective Xylulofuranosylation via a Conformationally-Restricted Donor

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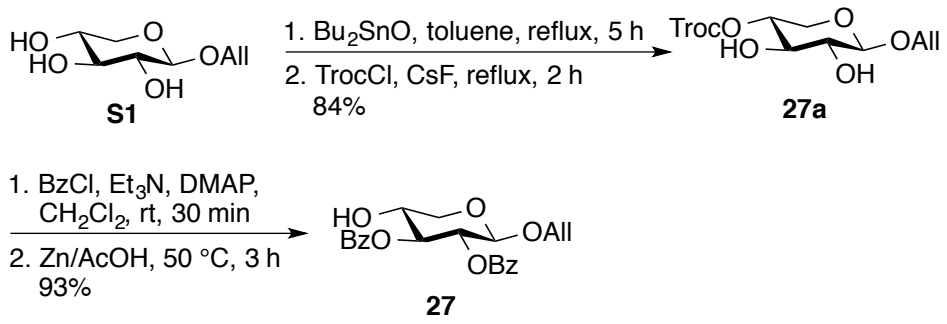
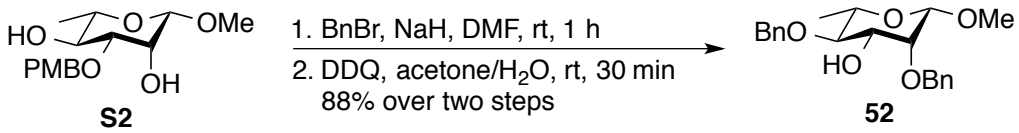
General Experimental Methods

Reactions were carried out in oven-dried glassware. All reagents used were purchased from commercial sources and were used without further purification unless noted. Solvents used in reactions were purified by successive passage through columns of alumina and copper under nitrogen. Unless stated otherwise, all reactions were carried out at rt under a positive pressure of argon and were monitored by TLC on silica gel 60 F_{254} (0.25 mm, E. Merck). Spots were detected under UV light or by charring with 10% H_2SO_4, in EtOH. Unless otherwise indicated, all column chromatography was performed on silica gel 60 (40–60 mM). Iatrobeads refers to a beaded silica gel 6RS–8060, which is manufactured by Iatron Laboratories (Tokyo). The ratio between silica gel and crude product ranged from 100 to 50:1 (w/w). Optical rotations were measured at 22 ± 2 °C at the sodium D line (589 nm) and are in units of deg·mL(dm·g)$^{-1}$. ^{1}H NMR spectra were recorded at 500 or 700 MHz, and chemical shifts are referenced to either $CHCl_3$ (7.26 ppm, $CDCl_3$) or HOD (4.78 ppm, D_2O). ^{13}C NMR spectra were recorded at 125 or 175 MHz, and ^{13}C chemical shifts were referenced to internal $CDCl_3$ (77.23 ppm, $CDCl_3$), external dioxane (67.40 ppm, D_2O). Assignments of resonances, including those for mixtures of compounds, were made on the basis of 2D NMR experiments including ^{1}H–^{1}H-COSY, HMQC, HMBC and ^{1}H–^{1}H-TROESY. Assignments with "app" represent apparent. In the processing of reaction mixtures, solutions of organic solvents were washed with equal amounts of aqueous solutions. Organic solutions were concentrated under vacuum at < 40 ºC (bath). Electrospray mass spectra were recorded on samples suspended in mixtures of THF with CH_3OH and added NaCl.

Scheme S1. Synthesis of **27**



Scheme S2. Synthesis of **52**



Scheme S3. Synthesis of **53**

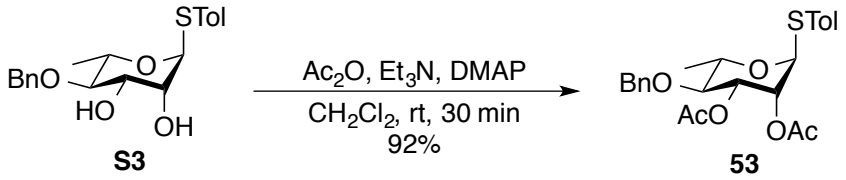


Figure S1. X-ray crystallography structure of compound **8**

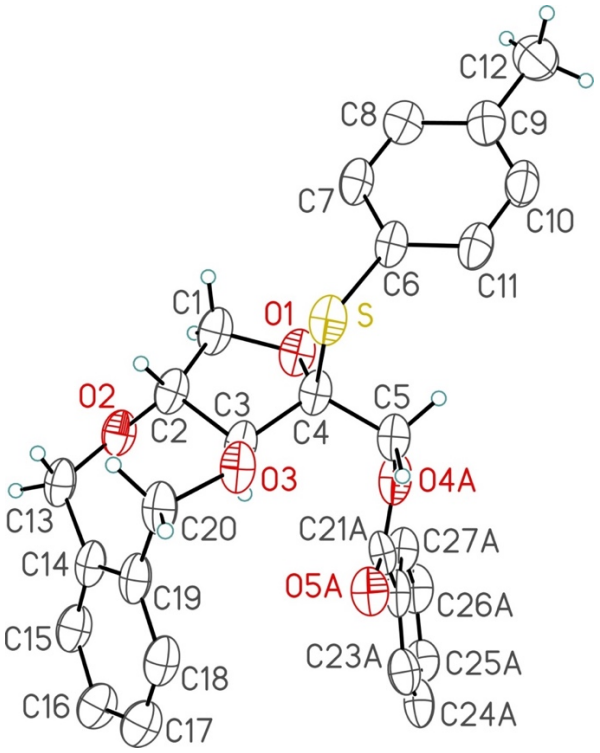
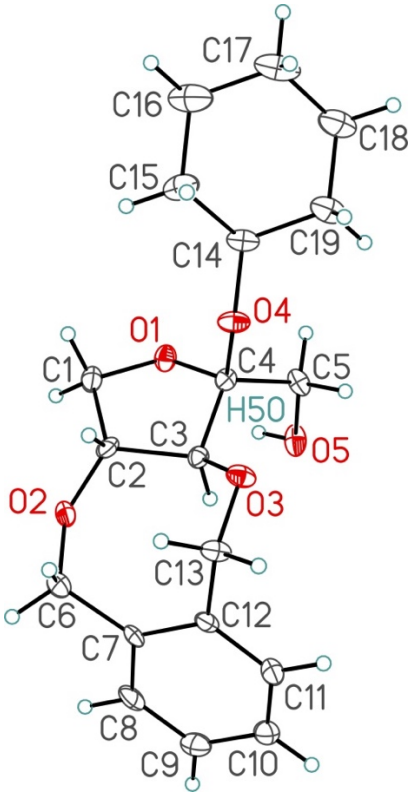
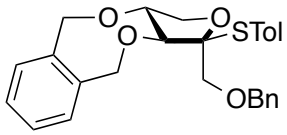


Figure S2. X-ray crystallography structure of compound **49β**

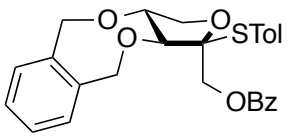


Experimental details and data for new compounds



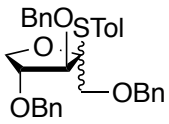
Tolyl 1-*O*-benzyl-2-thio-3,4-*O*-xylylene-β-D-*threo*-pent-2-ulofuranoside (7). To a solution of **16** (159 mg, 0.267 mmol) in tetrahydrofuran (2.7 mL) was added 1M tetrabutylammonium fluoride (399 μL, 0.399 mmol) at room temperature. After 4 h, the reaction mixture was added satd aq $NaHCO_3$ and then the solution was extracted with EtOAc. The organic layer was then washed with water and brine. The organic layer was dried with $MgSO_4$ and then filtered. The filtrate was concentrated and dried *in vacuo*. To a solution of the resulting residue in DMF (2.7 mL) was added benzyl bromide (54.8 mg, 38.0 μL, 0.320 mmol) and 60% NaH (12.8 mg, 0.320 mmol) at room temperature. After 1 h, CH_3OH was added. The mixture was concentrated and then diluted with CH_2Cl_2, and then washed with brine and water. The organic layers were dried with $MgSO_4$ and then filtered. The filtrate was concentrated under reduced pressure and then purified by column chromatography (8:1, hexane–EtOAc) to give **7** (105 mg, 88% over two steps) as a colorless oil. $[\alpha]^{25}_D$ –18.7 (*c* 0.7, $CHCl_3$); R_f 0.41 (4:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.48–7.38 (m, 4H, Ar), 7.38–7.34 (m, 2H, Ar), 7.31–7.24 (m, 3H, Ar), 7.14–7.10 (m, 2H, Ar), 7.10–7.06 (m, 2H, Ar), 5.04 (d, 1H, J_{gem} = 12.7 Hz, ArCH_2), 4.93 (d, 1H, J_{gem} = 12.7 Hz, ArCH_2), 4.85 (d, 1H, J_{gem} = 12.7 Hz, ArCH_2), 4.78 (d, 1H, J_{gem} = 12.7 Hz, ArCH_2), 4.58 (dd, 1H, $J_{5a,4}$ = 7.7 Hz, J_{gem} = 9.8 Hz, H-5a), 4.54–4.49 (m, 2H, H-4, ArCH_2), 4.48 (d, 1H, $J_{3,4}$ = 4.8 Hz, H-3), 4.33 (d, 1H, J_{gem} = 12.7 Hz, ArCH_2), 3.94 (dd, 1H, $J_{5b,4}$ = 3.2 Hz, J_{gem} = 9.8

Hz, H-5b), 3.69 (d, 1H, J_{gem} = 11.3 Hz, H-1a), 3.41 (d, 1H, J_{gem} = 11.3 Hz, H-1b), 2.33 (s, 3H, ArC*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.6 (Ar), 138.1 (Ar), 136.4 (Ar), 136.3 (2C, Ar), 135.7 (Ar), 131.7 (Ar), 131.5 (Ar), 129.7 (Ar), 129.65 (Ar), 129.4 (2C, Ar), 128.3 (2C, Ar), 127.7 (2C, Ar), 127.5 (Ar), 126.8 (Ar), 98.2 (C-2), 83.8 (C-3), 81.4 (C-4), 73.3 (Ar*C*H$_2$), 70.9 (C-5), 70.3 (C-1), 69.5 (Ar*C*H$_2$), 68.8 (Ar*C*H$_2$), 21.2 (CH_3); HRMS (ESI) calcd. for $C_{27}H_{28}NaO_4S$ $[M+Na]^+$ 471.1601; found 471.1598.



Tolyl 1-*O*-benzoyl-2-thio-3,4-*O*-xylylene-β-D-*threo*-pent-2-ulofuranoside (8). To a solution of **16** (106 mg, 0.178 mmol) in tetrahydrofuran (1.8 mL) was added 1M tetrabutylammonium fluoride (266 μL, 0.266 mmol) at room temperature. After 4 h, the reaction mixture was added to satd aq $NaHCO_3$ and then extracted with EtOAc. The organic layer was then washed with brine and water. The organic layer was dried with $MgSO_4$ and then filtered. The filtrate was concentrated and dried *in vacuo*. To a solution of the resulting residue in CH_2Cl_2 (1.8 mL) was added Et_3N (21.6 mg, 29.5 μL, 0.213 mmol), benzoyl chloride (30.0 mg, 24.7 μL, 0.213 mmol) and DMAP (2.2 mg, 0.0178 mmol) at room temperature. After 1 h, CH_3OH was added and the mixture was concentrated and then diluted with CH_2Cl_2, washed with brine and water. The organic layers were dried with $MgSO_4$ and then filtered. The filtrate was concentrated under reduced pressure and then purified by column chromatography (8:1, hexane–EtOAc) to give **8** (73 mg, 89% over two steps) as a colorless oil. $[\alpha]^{25}_D$ –78.1 (*c* 0.5, $CHCl_3$); R_f 0.51 (4:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.84–7.80 (m, 2H, ArH),

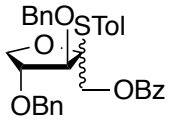
7.56–7.50 (m, 1H, ArH), 7.43–7.34 (m, 8H, ArH), 7.14–7.09 (m, 2H, ArH), 5.06 (d, 1H, J_{gem} = 12.5 Hz, ArCH_2), 4.89 (d, 1H, J_{gem} = 12.5 Hz, ArCH_2), 4.86 (d, 1H, J_{gem} = 12.5 Hz, ArCH_2), 4.79 (d, 1H, J_{gem} = 12.5 Hz, ArCH_2), 4.61 (dd, 1H, $J_{5a,4}$ = 7.9, J_{gem} = 9.7 Hz, H-5a), 4.56 (ddd, 1H, $J_{4,3}$ = 4.6 Hz, $J_{4,5a}$ = 7.9 Hz, $J_{4,5b}$ = 3.0 Hz, H-4), 4.43 (d, 1H, J_{gem} = 12.0 Hz, H-1a), 4.38 (d, 1H, J_{gem} = 12.0 Hz, H-1b), 4.35 (d, 1H, $J_{3,4}$ = 4.6 Hz, H-3), 3.92 (dd, 1H, $J_{5b,4}$ = 3.0 Hz, J_{gem} = 9.7 Hz, H-5b), 2.33 (s, 3H, ArCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 165.8 (C=O), 139.1 (Ar), 136.6 (Ar), 136.5 (2C, Ar), 135.2 (Ar), 133.0 (Ar), 131.8 (Ar), 131.4 (Ar), 129.9 (Ar), 129.8 (2C, Ar), 129.72 (2C, Ar), 129.67 (2C, Ar), 128.3 (2C, Ar), 126.0 (Ar), 96.5 (C-2), 84.1 (C-4), 81.6 (C-3), 71.1 (C-5), 69.5 (ArCH$_2$), 69.1 (ArCH$_2$), 64.5 (C-1), 21.1 (ArCH$_3$); HRMS (ESI) calcd. for $C_{27}H_{26}NaO_5S$ $[M+Na]^+$ 485.1393; found 485.1397.



***p*-Tolyl 1,3,4-tri-*O*-benzyl-2-thio-α/β-D-*threo*-pent-2-ulofuranoside (9)**. To a solution of **21** (116 mg, 0.173 mmol) in THF (1.7 mL) was added tetrabutylammonium fluoride (259 μL, 0.259 mmol) at room temperature and the mixture was stirred for 4 h. After the completion of the reaction, the reaction mixture was added satd aq NH_4Cl and extracted with EtOAc. The organic layer was then washed with water and brine. The organic layers were dried with $MgSO_4$ and then filtered. The filtrate was concentrated and dried *in vacuo*. To a solution of the resulting residue in DMF (1.7 mL) was added benzyl bromide (90.4 mg, 62.8 μL, 0.207 mmol), followed by the addition of sodium hydride (21.1 mg, 0.207 mmol) at room temperature and the mixture was stirred for 2

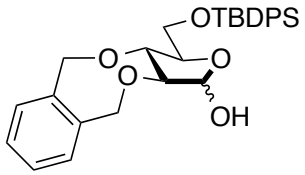
h. After the completion of the reaction, CH_3OH was added. The mixture was concentrated and then diluted with CH_2Cl_2, and then washed with brine and water. The organic layers were dried with $MgSO_4$ and then filtered. The filtrate was concentrated under reduced pressure and then purified by column chromatography (8:1, hexane–EtOAc) to give an inseparable α/β mixture of **9** (80 mg, 88% over two steps, α/β = 1:7) as a colorless oil. R_f 0.27 (8:1, hexane–EtOAc); Data for **9α**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.43–7.25 (m, 17H, ArH), 7.09–7.06 (m, 2H, ArH), 4.76 (d, 1H, J_{gem} = 11.8 Hz, ArCH_2), 4.62 (d, 1H, J_{gem} = 11.8 Hz, ArCH_2), 4.53 (d, 1H, J_{gem} = 11.8 Hz, ArCH_2), 4.51 (d, 1H, J_{gem} = 11.8 Hz, ArCH_2), 4.46–4.40 (m, 2H, ArCH_2), 4.24 (app dt, 1H, $J_{4,3}$ = 4.6 Hz, $J_{4,5a}$ = $J_{4,5b}$ = 7.4 Hz, H-4), 4.14 (dd, 1H, $J_{5a,4}$ = 7.4 Hz, J_{gem} = 8.9 Hz, H-5a), 4.09 (d, 1H, $J_{3,4}$ = 4.6 Hz, H-3), 3.95–3.91 (m, 1H, H-5b), 3.59 (d, 1H, J_{gem} = 10.0 Hz, H-1a), 3.46 (d, 1H, J_{gem} = 10.0 Hz, H-1b), 2.34 (s, 3H, ArCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 96.6 (C-2), 88.5 (C-3), 83.3 (C-4), 73.4 (Ar*C*H$_2$), 72.5 (Ar*C*H$_2$), 70.1 (C-1), 69.4 (C-5), 21.4 (Ar*C*H$_3$); Data for **9β**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.43–7.25 (m, 17H, ArH), 7.10 (d, 2H, J = 8.2 Hz, ArH), 4.80 (d, 1H, J_{gem} = 11.8 Hz, ArCH_2), 4.60 (d, 1H, J_{gem} = 11.8 Hz, ArCH_2), 4.55 (d, 1H, J_{gem} = 11.8 Hz, ArCH_2), 4.50 (d, 1H, $J_{3,4}$ = 3.7 Hz, H-3), 4.46 (d, 1H, J_{gem} = 11.8 Hz, ArCH_2), 4.43 (d, 1H, J_{gem} = 11.8 Hz, ArCH_2), 4.42 (dd, 1H, $J_{5a,4}$ = 6.2 Hz, J_{gem} = 9.5 Hz, H-5a), 4.37 (d, 1H, J_{gem} = 11.8 Hz, ArCH_2), 4.37–4.33 (m, 1H, H-4), 3.94 (dd, 1H, $J_{5b,4}$ = 3.0 Hz, J_{gem} = 9.5 Hz, H-5b), 3.66 (d, 1H, J_{gem} = 10.9 Hz, H-1a), 3.45 (d, 1H, J_{gem} = 10.9 Hz, H-1b), 2.35 (s, 3H, ArCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.5 (Ar), 138.1 (Ar), 138.0 (Ar), 137.9 (Ar), 136.5 (2C, Ar), 129.3 (2C, Ar), 128.44 (2C, Ar), 128.37 (2C, Ar), 128.3 (2C, Ar), 128.0 (2C, Ar), 127.9 (2C, Ar), 127.8 (2C, Ar), 127.77 (Ar), 127.75 (Ar), 127.6 (Ar), 127.3

(Ar), 98.3 (C-2), 86.0 (C-3), 84.2 (C-4), 73.5 (Ar*C*H_2), 72.9 (Ar*C*H_2), 71.9 (C-1), 71.7 (Ar*C*H_2), 69.5 (C-5), 21.3 (Ar*C*H_3); HRMS (ESI) calcd. for $C_{33}H_{34}NaO_4S$ $[M+Na]^+$ 549.2070; found 549.2067.



***p*-Tolyl 3,4-di-*O*-benzyl-1-*O*-benzoyl-2-thio-α/β-D-*threo*-pent-2-ulofuranoside (10)**. To a solution of **21** (143 mg, 0.212 mmol) in THF (2.1 mL) was added tetrabutylammonium fluoride (318 μL, 0.318 mmol) at room temperature and the mixture was stirred for 4 h. After the completion of the reaction, the reaction mixture was added satd aq NH_4Cl and extracted with EtOAc. The organic layer was then washed with H_2O and brine. The organic layers were dried with $MgSO_4$ and then filtered. The filtrate was concentrated and dried *in vacuo*. To a solution of the resulting residue in CH_2Cl_2 (2.1 mL) was added triethylamine (25.7 mg, 35.2 μL, 0.254 mmol), benzoyl chloride (35.8 mg, 29.6 μL, 0.254 mmol) and DMAP (2.6 mg, 0.0212 mmol) at room temperature and the mixture was stirred for 1 h. After the completion of the reaction, excess benzoyl chloride was quenched by the addition of CH_3OH and then concentrated under reduced pressure. The resulting residue was purified by column chromatography (8:1, hexane–EtOAc) to give an inseparable α/β mixture of **10** (102 mg, 89% over two steps, α/β = 1:7) as a colorless oil. R_f 0.30 (8:1, hexane–EtOAc); Data for **10α**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 8.05–8.01 (m, 2H, ArH), 7.54–7.50 (m, 2H, ArH), 7.49–7.43 (m, 2H, ArH), 7.41–7.24 (m, 11H, ArH), 7.14–7.10 (m, 2H, ArH), 4.73–4.56 (m, 3H, Ar*CH*$_2$), 4.53–4.37 (m, 3H, Ar*CH*$_2$, H-1a, H-1b), 4.27 (app dt, 1H,

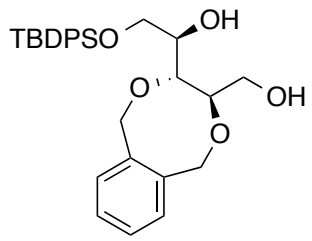
$J_{4,3}$ = 4.7 Hz, $J_{4,5a}$ = $J_{4,5b}$ = 7.2 Hz, H-4), 4.21 (dd, 1H, $J_{5b,4}$ = 7.2 Hz, J_{gem} = 8.9 Hz, H-5a), 4.19 (d, 1H, $J_{3,4}$ = 4.7 Hz, H-3), 4.04 (dd, 1H, $J_{5b,4}$ = 7.2 Hz, J_{gem} = 8.9 Hz, H-5b), 2.34 (s, 3H, ArCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 165.8 (C=O), 94.8 (C-2), 88.7 (C-3), 82.9 (C-4), 73.0 (ArCH$_2$), 72.4 (ArCH$_2$), 69.0 (C-5), 64.0 (C-1), 21.3 (ArCH$_3$); Data for **10β**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 8.00–7.95 (m, 2H, ArH), 7.54–7.50 (m, 2H, ArH), 7.45 (d, 2H, J = 8.0 Hz, ArH), 7.41-7.24 (m, 11H, ArH), 7.13 (d, 2H, J = 8.0 Hz, ArH), 4.84 (d, 1H, J_{gem} = 12.2 Hz, ArCH_2), 4.67 (d, 1H, J_{gem} = 12.2 Hz, ArCH_2), 4.50 (s, 2H, ArCH_2), 4.47 (dd, 1H, $J_{5a,4}$ = 5.8, J_{gem} = 9.8 Hz, H-5a), 4.45–4.40 (m, 3H, H-1a, H-3, H-4), 4.38 (d, 1H, J_{gem} = 11.9 Hz, H-1b), 3.99 (dd, 1H, $J_{5b,4}$ = 2.8 Hz, J_{gem} = 9.8 Hz, H-5b), 2.34 (s, 3H, ArCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 165.9 (C=O), 139.0 (Ar), 137.7 (Ar), 137.7 (Ar), 137.4 (Ar), 136.6 (2C, Ar), 133.0 (Ar), 130.6 (Ar), 129.8 (2C, Ar), 129.6 (2C, Ar), 128.9 (Ar), 128.5 (2C, Ar), 128.4 (2C, Ar), 128.3 (2C, Ar), 128.0 (2C, Ar), 127.92 (Ar), 127.88 (Ar), 127.78 (Ar), 96.5 (C-2), 85.9 (C-3), 84.1 (C-4), 73.1 (ArCH$_2$), 71.9 (ArCH$_2$), 69.7 (C-5), 65.6 (C-1), 21.3 (ArCH$_3$); HRMS (ESI) calcd. for $C_{33}H_{32}NaO_5S$ $[M+Na]^+$ 563.1863; found 563.1870.



5-*O*-*t*-butyldiphenylsilyl-2,3-*O*-xylylidene-α/β-D-arabinose (12). To a solution of the **11**[1] (10.0 g, 17.6 mmol) in CH_3OH (88.0 mL) was added sodium methoxide (70.4 mg, 1.76 mmol) at room temperature. After stirring for 3.5 h, sodium methoxide was neutralized by the addition of Amberlite IR-120 H^+ resin. The mixture was then filtered and the filtrate was concentrated under reduced pressure and dried *in vacuo*. To a

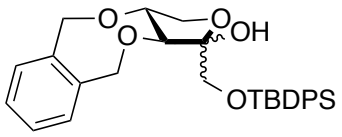
solution of the resulting residue in pyridine (52 mL) was added TBDPSCl (5.4 g, 5.1 mL, 19.4 mmol) and Et_3N (5.3 g, 7.3 mL, 52.8 mmol) at 0 °C. After stirring for 16 h at room temperature, the CH_3OH was added and the solution was co-evaporated with toluene. The crude residue was diluted with CH_2Cl_2 and washed with 1N HCl, water, satd aq $NaHCO_3$ and brine. The organic layers were dried with $MgSO_4$ and filtered. The filtrate was then concentrated under reduced pressure and dried *in vacuo*. The residue was then dissolved in DMF (88 mL), followed by addition of 60% NaH (1.76 g, 44.0 mol) and α,α'-dibromo-*o*-xylylene (5.1 g, 19.4 mmol) at 0 ºC. After stirring for 1.5 h at room temperature, satd aq NH_4Cl was added. Dilution of the mixture with CH_2Cl_2 provided a solution that was washed with water and brine. The organic layer was dried with $MgSO_4$, filtered and the filtrate was concentrated. The obtained residue was dissolved in mixture of acetone and water (80.0 mL, 9:1), followed by addition of *N*-bromosuccinimide (4.7 g, 26.4 mmol) at room temperature. After stirring for 30 min at room temperature, the mixture was concentrated. The crude residue was then diluted with CH_2Cl_2 and washed with water and brine. The organic layer was then dried over $MgSO_4$ and concentrated. The resulting residue was purified by column chromatography (4:1, hexane–EtOAc) to give an inseparable α/β mixture of **12** (4.0 g, 46% over four steps, α:β = 1.6:1) as a white foam. R_f 0.27 (4:1, hexane–EtOAc); Data for **12α**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.68–7.62 (m, 4H, ArH), 7.55–7.52 (m, 1H, ArH), 7.45–7.34 (m, 9H, ArH), 5.36 (d, 1H, $J_{1,2}$ = 2.5 Hz, H-1), 4.94 (d, 1H, J_{gem} = 12.5 Hz, ArCH_2), 4.71 (d, 1H, J_{gem} = 12.5 Hz, ArCH_2), 4.21 (ddd, 1H, $J_{4,3}$ = 8.3 Hz, $J_{4,5a}$ = 2.4 Hz, $J_{4,5b}$ = 3.9 Hz, H-4), 4.16 (dd, 1H, $J_{3,2}$ = 5.2 Hz, $J_{3,4}$ = 8.3 Hz, H-3), 4.00 (dd, 1H, $J_{2,1}$ = 2.5 Hz, $J_{2,3}$ = 5.2 Hz, H-2), 3.87 (dd, 1H, $J_{5a,4}$ = 2.4 Hz, J_{gem} = 11.5 Hz, H-

5a), 3.75 (dd, 1H, $J_{5b,4}$ = 3.9 Hz, J_{gem} = 11.5 Hz, H-5b), 2.80 (br s, 1H, OH), 1.01 (s, 9H, C(C*H*$_3$)$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 135.8 (Ar), 135.7 (2C, Ar), 135.6 (Ar), 131.77 (Ar), 131.74 (Ar), 131.45 (Ar), 131.44 (Ar), 129.71 (2C, Ar), 129.66 (Ar), 129.64 (Ar), 127.89 (Ar), 127.87 (Ar), 127.70 (2C, Ar), 127.67 (2C, Ar), 102.4 (C-1), 88.3 (C-2), 81.7 (C-4), 80.8 (C-3), 69.9 (Ar*C*H$_2$), 68.5 (Ar*C*H$_2$), 63.1 (C-5), 26.8 ((*C*H$_3$)$_3$C) 19.3 ((CH$_3$)$_3$*C*); Data for **12β**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.68–7.62 (m, 4H, ArH), 7.45–7.34 (m, 10H, ArH), 5.28 (dd, 1H, $J_{1,2}$ = 5.3 Hz, $J_{1,OH}$ = 7.8 Hz, H-1), 4.99 (d, 1H, J_{gem} = 12.5 Hz, ArC*H*$_2$), 4.95 (d, 1H, J_{gem} = 12.5 Hz, ArC*H*$_2$), 4.90 (d, 1H, J_{gem} = 12.5 Hz, ArC*H*$_2$), 4.71 (d, 1H, J_{gem} = 12.5 Hz, ArC*H*$_2$), 4.26 (app t, 1H, $J_{3,2}$ = $J_{3,4}$ = 5.3 Hz, H-3), 4.16 (app t, 1H, $J_{2,1}$ = $J_{2,3}$ = 5.3 Hz, H-2), 4.13 (d, 1H, $J_{OH,1}$ = 7.8 Hz, OH), 4.04 (app dt, 1H, $J_{4,3}$ = 5.3 Hz, $J_{4,5a}$ = $J_{4,5b}$ = 3.4 Hz, H-4), 3.79 (dd, 1H, $J_{5a,4}$ = 3.4 Hz, J_{gem} = 11.2 Hz, H-5a), 3.61 (dd, 1H, $J_{5b,4}$ = 3.4 Hz, J_{gem} = 11.2 Hz, H-5b), 1.00 (s, 9H, (C*H*$_3$)$_3$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 136.3 (Ar), 136.2 (Ar), 136.1 (Ar), 135.9 (Ar), 133.5 (Ar), 133.4 (Ar), 132.5 (Ar), 132.3 (Ar), 130.0 (Ar), 129.9 (Ar), 97.6 (C-1), 83.7 (C-4), 83.6 (C-2), 80.0 (C-3), 69.4 (Ar*C*H$_2$), 68.7 (Ar*C*H$_2$), 64.7 (C-5), 26.8 ((*C*H$_3$)$_3$C), 19.2 ((CH$_3$)$_3$*C*); HRMS (ESI) calcd. for $C_{29}H_{34}NaO_5Si$ $[M+Na]^+$ 513.2068; found 513.2061.



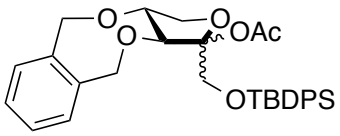
5-*O*-*t*-butyldiphenylsilyl-2,3-*O*-xylylidene-D-arabinitol (13). To a solution of **12** (250 mg, 0.508 mmol) in CH_3OH (5 mL) was added sodium borohydride (19.2 mg,

0.508 mmol) at room temperature. After stirring for 2 h, the reaction mixture was added to 1N HCl (10 mL) and then extracted with EtOAc. The organic layer was then washed with water and brine. The organic layer was dried with $MgSO_4$ and then filtered. The filtrate was concentrated and the resulting residue was purified by column chromatography (1:1, hexane–EtOAc) to give **13** (175.1 mg, 70%) as a white foam. $[\alpha]^{25}_D$ –28.7 (*c* 1.1, $CHCl_3$); R_f 0.35 (1:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 700 MHz) δ_H 7.75–7.71 (m, 2H, ArH), 7.70–7.68 (m, 2H, ArH), 7.51–7.40 (m, 6H, ArH), 7.24–7.21 (m, 2H, ArH), 7.11–7.07 (m, 1H, ArH), 7.06–7.02 (m, 1H, ArH), 5.10 (d, 1H, J_{gem} = 14.0 Hz, ArCH_2), 5.03 (d, 1H, J_{gem} = 14.0 Hz, ArCH_2), 5.00 (d, 1H, J_{gem} = 14.0 Hz, ArCH_2), 4.82 (d, 1H, J_{gem} = 14.0 Hz, ArCH_2), 3.94 (dd, 1H, $J_{5a,4}$ = 4.2 Hz, J_{gem} = 10.5 Hz, H-5a), 3.91 (dd, 1H, $J_{5b,4}$ = 5.6 Hz, J_{gem} = 10.5 Hz, H5-b), 3.91–3.82 (m, 1H, H-1a), 3.75–3.72 (m, 2H, H-2, H-4), 3.68–3.63 (m, 1H, H-1b), 3.26 (dd, 1H, *J* = 9.1, 7.0 Hz, H-3), 2.96 (d, 1H, *J* = 5.6 Hz, OH), 2.84 (br s, 1H, OH), 1.14 (s, 9H, (CH_3)$_3$C); ^{13}C NMR ($CDCl_3$, 175 MHz) δ_C 136.95 (Ar), 136.92 (Ar), 135.7 (2C, Ar), 135.65 (2C, Ar), 133.03 (Ar), 133.02 (Ar), 130.05 (Ar), 130.03 (Ar), 128.4 (Ar), 128.3 (Ar), 127.98 (2C, Ar), 127.96 (2C, 127.5 (2C, Ar), 84.2 (C-2), 82.0 (C-3), 75.1 (Ar*C*H$_2$), 74.9 (Ar*C*H$_2$), 72.4 (C-4), 64.5 (C-5), 63.7 (C-1), 26.9 ((*C*H$_3$)$_3$C) 19.2 ((CH$_3$)$_3$*C*); HRMS (ESI) calcd. for $C_{29}H_{36}NaO_5Si$ $[M+Na]^+$ 515.2224; found 515.2217.



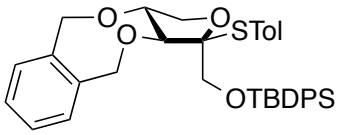
1-*O*-*tert*-butyldiphenylsilyl-3,4-*O*-xylylene-α/β-D-*threo*-pent-2-ulofuranose (14). To a solution of **13** (75.1 mg, 0.152 mmol) in CH_2Cl_2 (4 mL) was added bis(tri-*n*-

butyltin) oxide (116 μL, 136 mg, 0.229 mmol) at 0 ºC, followed by bromine (11.7 μL, 36.5 mg, 0.229 mmol) dropwise. After stirring for 2.5 h, the reaction mixture was concentrated. The resulting residue was purified by column chromatography (CH_2Cl_2, then 4:1, hexane–EtOAc) to give **14** (40 mg, 50%, α/β = 1:10) as a colorless oil. R_f 0.32 (2:1, hexane–EtOAc); Data for **14β**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.67–7.62 (m, 4H, ArH), 7.45–7.35 (m, 10H, ArH), 5.05 (d, 1H, J_{gem} = 12.4 Hz, ArC*H*$_2$), 4.88 (d, 1H, J_{gem} = 12.9 Hz, ArC*H*$_2$), 4.82 (d, 1H, J_{gem} = 12.4 Hz, ArC*H*$_2$), 4.78 (d, 1H, J_{gem} = 12.9 Hz, ArC*H*$_2$), 4.42 (app dt, 1H, $J_{4,3}$ = $J_{4,5b}$ = 4.6 Hz, $J_{4,5a}$ = 7.8 Hz, H-4), 4.35 (dd, 1H, $J_{5a,4}$ = 7.8 Hz, J_{gem} = 9.5 Hz, H5-a), 4.05 (d, 1H, $J_{3,4}$ = 4.6 Hz, H-3), 3.80 (dd, 1H, $J_{5b,4}$ = 4.6 Hz, J_{gem} = 9.5 Hz, H-5b), 3.69 (d, 1H, J_{gem} = 10.4 Hz, H-1a), 3.67 (s, 1H, OH), 3.61 (d, 1H, J_{gem} = 10.4 Hz, H-1b), 1.01 (s, 9H, (C*H*$_3$)$_3$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 136.7 (Ar), 135.9 (Ar), 135.81 (2C, Ar), 135.79 (2C, Ar), 135.7 (Ar), 133.22 (Ar), 133.18 (Ar), 131.8 (Ar), 131.7 (Ar), 130.0 (Ar), 129.9 (2C, Ar), 129.8 (Ar), 127.9 (3C, Ar), 104.0 (C-2), 81.7 (C-3), 81.0 (C-4), 70.3 (C-5), 69.2 (Ar*C*H$_2$), 69.1 (Ar*C*H$_2$), 65.9 (C-1), 26.7 ((*C*H$_3$)$_3$C), 19.2 ((CH$_3$)$_3$*C*); HRMS (ESI) calcd. for $C_{29}H_{34}NaO_5Si$ $[M+Na]^+$ 513.2068; found 513.2068.



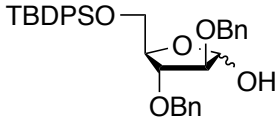
2-*O*-acetyl-1-*O*-*tert*-butyldiphenyl-3,4-*O*-xylylene-α/β-D-*threo*-pent-2-ulofuranoside (15). To a solution of **14** (4.34 g, 8.85 mmol) in tetrahydrofuran (88.5 mL) was added acetic anhydride (1.0 mL, 1.08 g, 10.6 mmol) at room temperature. The mixture was then cooled to –78 ºC and *n*-butyllithium (6.63 mL, 10.6 mmol) was added

dropwise. After stirring for 2 h, the reaction mixture was added satd aq $NaHCO_3$ and then extracted with EtOAc. The organic layer was then washed with brine and water. The organic layer was dried with $MgSO_4$ and then filtered. The filtrate was concentrated and the resulting residue was purified by column chromatography (8:1, hexane–EtOAc) to give **15** (4.50 g, 96%, α/β = 1:10) as a yellow oil. R_f 0.45 (4:1, hexane–EtOAc); Data for **15β**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.63–7.60 (m, 2H, ArH), 7.52–7.49 (m, 2H, ArH), 7.45–7.34 (m, 10H, ArH), 5.13 (d, 1H, J_{gem} = 12.4 Hz, ArCH_2), 4.94 (app dt, 1H, $J_{4,3}$ = $J_{4,5b}$ = 5.2 Hz, $J_{4,5a}$ = 8.3 Hz, H-4), 4.87 (d, 1H, J_{gem} = 12.9 Hz, ArCH_2), 4.80 (d, 1H, J_{gem} = 12.9 Hz, ArCH_2), 4.78 (d, 1H, J_{gem} = 12.4 Hz, ArCH_2), 4.59 (app t, 1H, $J_{5a,4}$ = J_{gem} = 8.3 Hz, H-5a), 4.57 (d, 1H, $J_{3,4}$ = 5.2 Hz, H-3), 3.89 (dd, 1H, $J_{5b,4}$ = 5.2 Hz, J_{gem} = 8.3 Hz, H-5b), 3.75 (d, 1H, J_{gem} = 10.6 Hz, H-1a), 3.60 (d, 1H, J_{gem} = 10.6 Hz, H-1b), 2.01 (s, 3H, CH_3CO), 0.89 (s, 9H, (CH_3)$_3$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 169.1 (C=O), 137.7 (Ar), 135.5 (2C, Ar), 134.8 (Ar), 133.0 (Ar), 132.96 (Ar), 131.7 (Ar), 131.2 (Ar), 129.7 (Ar), 129.64 (Ar), 129.62 (Ar), 129.5 (Ar), 127.66 (2C, Ar), 127.64 (2C, Ar), 127.61 (Ar), 127.58 (Ar), 109.4 (C-2), 82.7 (C-4), 80.5 (C-3), 73.9 (C-5), 70.1 (ArCH$_2$), 68.1 (ArCH$_2$), 64.2 (C-1), 26.5 ((CH$_3$)$_3$C), 21.8 (CH$_3$CO), 19.2 ((CH$_3$)$_3$$C$); HRMS (ESI) calcd. for $C_{31}H_{40}NO_6Si$ $[M+NH_4]^+$ 550.2619; found 550.2616.



Tolyl 1-*O*-*tert*-butyldiphenyl-2-thio-3,4-*O*-xylylene-β-D-*threo*-pent-2-ulofuranoside (16). To a solution of **15** (132 mg, 0.248 mmol) and thiocresol (36.9 mg, 0.297 mmol) in CH_2Cl_2 (2.5 mL) was added boron trifluoride diethyl etherate (39.8 μL,

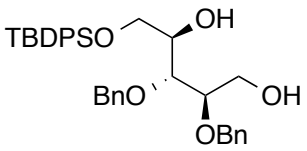
0.322 mmol) at 0 °C. After stirring for 2 h, the reaction mixture was added to satd aq $NaHCO_3$ and then extracted with EtOAc. The organic layer was then washed with brine and water. The organic layer was dried with $MgSO_4$ and then filtered. The filtrate was concentrated and the resulting residue was purified by column chromatography (8:1, hexane–EtOAc) to give **16** (106 mg, 72%) as a yellow oil. $[\alpha]^{25}_D$ –29.6 (*c* 2.2, $CHCl_3$); R_f 0.57 (4:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.53–7.50 (m, 2H, ArH), 7.47–7.44 (m, 2H, ArH), 7.42–7.37 (m, 5H, ArH), 7.36–7.31 (m, 3H, ArH), 7.25–7.21 (m, 2H, ArH), 7.20 (d, 2H, J = 7.8 Hz, ArH), 6.95 (d, 2H, J = 7.8 Hz, ArH), 5.07 (d, 1H, J_{gem} = 12.7 Hz, ArCH_2), 4.89 (d, 1H, J_{gem} = 12.7 Hz, ArCH_2), 4.83 (d, 1H, J_{gem} = 12.7 Hz, ArCH_2), 4.81 (d, 1H, J_{gem} = 12.7 Hz, ArCH_2), 4.63–4.61 (m, 1H, H-3), 4.60–4.52 (m, 2H, H-4, H-5a), 3.93–3.88 (m, 1H, H-5b), 3.85 (d, 1H, J_{gem} = 11.4 Hz, H-1a), 3.61 (d, 1H, J_{gem} = 11.4 Hz, H-1b), 2.28 (s, 3H, ArCH_3), 0.88 (s, 9H, (CH_3)$_3$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.2 (Ar), 136.8 (Ar), 136.0 (2C, Ar), 135.6 (2C, Ar), 135.5 (2C, Ar), 134.8 (Ar), 133.5 (Ar), 133.1 (Ar), 131.7 (Ar), 131.4 (Ar), 129.8 (Ar), 129.7 (Ar), 129.5 (Ar), 129.3 (Ar), 129.2 (2C, Ar), 127.8 (Ar), 127.6 (2C, Ar), 127.5 (2C, Ar), 98.7 (C-2), 82.7 (C-4), 81.9 (C-3), 71.0 (C-5), 69.4 (ArCH_2), 69.1(ArCH_2), 64.5 (C-1), 26.6 ((*C*H$_3$)$_3$C), 21.1 (Ar*C*H$_3$), 19.3 ((CH$_3$)$_3$*C*); HRMS (ESI) calcd. for $C_{36}H_{40}NaO_4SSi$ $[M+Na]^+$ 619.2309; found 619.2298.



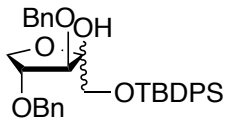
2,3-di-*O*-benzyl-5-*O*-*tert*-butyldiphenylsilyl-α/β-D-arabinofuranose (17). To a solution of **11**[1] (4 g, 7.15 mmol) in CH_3OH (35.7 mL) was added sodium methoxide

(38.6 mg, 0.715 mmol) at room temperature. The reaction mixture was stirred for 3.5 h at room temperature, then neutralized by addition of Amberlite IR-120 H^+ resin, filtered, and filtrate was concentrated. The resulting crude residue was dissolved in pyridine (27 mL), followed by the addition of TBDPSCl (2.03 mL, 7.85 mmol) and triethylamine (2.98 mL, 21.4 mmol). After stirring for 16 h at room temperature, CH_3OH was added, followed by co-evaporation with toluene. The crude residue was diluted with CH_2Cl_2 and washed with 1N HCl, H_2O, satd aq $NaHCO_3$ and brine. The organic layer was dried with $MgSO_4$ and then filtered, and the filtrate was concentrated and dried *in vacuo*. The resulting crude residue was then dissolved in DMF (27 mL), followed by the addition of benzyl bromide (2.68 g, 1.87 mL, 15.7 mmol) and 60% NaH (713 mg, 17.9 mmol). The reaction mixture was stirred for 1.5 h, satd aq NH_4Cl was added, and the solution was diluted with CH_2Cl_2. The organic layer was then washed with H_2O, satd aq $NaHCO_3$ and brine. The organic layer was subsequently dried with $MgSO_4$ and then filtered. The filtrate was then concentrated and dried *in vacuo*. The resulting crude residue was then dissolved in the mixture of acetone and H_2O (27 mL, 9:1), followed by the addition of *N*-bromosuccinimide (2.54 g, 14.3 mmol). The reaction mixture was stirred for 30 min at room temperature, then evaporated. The resulting residue was then diluted with CH_2Cl_2, and washed with satd aq $NaHCO_3$, H_2O, and brine. The organic layer was dried with $MgSO_4$ and then filtered. The filtrate was concentrated and the resulting residue was purified by column chromatography (4:1, hexane–EtOAc) to give an α/β mixture of **17** (2.72 g, 67% over four steps, α/β = 2:1) as a colorless oil. R_f 0.29 (4:1, hexane–EtOAc); Data for **17α**: ^{1}H NMR ($CDCl_3$, 700 MHz) δ_H 7.71–7.65 (m, 4H, ArH), 7.47–7.26 (m, 16H, ArH), 5.37 (dd, 1H, $J_{1,2}$ = 1.4 Hz, $J_{1,OH}$ = 8.8 Hz, H-1), 4.62

(d, 1H, J_{gem} = 12.1 Hz, ArCH_2), 4.57 (d, 1H, J_{gem} = 12.1 Hz, ArCH_2), 4.53 (d, 1H, J_{gem} = 12.1 Hz, ArCH_2), 4.49 (d, 1H, J_{gem} = 12.1 Hz, ArCH_2), 4.45 (ddd, 1H, $J_{4,3}$ = 2.8 Hz, $J_{4,5a}$ = 5.2 Hz, $J_{4,5b}$ = 7.7 Hz, H-4), 4.14–4.12 (m, 1H, H-3), 4.01 (d, 1H, $J_{2,1}$ = 1.4 Hz, H-2), 3.84 (dd, 1H, $J_{5a,4}$ = 5.2 Hz, J_{gem} = 10.5 Hz, H-5a), 3.75 (dd, 1H, $J_{5b,4}$ = 7.7 Hz, J_{gem} = 10.5 Hz, H-5b), 3.34 (d, 1H, $J_{OH,1}$ = 8.8 Hz, OH), 1.09 (s, 9H, (CH_3)$_3$C); ^{13}C NMR ($CDCl_3$, 175 MHz) δ_C 135.7 (Ar), 135.63 (Ar), 135.61 (3C, Ar), 129.8 (Ar), 129.7 (Ar), 128.55 (2C, Ar), 128.48 (2C, Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 127.83 (Ar), 127.81 (Ar), 127.75 (2C, Ar), 127.73 (2C, Ar), 127.71 (2C, Ar), 127.67 (2C, Ar), 101.2 (C-1), 86.1 (C-2), 84.0 (C-4), 82.3 (C-3), 72.0 (Ar*C*H$_2$), 71.7 (Ar*C*H$_2$), 64.0 (C-5), 26.90 ((*C*H$_3$)$_3$C) 19.29 ((CH$_3$)$_3$*C*); Data for **17β**: ^{1}H NMR ($CDCl_3$, 700 MHz) δ_H 7.71–7.65 (m, 4H, ArH), 7.47–7.26 (m, 16H, ArH), 5.40 (dd, 1H, $J_{1,2}$ = 4.3 Hz, $J_{1,OH}$ = 10.0 Hz, H-1), 4.67 (d, 1H, J_{gem} = 12.1 Hz, ArCH_2), 4.58 (d, 1H, J_{gem} = 12.1 Hz, ArCH_2), 4.57 (d, 1H, J_{gem} = 12.1 Hz, ArCH_2), 4.56 (d, 1H, J_{gem} = 12.1 Hz, ArCH_2), 4.25 (app t, 1H, $J_{3,2}$ = $J_{3,4}$ = 4.3 Hz, H-3), 4.08 (app dt, 1H, $J_{4,3}$ = 4.3 Hz, $J_{4,5a}$ = $J_{4,5b}$ = 5.0 Hz, H-4), 4.04 (app t, 1H, $J_{2,1}$ = $J_{2,3}$ = 4.3 Hz, H-2), 3.80 (dd, 1H, $J_{5a,4}$ = 5.0 Hz, J_{gem} = 11.2 Hz, H-5a), 3.78 (d, 1H, $J_{OH,1}$ = 10.0 Hz, OH), 3.75–3.72 (m, 1H, H-5b), 1.10 (s, 9H, (CH_3)$_3$C); ^{13}C NMR ($CDCl_3$, 175 MHz) δ_C 137.8 (Ar), 137.43 (2C, Ar), 137.35 (2C, Ar), 137.33 (Ar), 133.4 (2C, Ar), 133.3 (2C, Ar), 132.9 (Ar), 132.8 (Ar), 129.94 (2C, Ar), 129.86 (2C, Ar), 128.5 (2C, Ar), 128.4 (2C, Ar), 127.8 (2C, Ar), 127.7 (2C, Ar), 96.4 (C-1), 83.7 (C-2), 82.1 (C-4), 81.9 (C-3), 72.3 (Ar*C*H$_2$), 71.9 (Ar*C*H$_2$), 64.7 (C-5), 26.91 ((*C*H$_3$)$_3$C), 19.25 ((CH$_3$)$_3$*C*); HRMS (ESI) calcd. For $C_{35}H_{40}NaO_5Si$ $[M+Na]^+$ 591.2537; found 591.2539.

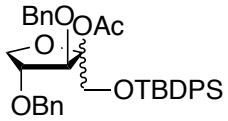


5-*O*-*t*-butyldiphenylsilyl-2,3-di-*O*-benzyl-D-arabinitol (18). To a solution of **17** (2.72 g, 4.78 mmol) in CH_3OH (35 mL) was added sodium borohydride (198 mg, 5.26 mmol) at room temperature. After stirring for 2 h at room temperature, 1N HCl was added to the reaction mixture and then the solution was extracted with EtOAc. The organic layer was then washed with satd aq $NaHCO_3$, H_2O and brine. The organic layer was dried with $MgSO_4$ and then filtered. The filtrate was concentrated and the resulting residue was purified by column chromatography (2:1, hexane–EtOAc) to give **18** (2.12 g, 78%) as a colorless oil. $[\alpha]^{25}_D$ –6.2 (*c* 2.7, $CHCl_3$); R_f 0.37 (1:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.70–7.64 (m, 4H, ArH), 7.48–7.43 (m, 2H, ArH), 7.42–7.36 (m, 4H, ArH), 7.34–7.25 (m, 8H, ArH), 7.22–7.18 (m, 2H, ArH), 4.65 (d, 1H, J_{gem} = 11.6, ArCH_2), 4.62 (d, 1H, J_{gem} = 11.6 Hz, ArCH_2), 4.61 (d, 1H, J_{gem} = 11.3 Hz, ArCH_2), 4.57 (d, 1H, J_{gem} = 11.3 Hz, ArCH_2), 3.98–3.92 (m, 1H, H-4), 3.88–3.77 (m, 6H, H-1a, H-1b, H-2, H-3, H-5a, H-5b), 3.06 (d, 1H, J = 5.3 Hz, OH), 2.30 (br s, 1H, OH) 1.10 (s, 9H, (CH_3)$_3$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.1 (Ar), 137.9 (Ar), 135.84 (2C, Ar), 135.78 (2C, Ar), 133.3 (Ar), 133.2 (Ar), 130.06 (2C, Ar), 130.05 (2C, Ar), 128.7 (2C, Ar), 128.6 (2C, Ar), 128.4 (2C, Ar), 128.3 (2C, Ar), 128.10 (Ar), 128.07 (Ar), 128.00 (2C, Ar), 79.6 (C-2), 78.6 (C-3), 73.7 (Ar*C*H$_2$), 72.8 (Ar*C*H$_2$), 71.6 (C-4), 64.9 (C-5), 61.7 (C-1), 26.9 ((*C*H$_3$)$_3$C) 19.3 ((CH$_3$)$_3$*C*); HRMS (ESI) calcd. for $C_{35}H_{42}NaO_5Si$ $[M+Na]^+$ 593.2694; found 593.2695.



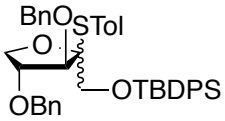
3,4-Di-*O*-benzyl-1-*O*-*tert*-butyldiphenylsilyl-α/β-D-*threo*-pent-2-ulofuranose (19). To a solution of **18** (2.12 g, 3.71 mmol) in CH_2Cl_2 (90 mL) was added bis(tri-*n*-butyltin) oxde (2.83 mL, 3.31 g, 5.58 mmol) at 0 ºC, followed by bromine (285 μL, 889 mg, 5.58 mmol) dropwise. After stirring for 2.5 h, the reaction mixture was concentrated. The resulting residue was purified by column chromatography (2:1, hexane–EtOAc) to give an inseparable α/β mixture of **19** (1.14 g, 54%, α/β = 1:7) as a colorless oil. R_f 0.34 (2:1, hexane–EtOAc): Data for **19α**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.76–7.65 (m, 4H, ArH), 7.45–7.27 (m, 16H, ArH), 4.74–4.69 (m, 1H, ArCH_2), 4.57–4.53 (m, 3H, ArCH_2), 4.18–4.11 (m, 1H, H-5a), 4.08–4.04 (m, 3H, H-3, H-4, H-5b), 3.94–3.90 (m, 2H, H-1a, OH), 3.85–3.79 (m, 1H, H-1b), 1.08 (s, 9H, (CH_3)$_3$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 105.6 (C-2), 86.0 (C-3), 81.7 (C-4), 72.4 (Ar*C*H$_2$), 72.0 (Ar*C*H$_2$), 70.9 (C-5), 65.1 (C-1), 26.9 ((*C*H$_3$)$_3$C) 19.29 ((CH$_3$)$_3$*C*); Data for **19β**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.76–7.65 (m, 4H, ArH), 7.45–7.27 (m, 16H, ArH), 4.70 (d, 1H, J_{gem} = 11.6 Hz, ArCH_2), 4.54 (d, 1H, J_{gem} = 11.6 Hz, ArCH_2), 4.47 (s, 2H, ArCH_2), 4.22–4.20 (m, 1H, H-4), 4.18–4.11 (m, 2H, H-3, H-5a), 4.03 (s, 1H, OH), 3.85–3.79 (m, 1H, H-5b), 3.76 (d, 1H, J_{gem} = 10.9 Hz, H-1a), 3.73 (d, 1H, J_{gem} = 10.9 Hz, H-1b), 1.07 (s, 9H, (CH_3)$_3$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 137.7 (Ar), 137.2 (Ar), 135.7 (2C, Ar), 135.64 (2C, Ar), 133.3 (Ar), 133.1 (Ar), 129.70 (2C, Ar), 129.68 (2C, Ar), 128.5 (2C, Ar), 128.46 (2C, Ar), 128.1 (2C, Ar), 128.0 (2C, Ar), 127.8 (2C, Ar), 127.9 (2C, Ar), 103.3 (C-2), 82.9 (C-3), 82.7 (C-4), 73.1 (Ar*C*H$_2$), 71.6 (Ar*C*H$_2$), 69.2 (C-5), 66.5 (C-1), 26.9 ((*C*H$_3$)$_3$C)

19.33 ((CH$_3$)$_3$*C*); HRMS (ESI) calcd. for $C_{35}H_{40}NaO_5Si$ $[M+Na]^+$ 591.2537; found 591.2539.



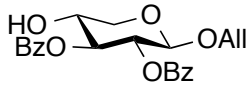
2-*O*-acetyl-3,4-di-*O*-benyl-1-*O*-*tert*-butyldiphenylsilyl-α/β-D-*threo*-pent-2-ulofuranose (20). To a solution of the **19** (1.14 g, 2.00 mmol) in tetrahydrofuran (20.0 mL) was added acetic anhydride (227 μL, 245 mg, 2.40 mmol) at room temperature. The mixture was cooled to –78 ºC and *n*-butyllithium (1.5 mL, 2.40 mmol) was added dropwise. After stirring for 2 h, satd aq NH_4Cl was added and the mixture was extracted with EtOAc. The organic layer was then washed with brine and water. The organic layer was dried with $MgSO_4$ and then filtered. The filtrate was concentrated and the resulting residue was purified by column chromatography (4:1, hexane–EtOAc) to give an inseparable α/β mixture of **20** (1.11 g, 91%, α/β = 1:7) as a yellow oil. R_f 0.31 (4:1, hexane–EtOAc); Data for **20β**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.70–7.67 (m, 4H, ArH), 7.46–7.40 (m, 2H, ArH), 7.39–7.28 (m, 14H, ArH), 4.68 (d, 1H, J_{gem} = 11.5 Hz, ArC*H*$_2$), 4.58–4.51 (m, 4H, H-3, H-4, 2 x ArC*H*$_2$), 4.50–4.43 (m, 2H, H-5a, ArC*H*$_2$), 4.22–4.20 (m, 1H, H-4), 3.95 (d, 1H, J_{gem} = 11.0 Hz, H-1a), 3.90–3.85 (m, 2H, H-1b, H-5b), 1.99 (s, 3H, C*H*$_3$CO), 1.08 (s, 9H, (C*H*$_3$)$_3$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 169.1 (C=O), 138.1 (Ar), 138.0 (Ar), 135.75 (2C, Ar), 135.72 (2C, Ar), 133.2 (Ar), 133.0 (Ar), 129.84 (Ar), 129.80 (Ar), 128.42 (2C, Ar), 128.39 (2C, Ar), 127.78 (2C, Ar), 127.75 (2C, Ar), 127.71 (2C, Ar), 127.66 (2C, Ar), 127.63 (2C, Ar), 108.6 (C-2), 84.4 (C-3), 84.0 (C-4), 72.8 (Ar*C*H$_2$), 72.6 (C-5), 71.9 (Ar*C*H$_2$), 65.8 (C-1), 26.9 ((*C*H$_3$)$_3$C) 21.9 (*C*H$_3$CO),

19.33 ($(CH_3)_3C$); HRMS (ESI) calcd. for $C_{37}H_{42}NaO_6Si$ $[M+Na]^+$ 633.2643; found 633.2643.



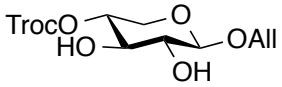
***p*-Tolyl 3,4-di-*O*-benyl-1-*O*-*tert*-butyldiphenylsilyl-2-thio-α/β-D-*threo*-pent-2-ulofuranoside (21).** To a solution of **20** (403 mg, 0.661 mmol) and thiocresol (98.3 mg, 0.791 mmol) in dichloromethane (6.6 mL) was added boron trifluoride diethyl etherate (106 μL, 0.859 mmol) at 0 °C. After stirring for 1 h, the reaction mixture was added satd aq $NaHCO_3$ and then the solution was extracted with EtOAc. The organic layer was then washed with brine and water. The organic layer was dried with $MgSO_4$ and then filtered. The filtrate was concentrated and the resulting residue was purified by column chromatography (8:1, hexane–EtOAc) to give an inseparable α/β mixture of **21** (357 mg, 80%, α/β = 1:7) as a yellow oil. R_f 0.23 (8:1, hexane–EtOAc); Data for **21α**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.66–7.61 (m, 4H, ArH), 7.45–7.24 (m, 14H, ArH), 7.02 (d, 2H, J = 8.5 Hz, ArH), 4.82 (d, 1H, J_{gem} = 12.0 Hz, ArCH_2), 4.75 (d, 1H, J_{gem} = 12.0 Hz, ArCH_2), 4.67–4.60 (m, 1H, ArCH_2), 4.57–4.51 (m, 2H, H-4, ArCH_2), 4.22 (dd, 1H, J = 7.5, 8.4 Hz, H-5a), 4.18 (d, 1H, J = 6.0 Hz, H-3), 3.93–3.91 (m, 1H, H-1a), 3.86-3.81 (m, 1H, H-5b), 3.70 (d, 1H, J_{gem} = 10.7 Hz, H-1b), 2.33 (s, 3H, CH_3), 1.01 (s, 9H, (CH_3)$_3$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 96.0 (C-2), 88.1 (C-3), 82.2 (C-4), 73.1 (ArCH$_2$), 72.4 (ArCH$_2$), 69.6 (C-5), 65.0 (C-1), 26.7 ((CH$_3$)$_3$C) 21.2 (ArCH$_3$), 19.4 ($(CH_3)_3C$); Data for **21β**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.61–7.57 (m, 4H, ArH), 7.45–7.24 (m, 14H, ArH), 6.98 (d, 2H, J = 8.5 Hz, ArH), 4.87 (d, 1H, J_{gem} = 12.0 Hz,

ArCH_2), 4.65 (d, 1H, J_{gem} = 12.0 Hz, ArCH_2), 4.64 (d, 1H, $J_{3,4}$ = 3.4 Hz, H-3), 4.50 (d, 1H, J_{gem} = 12.0 Hz, ArCH_2), 4.45 (d, 1H, J_{gem} = 12.0 Hz, ArCH_2), 4.41–4.36 (m, 2H, H-4, H-5a), 3.96–3.91 (m, 1H, H-5b), 3.87 (d, 1H, J_{gem} = 11.2 Hz, H-1a), 3.73 (d, 1H, J_{gem} = 11.2 Hz, H1-b), 2.33 (s, 3H, CH_3), 1.06 (s, 9H, (CH_3)$_3$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.02 (Ar), 137.98 (Ar), 137.9 (Ar), 136.0 (2C, Ar), 135.8 (2C, Ar), 135.7 (2C, Ar), 129.6 (Ar), 129.4 (Ar), 129.1 (2C, Ar), 128.4 (2C, Ar), 127.9 (2C, Ar), 127.72 (Ar), 127.69 (Ar), 127.66 (2C, Ar), 127.6 (2C, Ar), 127.5 (Ar), 99.0 (C-2), 85.5 (C-3), 84.1 (C-4), 73.0 (Ar*C*H$_2$), 71.5 (Ar*C*H$_2$), 69.7 (C-5), 65.6 (C-1), 26.9 ((*C*H$_3$)$_3$C), 21.2 (Ar*C*H$_3$), 19.4 ((CH$_3$)$_3$*C*); HRMS (ESI) calcd. for $C_{42}H_{46}NaO_4SSi$ $[M+Na]^+$ 697.2778; found 697.2788.



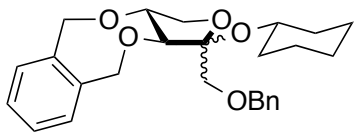
Allyl 2,3-di-*O*-benzoyl-β-D-xylopyranoside (27). To a solution of **27a** (119 mg, 0.326 mmol) in dichloromethane (3 mL) was added triethylamine (98.8 mg, 135 μL, 0.977 mmol), benzoyl chloride (137.2 mg, 113 μL, 0.977 mmol) and DMAP (4.0 mg, 0.0326 mmol), and the mixture was stirred for 30 min at room temperature. After completion of the reaction, the benzoyl chloride was quenched by the addition of CH_3OH and the solution was concentrated under reduced pressure. The residue was then diluted with CH_2Cl_2 and washed with 1N HCl, H_2O, satd aq $NaHCO_3$ and brine. The organic layers were dried with $MgSO_4$ and then filtered. The filtrate was then concentrated for the next step. To a solution of the residue in acetic acid (3 mL) was added activated zinc dust (2.4 g) and the reaction mixture was stirred at 50 °C for 3 h. After completion of the reaction, the reaction mixture was cooled and then passed through Celite. The

filtrate was then diluted with CH_2Cl_2 and washed with water, satd aq $NaHCO_3$ and brine. The organic layer was dried with $MgSO_4$ and then filtered. The filtrate was then concentrated under reduced pressure. The resulting residue was purified by column chromatography (3:1, hexane–EtOAc) to give **27** (120 mg, 93% over two steps) as a white foam. $[\alpha]^{25}_D$ +69.6 (*c* 0.6, $CHCl_3$); R_f 0.15 (4:1, hexane–EtOAc); ^1H NMR ($CDCl_3$, 500 MHz) δ_H 8.05–7.98 (m, 4H, ArH), 7.58–7.52 (m, 2H, ArH), 7.45–7.38 (m, 4H, ArH), 5.84 (dddd, 1H, *J* = 16.6, 10.6, 6.0, 5.0 Hz, OCH_2CH=CH_2), 5.40 (dd, 1H, $J_{2,1}$ = 6.2 Hz, $J_{2,3}$ = 8.1 Hz, H-2), 5.32–5.25 (m, 2H, OCH_2CH=CH_2, H-3), 5.17 (dq, 1H, *J* = 10.6, 1.2 Hz, OCH_2CH=CH_2), 4.78 (d, 1H, $J_{1,2}$ = 6.2 Hz, H-1), 4.34 (ddt, 1H, *J* = 13.4, 5.0, 1.6 Hz, OCH_2CH=CH_2), 4.24 (dd, 1H, $J_{5a,4}$ = 4.7 Hz, J_{gem} = 12.0 Hz, H-5a), 4.13 (ddt, 1H, *J* = 13.4, 6.0, 1.6 Hz, OCH_2CH=CH_2), 4.05–3.99 (m, 1H, H-4), 3.55 (dd, 1H, $J_{5b,4}$ = 8.0 Hz, J_{gem} = 12.0 Hz, H-5b), 3.08 (d, 1H, $J_{OH,4}$ = 5.8 Hz, OH); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 167.3 (*C*=O), 165.2 (*C*=O), 133.7 (OCH_2CH=CH_2), 133.6 (Ar), 133.4 (Ar), 130.1 (2C, Ar), 129.8 (2C, Ar), 129.4 (Ar), 129.0 (Ar), 128.52 (2C, Ar), 128.49 (2C, Ar), 117.7 (OCH_2CH=CH_2), 99.4 (C-1), 75.7 (C-3), 70.5 (C-2), 69.6 (OCH_2CH=CH_2), 68.8 (C-4), 64.6 (C-5); HRMS (ESI) calcd. for $C_{22}H_{22}NaO_7$ $[M+Na]^+$ 421.1258; found 421.1261.



Allyl 4-*O*-2,2,2-trichloroethoxycarbonyl-β-D-xylopyranoside (27a). To a solution of **S1**[2] (74 mg, 0.389 mmol) in toluene (20 mL) was added *n*-Bu_2SnO (145 mg, 0.584 mmol) at room temperature and the reaction mixture was stirred at reflux. After 5 h, the reaction mixture was cooled to room temperature and 2,2,2-trichloroethyl

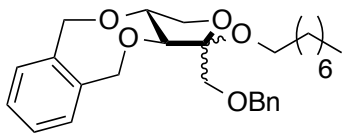
chloroformate (123.6 mg, 80.3 μL, 0.584 mmol) and CsF (88.6 mg, 0.584 mmol) were added. The reaction mixture was continuely stirred at reflux for 2 h. The solution was cooled to room temperature and then concentrated under reduced pressure. The resulting residue was purified by column chromatography (3:1, hexane–EtOAc) to give **27a** (119 mg, 84%) as a colorless oil. $[\alpha]^{25}_{D}$ –37.8 (*c* 1.4, $CHCl_3$); R_f 0.55 (1:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 5.93 (dddd, 1H, *J* = 16.7, 10.3, 6.3, 5.4 Hz, OCH_2CH=CH_2), 5.32 (dq, 1H, *J* = 17.1, 1.6 Hz, OCH_2CH=CH_2), 5.25 (dq, 1H, *J* = 10.3, 1.6 Hz, OCH_2CH=CH_2), 4.82 (d, 1H, J_{gem} = 11.8 Hz, Troc CH_2), 4.81–4.76 (m, 1H, H-4), 4.76 (d, 1H, J_{gem} = 11.8 Hz, Troc CH_2), 4.46 (d, 1H, $J_{1,2}$ = 6.3 Hz, H-1), 4.35 (ddt, 1H, *J* = 12.7, 5.3, 1.4 Hz, OCH_2CH=CH_2), 4.18 (dd, 1H, $J_{5a,4}$ = 4.7 Hz, J_{gem} = 12.1 Hz, H-5a), 4.13 (ddt, 1H, *J* = 12.7, 5.3, 1.3 Hz, OCH_2CH=CH_2), 3.84 (dt, 1H, $J_{3,2}$ = $J_{3,4}$ = 7.8 Hz, $J_{3,OH}$ = 4.6 Hz, H-3), 3.55 (ddd, 1H, $J_{2,1}$ = 6.3 Hz, $J_{2,3}$ = 7.8 Hz, $J_{2,OH}$ = 4.6 Hz, H-2), 3.47 (dd, 1H, $J_{5b,4}$ = 8.1 Hz, J_{gem} = 12.1 Hz, H-5b), 3.10 (d, 1H, $J_{OH,3}$ = 4.6 Hz, OH), 2.80 (d, 1H, $J_{OH,2}$ = 4.6 Hz, OH); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 153.5 (C=O), 133.5 (OCH_2CH=CH_2), 118.7 (OCH_2CH=CH_2), 101.5 (C-1), 77.5 (Troc CH_2), 75.7 (C-4), 72.5 (C-2), 72.2 (C-3), 70.3 (OCH_2CH=CH_2), 61.4 (C-5); HRMS (ESI) calcd. for $C_{11}H_{15}Cl_3NaO_7$ $[M+Na]^+$ 386.9776; found 386.9772.



Cyclohexyl 1-*O*-benzyl-3,4-*O*-xylylene-α-D-*threo*-pent-2-ulofuranoside (29α) and Cyclohexyl 1-*O*-benzyl-3,4-*O*-xylylene-β-D-*threo*-pent-2-ulofuranoside (29β). A mixture of **7** (56 mg, 0.156 mmol), **22** (18.7 mg, 0.187 mmol) and 4Å molecular sieves

in CH_2Cl_2 (6.2 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to –78 °C before *N*-iodosuccinimide (42.1 mg, 0.187 mmol) and silver triflate (4.0 mg, 0.0156 mmol) were added. After stirring at –78 °C for 2 h, triethylamine was added. The reaction mixture was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (9:1, hexane–EtOAc) to give **29α** (21.0 mg, 39%) as a colorless oil and **29β** (23.0 mg, 43%) as a colorless oil. Data for **29α**: $[\alpha]^{25}_D$ +47.8 (*c* 2.1, $CHCl_3$); R_f 0.33 (9:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.41–7.35 (m, 3H, ArH), 7.35–7.29 (m, 5H, ArH), 7.29–7.26 (m, 1H, ArH), 4.92 (d, 1H, J_{gem} = 12.0 Hz, ArC*H*$_2$), 4.91 (d, 1H, J_{gem} = 12.0 Hz, ArC*H*$_2$), 4.77 (d, 1H, J_{gem} = 12.0 Hz, ArC*H*$_2$), 4.76 (d, 1H, J_{gem} = 12.0 Hz, ArC*H*$_2$), 4.59 (d, 1H, J_{gem} = 12.0 Hz, ArC*H*$_2$), 4.56 (d, 1H, J_{gem} = 12.0 Hz, ArC*H*$_2$), 4.20 (dt, 1H, $J_{4,3}$ = 5.2 Hz, $J_{4,5a}$ = $J_{4,5b}$ = 8.1 Hz, H-4), 4.07 (app t, 1H, $J_{5a,4} = J_{gem}$ = 8.1 Hz, H-5a), 4.05 (d, 1H, $J_{3,4}$ = 5.2 Hz, H-3), 3.76 (app t, 1H, $J_{5b,4} = J_{gem}$ = 8.1 Hz, H-5b), 3.68–3.62 (m, 1H, cyclohexyl OC*H*), 3.63 (d, 1H, J_{gem} = 10.5 Hz, H-1a), 3.50 (d, 1H, J_{gem} = 10.5 Hz, H-1b), 1.83–1.76 (m, 1H, cyclohexyl C*H*$_2$), 1.73-1.61 (m, 3H, cyclohexyl C*H*$_2$), 1.52–1.44 (m, 1H, cyclohexyl C*H*$_2$), 1.30–1.07 (m, 5H, cyclohexyl C*H*$_2$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.8 (Ar), 136.7 (Ar), 136.3 (Ar), 131.8 (Ar), 131.6 (Ar), 129.66 (Ar), 129.63 (Ar), 128.4 (2C, Ar), 127.9 (2C, Ar), 127.6 (Ar), 109.4 (C-2), 87.5 (C-3), 81.4 (C-4), 73.7 (Ar*C*H$_2$), 71.2 (cyclohexyl O*C*H), 70.1 (C-1), 69.8 (Ar*C*H$_2$), 69.3 (Ar*C*H$_2$), 68.8 (C-5), 35.0 (cyclohexyl *C*H$_2$), 34.6 (cyclohexyl *C*H$_2$), 25.7 (cyclohexyl *C*H$_2$), 24.9 (2C,

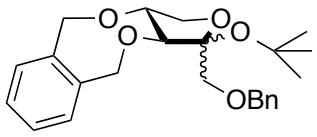
cyclohexyl CH_2); HRMS (ESI) calcd. for $C_{26}H_{32}NaO_5$ $[M+Na]^+$ 447.2142; found 447.2145. Data for **29β**: $[\alpha]^{25}_D$ +11.8 (*c* 2.8, $CHCl_3$); R_f 0.15 (9:1, hexane–EtOAc); ^1H NMR ($CDCl_3$, 500 MHz) δ_H 7.41–7.33 (m, 4H, ArH), 7.33–7.24 (m, 3H, ArH), 7.21–7.17 (m, 2H, ArH), 5.05 (d, 1H, J_{gem} = 12.8 Hz, ArC*H*$_2$), 4.85 (d, 1H, J_{gem} = 12.8 Hz, ArC*H*$_2$), 4.81 (d, 1H, J_{gem} = 12.8 Hz, ArC*H*$_2$), 4.79 (d, 1H, J_{gem} = 12.8 Hz, ArC*H*$_2$), 4.59 (d, 1H, J_{gem} = 12.2 Hz, ArC*H*$_2$), 4.44 (d, 1H, J_{gem} = 12.2 Hz, ArC*H*$_2$), 4.20 (ddd, 1H, $J_{4,3}$ = 5.4 Hz, $J_{4,5a}$ = 7.2 Hz, $J_{4,5b}$ = 3.9 Hz, H-4), 4.23 (dd, 1H, $J_{5a,4}$ = 7.2 Hz, J_{gem} = 9.4 Hz, H-5a), 4.20 (d, 1H, $J_{3,4}$ = 5.4 Hz, H-3), 3.76 (dd, 1H, $J_{5b,4}$ = 3.9 Hz, J_{gem} = 9.4 Hz, H-5b), 3.67 (app tt, 1H, *J* = 10.8, 4.1 Hz, cyclohexyl OC*H*), 3.53 (s, 2H, H-1), 1.80–1.74 (m, 1H, cyclohexyl C*H*$_2$), 1.73–1.65 (m, 3H, cyclohexyl C*H*$_2$), 1.56–1.48 (m, 1H, cyclohexyl C*H*$_2$), 1.44–1.29 (m, 2H, cyclohexyl C*H*$_2$), 1.28–1.14 (m, 2H, cyclohexyl C*H*$_2$), 1.12–1.02 (m, 1H, cyclohexyl C*H*$_2$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.3 (Ar), 137.0 (Ar), 136.3 (Ar), 131.8 (Ar), 131.5 (Ar), 129.51 (Ar), 129.47 (Ar), 128.5 (2C, Ar), 127.8 (2C, Ar), 127.7 (Ar), 107.1 (C-2), 82.9 (C-3), 81.2 (C-4), 73.6 (Ar*C*H$_2$), 71.0 (2C, cyclohexyl O*C*H, C-5), 70.0 (Ar*C*H$_2$), 69.1 (2C, C-1, Ar*C*H$_2$), 35.1 (cyclohexyl *C*H$_2$), 34.7 (cyclohexyl *C*H$_2$), 25.6 (cyclohexyl *C*H$_2$), 25.3 (cyclohexyl *C*H$_2$), 25.2 (cyclohexyl *C*H$_2$); HRMS (ESI) calcd. for $C_{26}H_{32}NaO_5$ $[M+Na]^+$ 447.2142; found 447.2144.



Octyl 1-*O*-benzyl-3,4-*O*-xylylidene-α-D-*threo*-pent-2-ulofuranoside (30α) and Octyl 1-*O*-benzyl-3,4-*O*-xylylidene-β-D-*threo*-pent-2-ulofuranoside (30β). A

mixture of **7** (27.4 mg, 0.0611 mmol), **23** (9.5 mg, 11.6 μL, 0.0733 mmol), and 4Å molecular sieves in CH_2Cl_2 (2.4 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to –78 °C and then *N*-iodosuccinimide (16.5 mg, 0.0733 mmol) and silver triflate (1.6 mg, 6.11 μmol) were added. After stirring for 1 h at –78 °C, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (15:1, hexane–EtOAc) to give **30α** (12.2 mg, 44%) as a colorless oil and **30β** (13.0 mg, 47%) as a colorless oil. Data for **30α**: $[\alpha]^{25}_D$ +56.2 (*c* 1.2, $CHCl_3$); R_f 0.61 (4:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.41–7.31 (m, 8H, ArH), 7.30–7.26 (m, 1H, ArH), 4.92 (d, 1H, J_{gem} = 12.5 Hz, ArCH_2), 4.91 (d, 1H, J_{gem} = 12.5 Hz, ArCH_2), 4.77 (d, 1H, J_{gem} = 12.5 Hz, ArCH_2), 4.76 (d, 1H, J_{gem} = 12.5 Hz, ArCH_2), 4.58 (d, 1H, J_{gem} = 12.2 Hz, ArCH_2), 4.56 (d, 1H, J_{gem} = 12.2 Hz, ArCH_2), 4.16 (app dt, 1H, $J_{4,3}$ = 5.0 Hz, $J_{4,5a}$ = $J_{4,5b}$ = 8.1 Hz, H-4), 4.07 (d, 1H, $J_{3,4}$ = 5.0 Hz, H-3), 4.04 (app t, 1H, $J_{5a,4}$ = 8.1 Hz, J_{gem} = 8.4 Hz, H-5a), 3.69 (app t, 1H, $J_{5b,4}$ = 8.1 Hz, J_{gem} = 8.4 Hz, H-5b), 3.59 (d, 1H, J_{gem} = 10.5 Hz, H-1a), 3.53 (d, 1H, J_{gem} = 10.5 Hz, H-1b), 3.46 (app t, 2H, *J* = 6.9 Hz, octyl OCH_2), 1.53–1.45 (m, 2H, octyl CH_2), 1.33–1.20 (m, 10H, octyl CH_2), 0.87 (t, 3H, *J* = 7.1 Hz, octyl CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.6 (Ar), 136.6 (Ar), 136.1 (Ar), 131.7 (Ar), 131.5 (Ar), 129.6 (Ar), 129.5 (Ar), 128.2 (2C, Ar), 127.8 (2C, Ar), 127.5 (Ar), 108.5 (C-2), 86.8 (C-3), 81.4 (C-4), 73.5 (ArCH_2), 69.8 (ArCH_2), 69.1 (ArCH_2), 68.6 (C-1), 68.2 (C-5), 61.7 (octyl OCH_2), 31.9 (octyl CH_2), 30.1 (octyl CH_2), 29.4 (octyl CH_2), 29.3 (octyl

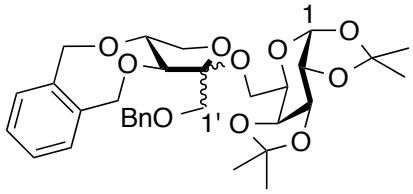
*C*H$_2$), 26.2 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.2 (octyl *C*H$_3$); HRMS (ESI) calcd. for $C_{28}H_{38}NaO_5$ [M+Na]$^+$ 477.2611; found 477.2616. Data for **30β**: $[\alpha]^{25}_D$ +14.6 (*c* 1.3, $CHCl_3$); R_f 0.48 (4:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.42–7.35 (m, 4H, ArH), 7.33–7.26 (m, 3H, ArH), 7.24–7.20 (m, 2H, ArH), 5.01 (d, 1H, J_{gem} = 12.8 Hz, ArC*H*$_2$), 4.90 (d, 1H, J_{gem} = 12.8 Hz, ArC*H*$_2$), 4.81 (d, 1H, J_{gem} = 12.8 Hz, ArC*H*$_2$), 4.76 (d, 1H, J_{gem} = 12.8 Hz, ArC*H*$_2$), 4.59 (d, 1H, J_{gem} = 12.2 Hz, ArC*H*$_2$), 4.48 (d, 1H, J_{gem} = 12.2 Hz, ArC*H*$_2$), 4.34 (ddd, 1H, $J_{4,5b}$ = 4.0 Hz, $J_{4,3}$ = 5.2 Hz, $J_{4,5a}$ = 7.6 Hz, H-4), 4.20 (d, 1H, $J_{3,4}$ = 5.2 Hz, H-3), 4.15 (dd, 1H, $J_{5a,4}$ = 7.6 Hz, J_{gem} = 9.6 Hz, H-5a), 3.79 (dd, 1H, $J_{5b,4}$ = 4.0 Hz, J_{gem} = 9.6 Hz, H-5b), 3.56 (d, 1H, J_{gem} = 10.8 Hz, H-1a), 3.54 (d, 1H, J_{gem} = 10.8 Hz, H-1b), 3.52 (app dt, 1H, *J* = 9.1, 7.6 Hz, OC*H*$_2$), 3.41 (app dt, 1H, *J* = 9.1, 7.6 Hz, OC*H*$_2$), 1.58–1.49 (m, 2H, octyl C*H*$_2$), 1.31–1.19 (m, 10H, octyl C*H*$_2$), 0.87 (t, 3H, *J* = 7.0 Hz, octyl C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.1 (Ar), 136.5 (Ar), 136.4 (Ar), 131.6 (Ar), 131.5 (Ar), 129.5 (2C, Ar), 128.4 (2C, Ar), 127.7 (2C, Ar), 127.6 (Ar), 106.4 (C-2), 83.2 (C-3), 80.8 (C-4), 73.4 (Ar*C*H$_2$), 70.8 (C-5), 69.8 (Ar*C*H$_2$), 68.6 (Ar*C*H$_2$), 68.2 (C-1), 61.7 (octyl O*C*H$_2$), 31.9 (octyl *C*H$_2$), 30.2 (octyl *C*H$_2$), 29.4 (octyl *C*H$_2$), 29.3 (octyl *C*H$_2$), 26.1 (octyl *C*H$_2$), 22.7 (octyl *C*H$_2$), 14.1 (octyl *C*H$_3$); HRMS (ESI) calcd. for $C_{28}H_{38}NaO_5$ [M+Na]$^+$ 477.2611; found 477.2619.



***tert*-Butyl 1-*O*-benzyl-3,4-*O*-xylylidene-α-D-*threo*-pent-2-ulofuranoside (31α)** and ***tert*-Butyl 1-*O*-benzyl-3,4-*O*-xylylidene-β-D-*threo*-pent-2-ulofuranoside (31β)**. A

mixture of the **7** (24.1 mg, 0.0537 mmol), **24** (4.8 mg, 0.0644 mmol), and 4Å molecular sieves in CH_2Cl_2 (2.14 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to –78 °C and *N*-iodosuccinimide (14.5 mg, 0.0644 mmol) and silver triflate (1.4 mg, 5.37 μmol) were added. After stirring for 4 h at –78 °C, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (10:1, hexane–EtOAc) to give **31α** (6.7 mg, 31%) and **31β** (9.8 mg, 46%), both as colorless oils. Data for **31α**: $[\alpha]^{25}_D$ +24.6 (*c* 0.7, $CHCl_3$); R_f 0.31 (6:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.41–7.37 (m, 3H, ArH), 7.34–7.25 (m, 6H, ArH), 4.93 (d, 1H, J_{gem} = 12.9 Hz, ArCH_2), 4.90 (d, 1H, J_{gem} = 12.9 Hz, ArCH_2), 4.80 (d, 1H, J_{gem} = 12.9 Hz, ArCH_2), 4.75 (d, 1H, J_{gem} = 12.9 Hz, ArCH_2), 4.54 (d, 1H, J_{gem} = 11.9 Hz, ArCH_2), 4.50 (d, 1H, J_{gem} = 11.9 Hz, ArCH_2), 4.27 (app dt, 1H, $J_{4,3}$ = 5.9 Hz, $J_{4,5a}$ = $J_{4,5b}$ = 8.0 Hz, H-4), 4.15 (d, 1H, $J_{3,4}$ = 5.9 Hz, H-3), 4.13 (dd, 1H, $J_{5a,4}$ = 8.0 Hz, J_{gem} = 8.4 Hz, H-5a), 3.78 (dd, 1H, $J_{5b,4}$ = 8.0 Hz, J_{gem} = 8.4 Hz, H-5b), 3.60 (d, 1H, J_{gem} = 10.0 Hz, H-1a), 3.49 (d, 1H, J_{gem} = 10.0 Hz, H-1b), 1.25 (s, 9H, (CH_3)$_3$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.9 (Ar), 136.8 (Ar), 136.6 (Ar), 131.8 (Ar), 131.4 (Ar), 129.59 (Ar), 129.55 (Ar), 128.3 (2C, Ar), 127.8 (2C, Ar), 127.5 (Ar), 110.3 (C-2), 88.8 (C-3), 80.5 (C-4), 76.0 (CH_3)$_3$*C*), 73.4 (Ar*C*H$_2$), 72.0 (C-1), 69.6 (C-5), 69.2 (Ar*C*H$_2$), 69.0 (Ar*C*H$_2$), 30.7 (3C, (*C*H$_3$)$_3$C); HRMS (ESI) calcd. for $C_{24}H_{30}NaO_5$ $[M+Na]^+$ 421.1985; found 421.1984. Data for **31β**: $[\alpha]^{25}_D$ +25.2 (*c* 1.0, $CHCl_3$); R_f 0.16 (6:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.40–7.20 (m, 7H, ArH), 7.22–

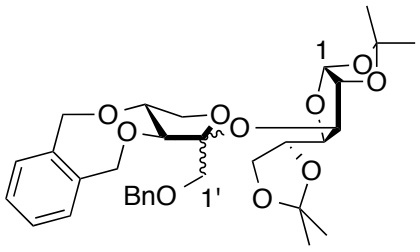
7.17 (m, 2H, ArH), 5.06 (d, 1H, J_{gem} = 12.9 Hz, ArCH_2), 4.83 (s, 2H, ArCH_2), 4.81 (d, 1H, J_{gem} = 12.9 Hz, ArCH_2), 4.59 (d, 1H, J_{gem} = 12.1 Hz, ArCH_2), 4.46 (d, 1H, J_{gem} = 12.1 Hz, ArCH_2), 4.39 (ddd, 1H, $J_{4,3}$ = 6.0 Hz, $J_{4,5a}$ = 7.6 Hz, $J_{4,5b}$ = 4.4 Hz, H-4), 4.22 (dd, 1H, $J_{5a,4}$ = 7.6 Hz, J_{gem} = 9.5 Hz, H-5a), 4.19 (d, 1H, $J_{3,4}$ = 6.0 Hz, H-3), 3.74 (dd, 1H, $J_{5b,4}$ = 4.4 Hz, J_{gem} = 9.5 Hz, H-5b), 3.71 (d, 1H, J_{gem} = 10.4 Hz, H-1a), 3.57 (d, 1H, J_{gem} = 10.4 Hz, H-1b), 1.29 (s, 9H, (CH_3)$_3$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.2 (Ar), 136.8 (Ar), 136.7 (Ar), 131.7 (Ar), 131.0 (Ar), 129.2 (Ar), 129.1 (Ar), 128.3 (2C, Ar), 127.7 (2C, Ar), 127.5 (Ar), 107.6 (C-2), 83.4 (C-3), 80.7 (C-4), 75.6 (CH$_3$)$_3$*C*), 73.4 (Ar*C*H$_2$), 70.4 (C-1), 70.0 (2C, C-5, Ar*C*H$_2$), 69.0 (Ar*C*H$_2$), 31.0 (3C, (*C*H$_3$)$_3$C); HRMS (ESI) calcd. for $C_{24}H_{30}NaO_5$ $[M+Na]^+$ 421.1985; found 421.1983.



1-*O*-benzyl-3,4-*O*-xylylidene-α-D-*threo*-pent-2-ulofuranosyl-(2→6)-1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranose (32α) and **1-*O*-benzyl-3,4-*O*-xylylidene-β-D-*threo*-pent-2-ulofuranosyl-(2→6)-1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranose (32β)**. A mixture of **7** (18.9 mg, 0.0421 mmol), **25** (10.4 mg, 0.0506 mmol), and 4Å molecular sieves in CH_2Cl_2 (1.7 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to –78 °C and *N*-iodosuccinimide (11.4 mg, 0.0506 mmol) and silver triflate (1.1 mg, 4.21 μmol) were added. After stirring for 1 h at –78 °C, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over

$MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (10:1, hexane–EtOAc) to give **32α** (7.6 mg, 31%) and **32β** (11.5 mg, 47%) both as colorless oils. Data for **32α**: $[\alpha]^{25}_D$ +15.4 (*c* 0.8, $CHCl_3$); R_f 0.47 (2:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.41–7.31 (m, 8H, ArH), 7.30–7.26 (m, 1H, ArH), 5.51 (d, 1H, $J_{1,2}$ = 4.9 Hz, H-1), 4.94 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.90 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.78 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.77 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.59 (d, 1H, J_{gem} = 12.2 Hz, ArCH_2), 4.56 (dd, 1H, $J_{3,2}$ = 2.4 Hz, $J_{3,4}$ = 7.9 Hz, H-3), 4.55 (d, 1H, J_{gem} = 12.2 Hz, ArCH_2), 4.28 (dd, 1H, $J_{2,1}$ = 4.9 Hz, $J_{2.3}$ = 2.4 Hz, H-2), 4.22 (dd, 1H, $J_{4,3}$ = 7.9 Hz, $J_{4,5}$ = 1.9 Hz, H-4), 4.17–4.13 (m, 2H, H-3', H-4'), 4.05–4.01 (m, 1H, H-5'a), 3.91 (app dt, 1H, $J_{5,4}$ = 1.9 Hz, $J_{5,6a}$ = $J_{5,6b}$ = 6.3 Hz, H-5), 3.80–3.73 (m, 2H, H-6a, H-5'b), 3.70 (dd, 1H, $J_{6b,5}$ = 6.3 Hz, J_{gem} = 10.3 Hz, H-6b), 3.63 (d, 1H, J_{gem} = 10.7 Hz, H-1'a), 3.58 (d, 1H, J_{gem} = 10.7 Hz, H-1'b), 1.52 (s, 3H, (CH_3)$_2$C), 1.42 (s, 3H, (CH_3)$_2$C), 1.33 (s, 3H, (CH_3)$_2$C), 1.32 (s, 3H, (CH_3)$_2$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.5 (Ar), 136.6 (Ar), 135.9 (Ar), 131.7 (Ar), 131.5 (Ar), 129.54 (Ar), 129.48 (Ar), 128.2 (2C, Ar), 127.7 (2C, Ar), 127.4 (Ar), 109.1 ((CH$_3$)$_2$*C*), 108.8 ((CH$_3$)$_2$*C*), 108.5 (C-2'), 96.3 (C-1), 87.1 (C-3'), 81.2 (C-4'), 73.6 (Ar*C*H$_2$), 71.0 (C-4), 70.7 (C-2), 70.6 (C-3), 69.6 (Ar*C*H$_2$), 69.2 (Ar*C*H$_2$), 69.1 (C-1'), 68.3 (C-5'), 67.3 (C-5), 60.9 (C-6), 26.1 ((*C*H$_3$)$_2$C), 26.0 ((*C*H$_3$)$_2$C), 25.0 ((*C*H$_3$)$_2$C), 24.4 ((*C*H$_3$)$_2$C); HRMS (ESI) calcd. for $C_{32}H_{40}NaO_{10}$ $[M+Na]^+$ 607.2514; found 607.2507. Data for **32β**: $[\alpha]^{25}_D$ –14.6 (*c* 0.4, $CHCl_3$); R_f 0.27 (2:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.44–7.35 (m, 4H, ArH), 7.33–7.25 (m, 3H, ArH), 7.24–7.21 (m, 2H, ArH), 5.39 (d, 1H, $J_{1,2}$ = 5.0 Hz, H-1), 5.01 (d, 1H, J_{gem} = 12.8 Hz, ArCH_2), 4.91 (d, 1H, J_{gem} = 12.8 Hz, ArCH_2), 4.83 (d, 1H, J_{gem} =

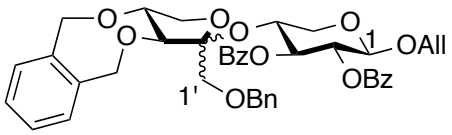
12.8 Hz, ArCH_2), 4.77 (d, 1H, J_{gem} = 12.8 Hz, ArCH_2), 4.58 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.55 (dd, 1H, $J_{3,2}$ = 2.2 Hz, $J_{3,4}$ = 7.9 Hz, H-3), 4.51 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.39–4.31 (m, 2H, H-4', H-5'a), 4.27 (dd, 1H, $J_{2,1}$ = 5.0 Hz, $J_{2,3}$ = 2.2 Hz, H-2), 4.22 (dd, 1H, $J_{4,3}$ = 7.9 Hz, $J_{4,5}$ = 1.9 Hz, H-4), 4.20 (d, 1H, $J_{3',4'}$ = 4.8 Hz, H-3'), 4.00 (ddd, 1H, $J_{5,4}$ = 1.9 Hz, $J_{5,6a}$ = 5.9 Hz, $J_{5,6b}$ = 8.7 Hz, H-5), 3.81 (app t, 1H, $J_{6a,5}$ = J_{gem} = 8.7 Hz, H-6a), 3.76 (dd, 1H, $J_{5b',4}$ = 3.1 Hz, J_{gem} = 8.6 Hz, H-5'b), 3.57 (s, 2H, H-1'a, H-1'b), 3.55 (dd, 1H, $J_{6b,5}$ = 5.9 Hz, J_{gem} = 8.7 Hz, H-6b), 1.53 (s, 3H, (CH_3)$_2$C), 1.42 (s, 3H, (CH_3)$_2$C), 1.32 (s, 3H, (CH_3)$_2$C), 1.28 (s, 3H, (CH_3)$_2$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.0 (Ar), 136.4 (Ar), 136.3 (Ar), 131.5 (Ar), 131.4 (Ar), 129.4 (2C, Ar), 128.3 (2C, Ar), 127.7 (2C, Ar), 127.6 (Ar), 108.8 ((CH$_3$)$_2$*C*), 108.4 ((CH$_3$)$_2$*C*), 106.3 (C-2'), 96.1 (C-1), 83.3 (C-3'), 80.7 (C-4'), 73.4 (Ar*C*H$_2$), 70.8 (C-2), 70.7 (C-5'), 70.5 (C-4), 70.4 (C-3), 69.6 (Ar*C*H$_2$), 68.7 (Ar*C*H$_2$), 68.1 (C-1'), 66.2 (C-5), 59.8 (C-6), 26.1 ((*C*H$_3$)$_2$C), 26.0 ((*C*H$_3$)$_2$C), 24.9 ((*C*H$_3$)$_2$C), 24.4 ((*C*H$_3$)$_2$C); HRMS (ESI) calcd. for $C_{32}H_{40}NaO_{10}$ $[M+Na]^+$ 607.2514; found 607.2502.



1-*O*-benzyl-3,4-*O*-xylylidene-α-D-*threo*-pent-2-ulofuranosyl-(2→3)-1,2,5,6-di-*O*-isopropylidene-α-D-glucopyranose (33*α*) and **1-*O*-benzyl-3,4-*O*-xylylidene-β-D-*threo*-pent-2-ulofuranosyl-(2→3)-1,2,3,4-di-*O*-isopropylidene-α-D-glucopyranose (33β)**. A mixture of the **7** (25.1 mg, 0.0560 mmol), **26** (17.5 mg, 0.0671 mmol), and 4Å molecular sieves in CH_2Cl_2 (2.24 mL) was stirred under an Ar atmosphere at room

temperature for 30 min. The mixture was then cooled to –78 °C and *N*-iodosuccinimide (15.1 mg, 0.0671 mmol) and silver triflate (1.4 mg, 5.60 μmol) were added. After stirring for 1 h at –78 °C, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (8:1, hexane–EtOAc) to give **33α** (4.8 mg, 15%) and **33β** (21.1 mg, 65%) both as colorless oils. Data for **33α**: $[\alpha]^{25}_D$ +35.1 (*c* 0.5, $CHCl_3$); R_f 0.25 (4:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.42–7.27 (m, 9H, ArH), 5.82 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.95 (d, 1H, J_{gem} = 12.8 Hz, ArCH_2), 4.88 (d, 1H, J_{gem} = 12.8 Hz, ArCH_2), 4.76 (d, 2H, J_{gem} = 12.8 Hz, ArCH_2), 4.55 (d, 1H, J_{gem} = 11.7 Hz, ArCH_2), 4.52 (d, 1H, J_{gem} = 11.7 Hz, ArCH_2), 4.41 (d, 1H, $J_{2,1}$ = 3.7 Hz, H-2), 4.32–4.15 (m, 5H, H-3, H-4, H-5, H-4', H-5'a), 4.05 (d, 1H, $J_{3',4'}$ = 5.9 Hz, H-3'), 3.96–3.91 (m, 2H, H-6a, H-6b), 3.74 (dd, 1H, *J* = 8.0, 8.7 Hz, H-5'b), 3.65 (d, 1H, J_{gem} = 10.8 Hz, H-1'a), 3.54 (d, 1H, J_{gem} = 10.8 Hz, H-1'b), 1.45 (s, 3H, (CH_3)$_2$C), 1.35 (s, 3H, (CH_3)$_2$C), 1.25 (s, 6H, (CH_3)$_2$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.4 (Ar), 136.3 (Ar), 136.0 (Ar), 131.5 (2C, Ar), 129.69 (Ar), 129.66 (Ar), 128.3 (2C, Ar), 127.63 (2C, Ar), 127.55 (Ar), 111.7 ((CH$_3$)$_2$*C*), 110.0 (C-2'), 108.5 ((CH$_3$)$_2$*C*), 105.1 (C-1), 86.6 (C-3'), 84.3 (C-2), 81.0 (C-4'), 80.5 (C-4), 75.9 (C-3), 73.7 (Ar*C*H$_2$), 73.1 (C-5), 69.7 (2C, C-1', C-5'), 69.5 (Ar*C*H$_2$), 68.9 (Ar*C*H$_2$), 66.2 (C-6), 26.9 ((*C*H$_3$)$_2$C), 26.6 ((*C*H$_3$)$_2$C), 26.4 ((*C*H$_3$)$_2$C), 25.3 ((*C*H$_3$)$_2$C); HRMS (ESI) calcd. for $C_{32}H_{40}NaO_{10}$ $[M+Na]^+$ 607.2514; found 607.2514. Data for **33β**: $[\alpha]^{25}_D$ +1.9 (*c* 1.0, $CHCl_3$); R_f 0.17 (4:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.43–7.26 (m, 7H, ArH), 7.24–

7.21 (m, 2H, ArH), 5.87 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 4.99 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.87 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.81 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.77 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.57 (d, 1H, J_{gem} = 12.3 Hz, ArCH_2), 4.53 (d, 1H, J_{gem} = 12.3 Hz, ArCH_2), 4.51 (d, 1H, $J_{2,1}$ = 3.8 Hz, H-2), 4.44 (dd, 1H, $J_{5'a,4'}$ = 7.9 Hz, J_{gem} = 9.0 Hz, H-5'a), 4.41–4.35 (m, 1H, H-4'), 4.33 (d, 1H, $J_{3,4}$ = 3.5 Hz, H-3), 4.31–4.25 (m, 1H, H-5), 4.16 (d, 1H, $J_{3',4'}$ = 5.5 Hz, H-3'), 4.15 (dd, 1H, $J_{4,3}$ = 3.5 Hz, $J_{4,5}$ = 7.4 Hz, H-4), 4.04 (dd, 1H, $J_{6a,5}$ = 6.2 Hz, J_{gem} = 8.5 Hz, H-6a), 3.96 (dd, 1H, $J_{6b,5}$ = 6.6 Hz, J_{gem} = 8.5 Hz, H-6b), 3.72 (dd, 1H, $J_{5'b,4'}$ = 4.8 Hz, J_{gem} = 9.0 Hz, H-5'b), 3.57 (d, 1H, J_{gem} = 10.6 Hz, H-1'a), 3.46 (d, 1H, J_{gem} = 10.6 Hz, H-1'b), 1.47 (s, 3H, (CH_3)$_2$C), 1.39 (s, 3H, (CH_3)$_2$C), 1.26 (s, 3H, (CH_3)$_2$C), 1.24 (s, 3H, (CH_3)$_2$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 137.8 (Ar), 136.5 (Ar), 136.2 (Ar), 131.5 (Ar), 131.4 (Ar), 129.59 (Ar), 129.55 (Ar), 128.4 (2C, Ar), 127.8 (Ar), 127.70 (2C, Ar), 111.4 ((CH$_3$)$_2$*C*), 108.9 ((CH$_3$)$_2$*C*), 107.2 (C-2'), 105.0 (C-1), 84.9 (C-2), 83.9 (C-3'), 81.2 (C-4), 80.7 (C-4'), 74.6 (C-3), 73.5 (Ar*C*H$_2$), 72.4 (C-5), 70.7 (C-5') 70.4 (C-1'), 69.4 (Ar*C*H$_2$), 69.1 (Ar*C*H$_2$), 67.3 (C-6), 26.9 ((*C*H$_3$)$_2$C), 26.7 ((*C*H$_3$)$_2$C), 26.4 ((*C*H$_3$)$_2$C), 25.5 ((*C*H$_3$)$_2$C); HRMS (ESI) calcd. for $C_{32}H_{40}NaO_{10}$ $[M+Na]^+$ 607.2514; found 607.2518.

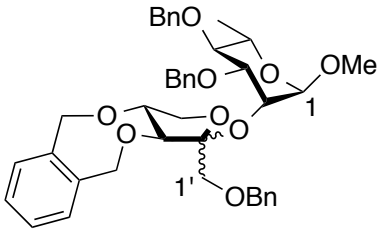


Allyl 1-*O*-benzyl-3,4-*O*-xylylidene-α-D-*threo*-pent-2-ulofuranosyl-(2→4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside (34α) and **Allyl 1-*O*-benzyl-3,4-*O*-xylylidene-β-D-*threo*-pent-2-ulofuranosyl-(2→4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside (34β)**. A mixture of **7** (24.0 mg, 0.0535 mmol), **27** (17.8 mg, 0.0446 mmol), and 4Å molecular

sieves in CH_2Cl_2 (1.8 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to –78 ºC and *N*-iodosuccinimide (14.4 mg, 0.0642 mmol) and silver triflate (1.4 mg, 5.35 μmol) were added. After stirring for 1 h at –78 ºC, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (8:1, Hexane–EtOAc) to give **34α** (5.0 mg, 15%) as a colorless oil and **34β** (23.2 mg, 72%) as a colorless oil. Data for **34α**: $[\alpha]^{25}_D$ +73.1 (*c* 0.5, $CHCl_3$); R_f 0.63 (2:1, Hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 700 MHz) δ_H 7.97–7.95 (m, 2H, ArH), 7.94–7.92 (m, 2H, ArH), 7.52–7.48 (m, 2H, ArH), 7.39–7.33 (m, 6H, ArH), 7.32–7.30 (m, 1H, ArH), 7.28–7.26 (m, 1H, ArH), 7.25–7.21 (m, 3H, ArH), 7.16–7.13 (m, 2H, ArH), 5.83 (m, 1H, OCH_2CH=CH_2), 5.48 (app t, 1H, $J_{3,2} = J_{3,4}$ = 8.1 Hz, H-3), 5.26 (dd, 1H, $J_{2,1}$ = 6.5 Hz, $J_{2,3}$ = 8.1 Hz, H-2), 5.23 (dq, 1H, J = 17.1, 1.6 Hz, OCH_2CH=CH_2), 5.12 (dq, 1H, J = 10.5, 1.6 Hz, OCH_2CH=CH_2), 4.85 (d, 1H, J_{gem} = 12.7 Hz, $ArCH_2$), 4.78 (d, 1H, J_{gem} = 12.7 Hz, $ArCH_2$), 4.70 (d, 1H, J_{gem} = 12.7 Hz, $ArCH_2$), 4.68 (d, 1H, $J_{1,2}$ = 6.5 Hz, H-1), 4.64 (d, 1H, J_{gem} = 12.7 Hz, $ArCH_2$), 4.33 (s, 2H, $ArCH_2$), 4.29 (ddt, 1H, J = 13.0, 5.0, 1.4 Hz, OCH_2CH=CH_2), 4.24 (app dt, 1H, $J_{4,5a}$ = 4.9 Hz, $J_{4,3} = J_{4,5b}$ = 8.1 Hz, H-4), 4.15–4.10 (m, 2H, H-5a, H-4'), 4.08 (ddt, 1H, J = 13.0, 6.1, 1.4 Hz, OCH_2CH=CH_2), 4.05 (app t, 1H, $J_{5'a,4'} = J_{gem}$ = 8.0 Hz, H-5'a), 4.02 (d, 1H, $J_{3',4'}$ = 5.7 Hz, H-3'), 3.70 (app t, 1H, $J_{5'b,4'} = J_{gem}$ = 8.0 Hz, H-5'b), 3.50 (d, 1H, J_{gem} = 10.5 Hz, H-1'a), 3.44 (d, 1H, J_{gem} = 10.5 Hz, H-1'b), 3.50 (dd, 1H, $J_{5b,4}$ = 8.1 Hz, J_{gem} = 11.8 Hz, H-5b); ^{13}C NMR ($CDCl_3$, 175 MHz) δ_C 165.7 (C=O), 165.5

(C=O), 138.3 (Ar), 136.5 (Ar), 135.9 (Ar), 133.7 ($OCH_2CH=CH_2$), 132.99 (Ar), 132.98 (Ar), 131.6 (Ar), 131.5 (Ar), 129.90 (Ar), 129.87 (Ar), 129.8 (Ar), 129.7 (Ar), 129.6 (Ar), 129.5 (Ar), 128.3 (Ar), 128.2 (Ar), 127.6 (Ar), 127.4 (Ar), 117.5 ($OCH_2CH=CH_2$), 109.6 (C-2'), 99.5 (C-1), 88.2 (C-3'), 80.8 (C-4'), 73.4 ($ArCH_2$), 72.4 (C-3), 71.3 (C-2), 69.6 (C-1'), 69.58 ($OCH_2CH=CH_2$), 69.44 ($ArCH_2$), 69.35 ($ArCH_2$), 68.92 (C-5'), 68.86 (C-4), 64.6 (C-5); HRMS (ESI) calcd. for $C_{42}H_{42}NaO_{11}$ $[M+Na]^+$ 745.2619; found 745.2623. Data for **34β**: $[\alpha]^{25}_D$ +25.6 (*c* 2.3, $CHCl_3$); R_f 0.53 (2:1, Hexane–EtOAc); ^1H NMR ($CDCl_3$, 700 MHz) δ_H 7.94 (d, 2H, J = 8.1 Hz, ArH), 7.87 (d, 2H, J = 8.1 Hz, ArH), 7.50–7.45 (m, 2H, ArH), 7.39–7.32 (m, 6H, ArH), 7.31–7.27 (m, 4H, ArH), 7.22–7.20 (m, 1H, ArH), 7.20–7.17 (m, 2H, ArH), 5.82–5.76 (m, 1H, $OCH_2CH=CH_2$), 5.61 (app t, 1H, $J_{3,2} = J_{3,4}$ = 8.8 Hz, H-3), 5.31 (dd, 1H, $J_{2,1}$ = 7.4 Hz, $J_{2,3}$ = 8.8 Hz, H-2), 5.22 (dq, 1H, J = 17.1, 1.6 Hz, $OCH_2CH=CH_2$), 5.12 (dq, 1H, J = 10.4, 1.6 Hz, $OCH_2CH=CH_2$), 4.84 (d, 1H, J_{gem} = 12.7 Hz, $ArCH_2$), 4.67 (d, 1H, J_{gem} = 12.7 Hz, $ArCH_2$), 4.66 (d, 1H, J_{gem} = 12.7 Hz, $ArCH_2$), 4.65 (d, 1H, $J_{1,2}$ = 7.4 Hz, H-1), 4.53 (d, 1H, J_{gem} = 12.4 Hz, $ArCH_2$), 4.51 (d, 1H, J_{gem} = 12.7 Hz, $ArCH_2$), 4.47 (d, 1H, J_{gem} = 12.4 Hz, $ArCH_2$), 4.29 (ddt, 1H, J = 13.6, 5.1, 1.6 Hz, $OCH_2CH=CH_2$), 4.24 (app dt, 1H, $J_{4,3}$ = 8.8 Hz, $J_{4,5a} = J_{4,5b}$ = 5.1 Hz, H-4), 4.10–4.04 (m, 3H, H-5a, H-3', $OCH_2CH=CH_2$), 4.03–3.97 (m, 2H, H-5'a, H-4'), 3.54–3.47 (m, 3H, H-5b, H-1'a, H-5'b), 3.38 (d, 1H, J_{gem} = 10.7 Hz, H-1'b); ^{13}C NMR ($CDCl_3$, 175 MHz) δ_C 165.6 (C=O), 165.4 (C=O), 137.7 (Ar), 136.5 (Ar), 136.0 (Ar), 133.6 ($OCH_2CH=CH_2$), 133.13 (Ar), 133.06 (Ar), 131.4 (Ar), 131.3 (Ar), 129.8 (Ar), 129.67 (Ar), 129.64 (Ar), 129.55 (Ar), 129.4 (Ar), 129.3 (Ar), 128.44 (Ar), 128.43 (Ar), 128.3 (Ar), 127.7 (Ar), 127.66 (Ar), 117.5 ($OCH_2CH=CH_2$), 106.8 (C-2'), 100.0 (C-1), 83.0 (C-3'), 80.2 (C-4'), 73.4

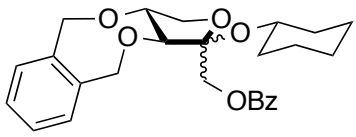
(Ar*C*H$_2$), 73.0 (C-3), 71.8 (C-2), 70.4 (C-5'), 70.1 (C-1'), 69.8 (O*C*H$_2$CH=CH$_2$), 69.3 (Ar*C*H$_2$), 69.0 (Ar*C*H$_2$), 67.8 (C-4), 65.3 (C-5); HRMS (ESI) calcd. for $C_{42}H_{42}NaO_{11}$ $[M+Na]^+$ 745.2626; found 745.2619.



Methyl 1-*O*-benzyl-3,4-*O*-xylylidene-α-D-*threo*-pent-2-ulofuranosyl-(2→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (35α) and **Methyl 1-*O*-benzyl-3,4-*O*-xylylidene-β-D-*threo*-pent-2-ulofuranosyl-(2→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (35β)**. A mixture of **7** (21.8 mg, 0.0485 mmol), **28**[3] (14.5 mg, 0.0404 mmol), and 4Å molecular sieves in CH_2Cl_2 (1.35 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to –78 °C and *N*-iodosuccinimide (13.1 mg, 0.0582 mmol) and silver triflate (1.2 mg, 4.85 μmol) were added. After stirring for 2 h at –78 °C, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (8:1, hexane–EtOAc) to give **35α** (8.2 mg, 30%) and **35β** (16.5 mg, 60%) both as colorless oils. Data for **35α**: $[\alpha]^{25}_D$ +36.4 (*c* 0.1, $CHCl_3$); R_f 0.27 (4:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.39–7.18 (m, 19H, ArH), 4.95 (d, 1H, J_{gem} = 11.2 Hz, ArCH_2), 4.89 (d, 1H, J_{gem} = 12.3 Hz, ArCH_2), 4.79 (d, 1H, J_{gem} = 13.0 Hz, ArCH_2), 4.71 (d, 1H, J_{gem} = 12.3 Hz, ArCH_2),

4.69 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 4.68 (d, 1H, J_{gem} = 12.1 Hz, ArCH_2), 4.64 (d, 1H, J_{gem} = 13.0 Hz, ArCH_2), 4.63 (d, 1H, J_{gem} = 11.2 Hz, ArCH_2), 4.55 (d, 1H, J_{gem} = 11.9 Hz, ArCH_2), 4.53 (d, 1H, J_{gem} = 11.9 Hz, ArCH_2), 4.52 (d, 1H, J_{gem} = 12.1 Hz, ArCH_2), 4.32 (dd, 1H, $J_{2,1}$ = 1.7 Hz, $J_{2,3}$ = 3.2 Hz, H-2), 4.21 (d, 1H, $J_{3',4'}$ = 5.5 Hz, H-3'), 4.09–4.04 (m, 1H, H-4'), 4.00 (app t, 1H, $J_{5'a,4'}$ = J_{gem} = 8.5 Hz, H-5'a), 3.88 (app t, 1H, $J_{5'b,4'}$ = J_{gem} = 8.5 Hz, H-5'b), 3.76 (dd, 1H, $J_{3,2}$ = 3.2 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 3.67 (d, 1H, J_{gem} = 10.8 Hz, H-1'a), 3.64–3.58 (m, 1H, H-5), 3.56 (d, 1H, J_{gem} = 10.8 Hz, H-1'b), 3.48 (app t, 1H, $J_{4,3}$ = $J_{4,5}$ = 9.6 Hz, H-4), 3.22 (s, 3H, OCH_3), 1.28 (d, 3H, $J_{6,5}$ = 6.3 Hz, H-6); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.8 (Ar), 138.4 (Ar), 137.1 (Ar), 135.7 (Ar), 131.6 (Ar), 131.5 (Ar), 129.5 (Ar), 129.4 (Ar), 128.33 (Ar), 128.26 (Ar), 128.1 (Ar), 127.8 (Ar), 127.7 (Ar), 127.5 (Ar), 127.3 (Ar), 109.3 (C-2'), 101.0 (C-1, $J_{C1,H1}$ = 171.8 Hz), 88.1 (C-3'), 80.3 (C-4'), 79.8 (C-4), 79.1 (C-3), 75.1 (ArCH$_2$), 73.9 (ArCH$_2$), 71.8 (ArCH$_2$), 71.3 (C-1'), 69.44 (C-2), 69.35 (ArCH$_2$), 69.2 (ArCH$_2$), 68.9 (C-5'), 67.9 (C-5), 54.7 (OCH$_3$), 18.1 (C-6); HRMS (ESI) calcd. for $C_{41}H_{46}NaO_9$ $[M+Na]^+$ 705.3034; found 705.3021. Data for **35β**: $[\alpha]^{25}_D$ +12.2 (*c* 0.3, $CHCl_3$); R_f 0.14 (4:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.40–7.24 (m, 17H, ArH), 7.15–7.11 (m, 2H, ArH), 5.04 (d, 1H, J_{gem} = 13.3 Hz, ArCH_2), 4.89 (d, 1H, J_{gem} = 13.0 Hz, ArCH_2), 4.87 (d, 1H, J_{gem} = 11.2 Hz, ArCH_2), 4.82 (d, 1H, J_{gem} = 13.0 Hz, ArCH_2), 4.80 (d, 1H, J_{gem} = 13.3 Hz, ArCH_2), 4.64–4.58 (m, 3H, H-1, ArCH_2), 4.58 (d, 1H, J_{gem} = 11.2 Hz, ArCH_2), 4.47 (d, 1H, J_{gem} = 12.1 Hz, ArCH_2), 4.46–4.43 (m, 1H, H-4'), 4.31 (d, 1H, J_{gem} = 12.1 Hz, ArCH_2), 4.27 (d, 1H, $J_{3',4'}$ = 6.5 Hz, H-3'), 4.22 (dd, 1H, $J_{5'a,4'}$ = 8.1 Hz, J_{gem} = 9.4 Hz, H-5'a), 4.09 (dd, 1H, $J_{2,1}$ = 1.7 Hz, $J_{2,3}$ = 3.0 Hz, H-2), 3.79 (dd, 1H, $J_{5'b,4}$ = 5.6 Hz, J_{gem} = 9.4 Hz, H-5'b), 3.76 (dd, 1H, $J_{3,2}$ = 3.0 Hz, $J_{3,4}$ = 9.1 Hz, H-3),

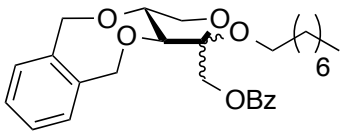
3.65–3.58 (m, 1H, H-5), 3.55 (s, 2H, H-1'a, H-1'b), 3.49 (app t, 1H, $J_{4,3} = J_{4,5} = 9.1$ Hz, H-4), 3.27 (s, 3H, OCH_3), 1.26 (d, 3H, $J_{6,5} = 6.1$ Hz, H-6); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.8 (Ar), 138.7 (Ar), 138.2 (Ar), 136.8 (Ar), 136.6 (Ar), 131.6 (Ar), 131.1 (Ar), 129.3 (Ar), 129.2 (Ar), 128.34 (Ar), 128.32 (Ar), 128.0 (Ar), 127.9 (Ar), 127.59 (Ar), 127.57 (Ar), 127.51 (Ar), 127.48 (Ar), 107.2 (C-2'), 100.3 (C-1, $J_{C1,H1}$ = 172.1 Hz), 82.2 (C-3'), 80.4 (C-4), 79.8 (C-4'), 78.9 (C-3), 74.9 (ArCH$_2$), 73.3 (ArCH$_2$), 72.4 (ArCH$_2$), 70.5 (C-5'), 69.6 (C-2), 69.5 (ArCH$_2$), 69.2 (ArCH$_2$), 69.0 (C-1'), 67.9 (C-5), 54.7 (OCH$_3$), 18.1 (C-6); HRMS (ESI) calcd. for $C_{41}H_{46}NaO_9$ $[M+Na]^+$ 705.3034; found 705.3026.



Cyclohexyl 1-*O*-benzoyl-3,4-*O*-xylylidene-α-D-*threo*-pent-2-ulofuranoside (**36α**) and **Cyclohexyl 1-*O*-benzoyl-3,4-*O*-xylylidene-β-D-*threo*-pent-2-ulofuranoside** (**36β**). A mixture of **8** (48 mg, 0.104 mmol), **22** (12.5 mg, 13.0 μL, 0.125 mmol), and 4Å molecular sieves in CH_2Cl_2 (4.2 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to –78 °C and *N*-iodosuccinimide (28.0 mg, 0.125 mmol) and silver triflate (2.7 mg, 10.4 μmol) were added. After stirring for 4 h at –78 °C, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (9:1, hexane–EtOAc) to give **36α**

(13.7 mg, 29%) as a colorless oil and **36β** (27.3 mg, 58%) as a colorless oil. Data for **36α**: $[\alpha]^{25}_{D}$ +17.8 (*c* 0.4, $CHCl_3$); R_f 0.29 (9:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.97–7.94 (m, 2H, Ar), 7.57–7.52 (m, 1H, Ar), 7.42–7.30 (m, 5H, Ar), 7.25–7.23 (m, 1H, Ar), 4.94 (d, 1H, J_{gem} = 12.4 Hz, ArC*H*$_2$), 4.84 (d, 1H, J_{gem} = 12.4 Hz, ArC*H*$_2$), 4.76 (d, 1H, J_{gem} = 12.4 Hz, ArC*H*$_2$), 4.73 (d, 1H, J_{gem} = 12.4 Hz, ArC*H*$_2$), 4.45 (d, 1H, J_{gem} = 11.8 Hz, H-1a), 4.41 (d, 1H, J_{gem} = 11.8 Hz, H-1b), 4.17 (ddd, 1H, $J_{4,3}$ = 5.5 Hz, $J_{4,5a}$ = 7.7 Hz, $J_{4,5b}$ = 8.8 Hz, H-4), 4.10 (d, 1H, $J_{3,4}$ = 5.5 Hz, H-3), 4.06 (dd, 1H, $J_{5a,4}$ = 7.7 Hz, J_{gem} = 8.8 Hz, H-5a), 3.80 (app t, 1H, $J_{5b,4}$ = J_{gem} = 8.8 Hz, H-5b), 3.76–3.69 (m, 1H, cyclohexyl OC*H*), 1.80–1.64 (m, 4H, cyclohexyl C*H*$_2$), 1.52–1.46 (m, 1H, cyclohexyl C*H*$_2$), 1.36–1.19 (m, 1H, cyclohexyl C*H*$_2$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 166.1 (C=O), 136.7 (Ar), 136.0 (Ar), 133.0 (Ar), 131.8 (Ar), 131.6 (Ar), 130.6 (Ar), 129.83 (2C, Ar), 129.77 (Ar), 129.67 (Ar), 128.5 (2C, Ar), 108.6 (C-2), 88.3 (C-3), 81.1 (C-4), 71.2 (cyclohexyl O*C*H), 69.7 (Ar*C*H$_2$), 68.9 (Ar*C*H$_2$), 68.5 (C-5), 62.8 (C-1), 35.0 (cyclohexyl *C*H$_2$), 34.4 (cyclohexyl *C*H$_2$), 25.5 (cyclohexyl *C*H$_2$), 24.65 (cyclohexyl *C*H$_2$), 24.63 (cyclohexyl *C*H$_2$); HRMS (ESI) calcd. for $C_{26}H_{30}NaO_6$ $[M+Na]^+$ 461.1935; found 461.1940. Data for **36β**: $[\alpha]^{25}_{D}$ +12.9 (*c* 0.9, $CHCl_3$); R_f 0.19 (9:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.89–7.84 (m, 2H, Ar), 7.58–7.53 (m, 1H, Ar), 7.43–7.37 (m, 2H, Ar), 7.37–7.30 (m, 3H, Ar), 7.28–7.25 (m, 1H, Ar), 5.06 (d, 1H, J_{gem} = 12.9 Hz, ArC*H*$_2$), 4.85–4.77 (m, 3H, ArC*H*$_2$), 4.61 (d, 1H, J_{gem} = 11.8 Hz, H-1a), 4.47 (ddd, 1H, $J_{4,3}$ = 5.1 Hz, $J_{4,5a}$ = 7.7 Hz, $J_{4,5b}$ = 3.8 Hz, H-4), 4.26 (dd, 1H, $J_{5a,4}$ = 7.7 Hz, J_{gem} = 9.8 Hz, H-5a), 4.21 (d, 1H, J_{gem} = 11.8 Hz, H-1b), 4.11 (d, 1H, $J_{3,4}$ = 5.1 Hz, H-3), 3.81–3.76 (m, 1H, cyclohexyl OC*H*), 3.76 (dd, 1H, $J_{5b,4}$ = 3.8 Hz, J_{gem} = 9.8 Hz, H-5b), 1.86–1.70 (m, 4H, cyclohexyl C*H*$_2$), 1.59–1.36 (m, 4H,

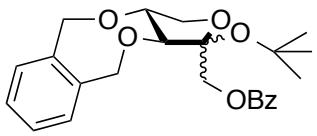
cyclohexyl C*H*$_2$), 1.30–1.20 (m, 2H, cyclohexyl C*H*$_2$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 165.9 (C=O), 137.0 (Ar), 135.7 (Ar), 133.2 (Ar), 131.7 (Ar), 131.6 (Ar), 130.0 (Ar), 129.9 (2C, Ar), 129.57 (Ar), 129.55 (Ar), 128.5 (2C, Ar) 105.4 (C-2), 83.5 (C-3), 81.3 (C-4), 71.0 (2C, cyclohexyl O*C*H, C-5), 69.7 (Ar*C*H$_2$), 69.1 (Ar*C*H$_2$), 62.8 (C-1), 34.6 (cyclohexyl *C*H$_2$), 34.5 (cyclohexyl *C*H$_2$), 25.4 (cyclohexyl *C*H$_2$), 25.1 (cyclohexyl *C*H$_2$), 25.0 (cyclohexyl *C*H$_2$); HRMS (ESI) calcd. for $C_{26}H_{30}NaO_6$ $[M+Na]^+$ 461.1935; found 461.1930.



Octyl 1-*O*-benzoyl-3,4-*O*-xylylidene-α-D-*threo*-pent-2-ulofuranoside (**37α**) and **Octyl 1-*O*-benzoyl-3,4-*O*-xylylidene-β-D-*threo*-pent-2-ulofuranoside** (**37β**). A mixture of the **8** (19.9 mg, 0.0430 mmol), **23** (6.7 mg, 0.0516 mmol), and 4Å molecular sieves in CH_2Cl_2 (1.72 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to –78 °C and *N*-iodosuccinimide (11.6 mg, 0.0516 mmol) and silver triflate (1.1 mg, 4.30 μmol) were added. After stirring for 1 h at –78 °C, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (15:1, hexane–EtOAc) to give **37α** (4.5 mg, 23%) and **37β** (13.3 mg, 68%) both as colorless oils. Data for **37α**: $[\alpha]^{25}_D$ +62.9 (*c* 0.5, $CHCl_3$); R_f 0.14 (15:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.99–7.95 (m, 2H, ArH), 7.58–7.52

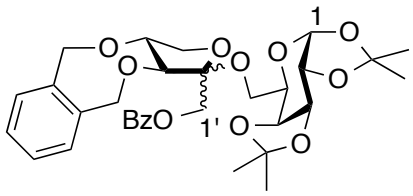
(m, 1H, ArH), 7.44–7.32 (m, 5H, ArH), 7.29–7.26 (m, 1H, ArH), 4.95 (d, 1H, J_{gem} = 12.7 Hz, ArCH_2), 4.87 (d, 1H, J_{gem} = 12.7 Hz, ArCH_2), 4.77 (d, 1H, J_{gem} = 12.7 Hz, ArCH_2), 4.74 (d, 1H, J_{gem} = 12.7 Hz, ArCH_2), 4.47 (d, 1H, J_{gem} = 11.7 Hz, H-1a), 4.40 (d, 1H, J_{gem} = 11.7 Hz, H-1b), 4.18 (ddd, 1H, $J_{4,3}$ = 5.3 Hz, $J_{4,5a}$ = 7.8 Hz, $J_{4,5b}$ = 8.8 Hz, H-4), 4.11 (d, 1H, $J_{3,4}$ = 5.3 Hz, H-3), 4.07 (dd, 1H, $J_{5a,4}$ = 7.8 Hz, J_{gem} = 8.8 Hz, H-5a), 3.74 (app t, 1H, $J_{5b,4}$ = J_{gem} = 8.8 Hz, H-5b), 3.55 (app dt, 1H, J = 6.8, 9.2 Hz, octyl OCH_2), 3.48 (app dt, 1H, J = 6.8, 9.2 Hz, octyl OCH_2), 1.56–1.47 (m, 2H, octyl CH_2), 1.33–1.18 (m, 10H, octyl CH_2), 0.86 (t, 3H, J = 7.2 Hz, octyl CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 166.1 (C=O), 136.5 (Ar), 135.9 (Ar), 132.9 (Ar), 131.7 (Ar), 131.5 (Ar), 130.4 (Ar), 129.72 (2C, Ar), 129.68 (Ar), 129.58 (Ar), 128.4 (2C, Ar), 107.9 (C-2), 87.6 (C-3), 81.1 (C-4), 69.8 (ArCH_2), 68.9 (ArCH_2), 68.3 (C-5), 62.1 (C-1), 61.8 (octyl OCH_2), 31.9 (octyl CH_2), 30.1 (octyl CH_2), 29.4 (octyl CH_2), 29.3 (octyl CH_2), 26.2 (octyl CH_2), 22.7 (octyl CH_2), 14.1 (octyl CH_3); HRMS (ESI) calcd. for $C_{28}H_{36}NaO_6$ $[M+Na]^+$ 491.2404; found 491.2412. Data for **37β**: $[\alpha]^{25}_D$ +21.4 (*c* 1.3, $CHCl_3$); R_f 0.09 (15:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.92–7.87 (m, 2H, ArH), 7.58–7.53 (m, 1H, ArH), 7.44–7.29 (m, 6H, ArH), 5.03 (d, 1H, J_{gem} = 12.7 Hz, ArCH_2), 4.88 (d, 1H, J_{gem} = 12.7 Hz, ArCH_2), 4.82 (d, 1H, J_{gem} = 12.7 Hz, ArCH_2), 4.78 (d, 1H, J_{gem} = 12.7 Hz, ArCH_2), 4.59 (d, 1H, J_{gem} = 11.8 Hz, H-1a), 4.39 (ddd, 1H, $J_{4,3}$ = 4.9 Hz, $J_{4,5a}$ = 7.5 Hz, $J_{4,5b}$ = 3.7 Hz, H-4), 4.30 (d, 1H, J_{gem} = 11.8 Hz, H-1b), 4.18 (dd, 1H, $J_{5a,4}$ = 7.5 Hz, J_{gem} = 9.9 Hz, H-5a), 4.14 (d, 1H, $J_{3,4}$ = 4.9 Hz, H-3), 3.78 (dd, 1H, $J_{5b,4}$ = 3.7 Hz, J_{gem} = 9.9 Hz, H-5b), 3.62 (app dt, 1H, J = 7.5, 9.2 Hz, octyl OCH_2), 3.54 (app dt, 1H, J = 6.6, 9.2 Hz, octyl OCH_2), 1.65–1.54 (m, 2H, octyl CH_2), 1.35–1.18 (m, 10H, octyl CH_2), 0.87 (t, 3H, J = 7.2 Hz, octyl CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C

165.9 (C=O), 136.6 (Ar), 135.8 (Ar), 133.1 (Ar), 131.6 (Ar), 131.4 (Ar), 129.9 (Ar), 129.8 (2C, Ar), 129.5 (2C, Ar), 128.4 (2C, Ar), 105.1 (C-2), 83.7 (C-3), 81.0 (C-4), 71.0 (C-5), 69.7 (Ar*C*H_2), 68.9 (Ar*C*H_2), 62.4 (C-1), 62.0 (octyl O*C*H_2), 31.9 (octyl *C*H_2), 30.1 (octyl *C*H_2), 29.4 (octyl *C*H_2), 29.3 (octyl *C*H_2), 26.1 (octyl *C*H_2), 22.7 (octyl *C*H_2), 14.1 (octyl *C*H_3); HRMS (ESI) calcd. for $C_{28}H_{38}NaO_5$ $[M+Na]^+$ 491.2404; found 491.2411.



***tert*-Butyl 1-*O*-benzoyl-3,4-*O*-xylylidene-α-D-*threo*-pent-2-ulofuranoside (38α)** and ***tert*-Butyl 1-*O*-benzoyl-3,4-*O*-xylylidene-β-D-*threo*-pent-2-ulofuranoside (38β).** A mixture of **8** (23.2 mg, 0.0502 mmol), **24** (4.5 mg, 0.0602 mmol), and 4Å molecular sieves in CH_2Cl_2 (2.01 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to –78 °C and *N*-iodosuccinimide (13.5 mg, 0.0602 mmol) and silver triflate (1.3 mg, 5.02 μmol) were added. After stirring for 6 h at –78 °C, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (10:1, hexane–EtOAc) to give **38α** (6.6 mg, 32%) and **38β** (11.9 mg, 58%) both as colorless oils. Data for **38α**: $[\alpha]^{25}_D$ +36.8 (*c* 0.7, $CHCl_3$); R_f 0.51 (4:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.90–7.86 (m, 2H, ArH), 7.56–7.50 (m, 1H, ArH), 7.40–7.34 (m, 3H, ArH), 7.33–7.29 (m,

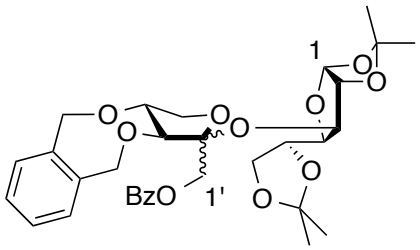
2H, ArH), 7.27–7.24 (m, 1H, ArH), 4.97 (d, 1H, J_{gem} = 12.8 Hz, ArCH_2), 4.83 (d, 1H, J_{gem} = 12.8 Hz, ArCH_2), 4.75 (d, 1H, J_{gem} = 12.8 Hz, ArCH_2), 4.74 (d, 1H, J_{gem} = 12.8 Hz, ArCH_2), 4.49 (d, 1H, J_{gem} = 11.2 Hz, H-1a), 4.37 (d, 1H, J_{gem} = 11.2 Hz, H-1b), 4.21–4.13 (m, 2H, H-3, H-4), 4.07 (dd, 1H, $J_{5a,4}$ = 7.6 Hz, J_{gem} = 8.2 Hz, H-5a), 3.83 (app t, 1H, $J_{5b,4}$ = J_{gem} = 8.2 Hz, H-5b), 1.32 (s, 9H, (CH_3)$_3$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 166.0 (C=O), 136.8 (Ar), 135.8 (Ar), 132.7 (Ar), 131.6 (Ar), 131.3 (Ar), 130.5 (Ar), 129.6 (2C, Ar), 129.5 (Ar), 129.4 (Ar), 128.3 (2C, Ar), 109.5 (C-2), 90.4 (C-3), 80.0 (C-4), 76.4 ((CH$_3$)$_3$*C*), 69.4 (Ar*C*H$_2$), 69.1 (Ar*C*H$_2$), 68.7 (C-5), 64.8 (C-1), 30.9 (3C, (*C*H$_3$)$_3$C); HRMS (ESI) calcd. for $C_{24}H_{28}NaO_6$ $[M+Na]^+$ 435.1778; found 435.1782. Data for **38β**: $[\alpha]^{25}_D$ +20.2 (*c* 1.2, $CHCl_3$); R_f 0.29 (4:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.86–7.81 (m, 2H, ArH), 7.57–7.52 (m, 1H, ArH), 7.41–7.28 (m, 5H, ArH), 7.26–7.23 (m, 1H, ArH), 5.08 (d, 1H, J_{gem} = 12.9 Hz, ArCH_2), 4.84 (d, 1H, J_{gem} = 12.9 Hz, ArCH_2), 4.81 (d, 1H, J_{gem} = 12.9 Hz, ArCH_2), 4.80 (d, 1H, J_{gem} = 12.9 Hz, ArCH_2), 4.79 (d, 1H, J_{gem} = 11.6 Hz, H-1a), 4.42 (ddd, 1H, $J_{4,3}$ = 5.8 Hz, $J_{4,5a}$ = 7.5 Hz, $J_{4,5b}$ = 4.3 Hz, H-4), 4.27 (d, 1H, J_{gem} = 11.6 Hz, H-1a), 4.25 (dd, 1H, $J_{5a,4}$ = 7.5 Hz, J_{gem} = 9.6 Hz, H-5a), 4.08 (d, 1H, $J_{3,4}$ = 5.8 Hz, H-3), 3.72 (dd, 1H, $J_{5b,4}$ = 4.3 Hz, J_{gem} = 9.6 Hz, H-5b), 1.37 (s, 9H, (CH_3)$_3$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 165.9 (C=O), 137.0 (Ar), 136.0 (Ar), 133.0 (Ar), 131.5 (Ar), 131.1 (Ar), 129.9 (Ar), 129.7 (2C, Ar), 129.3 (Ar), 129.2 (Ar), 128.4 (2C, Ar), 106.0 (C-2), 83.8 (C-3), 81.0 (C-4), 76.2 ((CH$_3$)$_3$*C*), 70.2 (C-5), 69.8 (Ar*C*H$_2$), 69.2 (Ar*C*H$_2$), 64.0 (C-1), 31.0 (3C, (*C*H$_3$)$_3$C); HRMS (ESI) calcd. for $C_{24}H_{28}NaO_6$ $[M+Na]^+$ 435.1780; found 435.1778.



1-*O*-benzoyl-3,4-*O*-xylylidene-α-D-*threo*-pent-2-ulofuranosyl-(2→6)-1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranose (39α) and **1-*O*-benzoyl-3,4-*O*-xylylidene-β-D-*threo*-pent-2-ulofuranosyl-(2→6)-1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranose (39β)**. A mixture of **8** (22.1 mg, 0.0478 mmol), **25** (14.9 mg, 0.0573 mmol), and 4Å molecular sieves in CH_2Cl_2 (1.91 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to –78 °C and *N*-iodosuccinimide (12.9 mg, 0.0573 mmol) and silver triflate (1.2 mg, 4.78 μmol) were added. After stirring for 1 h at –78 °C, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (10:1, hexane–EtOAc) to give **39α** (6.0 mg, 21%) and **39β** (21.6 mg, 76%) both as colorless oils. Data for **39α**: $[\alpha]^{25}_D$ +10.0 (*c* 0.6, $CHCl_3$); R_f 0.47 (2:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 8.00–7.95 (m, 2H, ArH), 7.56–7.51 (m, 1H, ArH), 7.43–7.31 (m, 5H, ArH), 7.26–7.23 (m, 1H, ArH), 5.49 (d, 1H, $J_{1,2}$ = 5.0 Hz, H-1), 4.95 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.85 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.76 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.73 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.54 (dd, 1H, $J_{3,2}$ = 2.5 Hz, $J_{3,4}$ = 8.0 Hz, H-3), 4.49 (d, 1H, J_{gem} = 11.8 Hz, H-1'a), 4.40 (d, 1H, J_{gem} = 11.8 Hz, H-1'b), 4.27 (dd, 1H, $J_{2,1}$ = 5.0 Hz, $J_{2,3}$ = 2.5 Hz, H-2), 4.24 (dd, 1H, $J_{4,3}$ = 8.0 Hz, $J_{4,5}$ = 2.0 Hz, H-4), 4.19–4.13 (m, 2H, H-3',

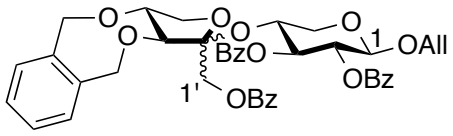
H-4'), 4.07 (dd, 1H, $J_{5',a,4}$ = 7.4 Hz, J_{gem} = 8.4 Hz, H-5'a), 3.88 (ddd, 1H, $J_{5,4}$ = 2.0 Hz, $J_{5,6a}$ = 7.0 Hz, $J_{5,6b}$ = 6.2 Hz, H-5), 3.77 (app t, 1H, $J_{5b,4}$ = J_{gem} = 8.4 Hz, H-5'b), 3.76 (dd, 1H, $J_{6a,5}$ = 7.0 Hz, J_{gem} = 9.7 Hz, H-6a), 3.72 (dd, 1H, $J_{6b,5}$ = 6.2 Hz, J_{gem} = 9.7 Hz, H-6b), 1.48 (s, 3H, (CH_3)$_2$C), 1.37 (s, 3H, (CH_3)$_2$C), 1.31 (s, 3H, (CH_3)$_2$C), 1.22 (s, 3H, (CH_3)$_2$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 166.1 (C=O), 136.6 (Ar), 135.7 (Ar), 132.8 (Ar), 131.7 (Ar), 131.5 (Ar), 130.5 (Ar), 129.8 (2C, Ar), 129.7 (Ar), 129.6 (Ar), 128.3 (2C, Ar), 109.2 ((CH$_3$)$_2$*C*), 108.6 ((CH$_3$)$_2$*C*), 108.2 (C-2'), 96.4 (C-1), 87.6 (C-3'), 81.1 (C-4'), 70.9 (C-2), 70.7 (C-4), 70.6 (C-3), 69.7 (Ar*C*H$_2$), 68.9 (Ar*C*H$_2$), 68.4 (C-5'), 66.9 (C-5), 62.2 (C-1'), 60.6 (C-6), 26.1 ((*C*H$_3$)$_2$C), 26.0 ((*C*H$_3$)$_2$C), 25.0 ((*C*H$_3$)$_2$C), 24.4 ((*C*H$_3$)$_2$C); HRMS (ESI) calcd. for $C_{32}H_{38}NaO_{11}$ $[M+Na]^+$ 621.2306; found 621.2307. Data for **39β**: $[\alpha]^{25}_D$ –22.4 (*c* 1.0, $CHCl_3$); R_f 0.27 (2:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.92–7.88 (m, 2H, ArH), 7.57–7.52 (m, 1H, ArH), 7.43–7.28 (m, 6H, ArH), 5.50 (d, 1H, $J_{1,2}$ = 5.0 Hz, H-1), 5.00 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.87 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.80 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.77 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.60 (d, 1H, J_{gem} = 11.8 Hz, H-1'a), 4.56 (dd, 1H, $J_{3,2}$ = 2.1 Hz, $J_{3,4}$ = 8.0 Hz, H-3), 4.40–4.35 (m, 2H, H-4', H-5'a), 4.33 (d, 1H, J_{gem} = 11.8 Hz, H-1'b), 4.27 (dd, 1H, $J_{2,1}$ = 5.0 Hz, $J_{2,3}$ = 2.1 Hz, H-2), 4.24 (dd, 1H, $J_{4,3}$ = 8.0 Hz, $J_{4,5}$ = 1.8 Hz, H-4), 4.14 (d, 1H, $J_{3',4'}$ = 4.4 Hz, H-3'), 4.04 (ddd, 1H, $J_{5,4}$ = 1.8 Hz, $J_{5,6a}$ = 7.8 Hz, $J_{5,6b}$ = 6.0 Hz, H-5), 3.87 (dd, 1H, $J_{6a,5}$ = 7.8 Hz, J_{gem} = 9.6 Hz, H-6a), 3.78–3.73 (m, 1H, H-5'b), 3.70 (dd, 1H, $J_{6b,5}$ = 6.0 Hz, J_{gem} = 9.6 Hz, H-6b), 1.51 (s, 3H, (CH_3)$_2$C), 1.42 (s, 3H, (CH_3)$_2$C), 1.31 (s, 3H, (CH_3)$_2$C), 1.29 (s, 3H, (CH_3)$_2$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 165.8 (C=O), 136.6 (Ar), 135.8 (Ar), 133.0 (Ar), 131.6 (Ar), 131.4 (Ar), 129.9 (Ar), 129.8 (2C, Ar), 129.5 (2C, Ar), 128.3 (2C, Ar), 109.0

(($CH_3)_2C$), 108.5 (($CH_3)_2C$), 105.2 (C-2'), 96.2 (C-1), 83.7 (C-3'), 80.9 (C-4'), 71.0 (C-5'), 70.8 (C-2), 70.7 (C-4), 70.6 (C-3), 69.6 (ArCH_2), 69.0 (ArCH_2), 66.4 (C-5), 62.6 (C-1'), 60.3 (C-6), 26.12 (($CH_3)_2C$), 26.06 (($CH_3)_2C$), 24.9 (($CH_3)_2C$), 24.5 (($CH_3)_2C$); HRMS (ESI) calcd. for $C_{32}H_{38}NaO_{11}$ $[M+Na]^+$ 621.2306; found 621.2304.



1-*O*-benzoyl-3,4-*O*-xylylidene-α-D-*threo*-pent-2-ulofuranosyl-(2→3)-1,2,5,6-di-*O*-isopropylidene-α-D-glucopyranose (40α) and **1-*O*-benzoyl-3,4-*O*-xylylidene-β-D-*threo*-pent-2-ulofuranosyl-(2→6)-1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranose (40β)**. A mixture of the **8** (23.7 mg, 0.0512 mmol), **26** (16.0 mg, 0.0615 mmol), and 4Å molecular sieves in CH_2Cl_2 (2.04 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to –78 °C and *N*-iodosuccinimide (13.8 mg, 0.0615 mmol) and silver triflate (1.3 mg, 5.12 μmol) were added. After stirring for 1 h at –78 °C, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (4:1, hexane–EtOAc) to give an inseparable mixture of **40α** and **40β** (23.0 mg, 75%, α/β = 1:5.9) as a colorless oil. R_f 0.30 (3:1, hexane–EtOAc). Data for major isomer, **40β**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.98–7.93 (m, 2H, ArH), 7.62–7.56 (m, 1H, ArH), 7.48–7.32 (m, 5H, ArH), 7.31–

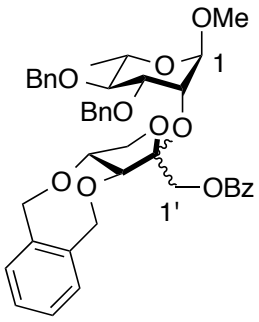
7.28 (m, 1H, ArH), 5.90 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 4.98 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.88 (d, 1H, J_{gem} = 12.5 Hz, ArCH_2), 4.78 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.77 (d, 1H, J_{gem} = 12.6 Hz, ArCH_2), 4.58 (d, 1H, $J_{2,1}$ = 3.8 Hz, H-2), 4.55 (d, 1H, J_{gem} = 11.6 Hz, H-1'a), 4.51 (dd, 1H, $J_{6a,5}$ = 8.1 Hz, J_{gem} = 9.5 Hz, H-6a), 4.43 (d, 1H, $J_{3,4}$ = 3.5 Hz, H-3), 4.41 (m, 1H, H-4'), 4.35–4.30 (m, 1H, H-5), 4.29 (d, 1H, J_{gem} = 11.6 Hz, H-1'b), 4.19 (dd, 1H, $J_{4,3}$ = 3.5 Hz, $J_{4,5}$ = 7.0 Hz, H-4), 4.17 (d, 1H, $J_{3',4'}$ = 5.6 Hz, H-3'), 4.08 (dd, 1H, $J_{5'b,4'}$ = 8.4 Hz, J_{gem} = 6.3 Hz, H-5'a), 4.00 (dd, 1H, $J_{5'b,4'}$ = 8.4 Hz, J_{gem} = 6.3 Hz, H-5'b), 3.74 (dd, 1H, $J_{6b,5}$ = 4.9 Hz, J_{gem} = 9.5 Hz, H-6b), 1.48 (s, 3H, (CH_3)$_2$C), 1.42 (s, 3H, (CH_3)$_2$C), 1.28 (s, 3H, (CH_3)$_2$C), 1.27 (s, 3H, (CH_3)$_2$C); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 165.8 (C=O), 136.4 (Ar) 135.7 (Ar), 133.2 (Ar), 131.5 (Ar), 131.3 (Ar), 129.8 (2C, Ar), 129.59 (Ar), 129.58 (Ar), 128.4 (2C, Ar), 111.6 ((CH$_3$)$_2$*C*), 109.0 ((CH$_3$)$_2$*C*), 105.9 (C-2'), 105.0 (C-1), 84.8 (C-2), 83.9 (C-3'), 81.2 (C-4), 80.6 (C-4'), 74.8 (C-3), 72.3 (C-5), 70.9 (C-6), 69.3 (Ar*C*H$_2$), 69.1 (Ar*C*H$_2$), 67.3 (C-5'), 64.4 (C-1'), 26.8 ((*C*H$_3$)$_2$C), 26.7 ((*C*H$_3$)$_2$C), 26.3 ((*C*H$_3$)$_2$C), 25.5 ((*C*H$_3$)$_2$C); HRMS (ESI) calcd. for $C_{32}H_{38}NaO_{11}$ $[M+Na]^+$ 621.2306; found 621.2304.



Allyl 1-*O*-benzoyl-3,4-*O*-xylylidene-α-D-*threo*-pent-2-ulofuranosyl-(2→4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside (41α) and **Allyl 1-*O*-benzoyl-3,4-*O*-xylylidene-β-D-*threo*-pent-2-ulofuranosyl-(2→4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside (41β)**. A mixture of **8** (65.0 mg, 0.140 mmol), **27** (46.7 mg, 0.117 mmol), and 4Å molecular sieves in CH_2Cl_2 (3.9 mL) was stirred under an Ar atmosphere at room temperature for

30 min. The mixture was then cooled to –78 °C and *N*-iodosuccinimide (38.0 mg, 0.169 mmol) and silver triflate (3.6 mg, 14.0 μmol) were added. After stirring for 30 min at –78 °C, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (4:1, hexane–EtOAc) to give an inseparable mixture of **41α** and **41β** (76.0 mg, 88%, α/β = 1:10.1) as a colorless oil. R_f 0.42 (2:1, hexane–EtOAc). Data for major isomer, **41β**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.98–7.87 (m, 6H, ArH), 7.58–7.45 (m, 3H, ArH), 7.44–7.27 (m, 8H, ArH), 7.25–7.21 (m, 1H, ArH), 7.14–7.10 (m, 1H, ArH), 5.89–5.76 (m, 1H, $OCH_2CH{=}CH_2$), 5.67 (app t, 1H, $J_{3,2} = J_{3,4}$ = 8.4 Hz, H-3), 5.35 (dd, 1H, $J_{2,1}$ = 7.0 Hz, $J_{2,3}$ = 8.4 Hz, H-2), 5.24 (dq, 1H, J = 17.3, 1.6 Hz, $OCH_2CH{=}CH_2$), 5.13 (dq, 1H, J = 10.4, 1.6 Hz, $OCH_2CH{=}CH_2$), 4.83 (d, 1H, J_{gem} = 12.8 Hz, $ArCH_2$), 4.72 (d, 1H, $J_{1,2}$ = 7.0 Hz, H-1), 4.67 (d, 1H, J_{gem} = 12.8 Hz, $ArCH_2$), 4.62 (d, 1H, J_{gem} = 12.8 Hz, $ArCH_2$), 4.55 (d, 1H, J_{gem} = 12.8 Hz, $ArCH_2$), 4.45 (d, 1H, J_{gem} = 11.8 Hz, H-1'a), 4.31 (ddt, 1H, J = 13.3, 5.0, 1.6 Hz, $OCH_2CH{=}CH_2$), 4.27–4.19 (m, 3H, H-4, H-5a, H-1'b), 4.15–4.01 (m, 4H, H-5'a, H-3', H-4', $OCH_2CH{=}CH_2$), 3.63 (dd, 1H, $J_{5b,4}$ = 8.5 Hz, J_{gem} = 11.5 Hz, H-5b), 3.51 (dd, 1H, $J_{5',b,4'}$ = 4.9 Hz, J_{gem} = 9.5 Hz, H-5'b); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 165.7 (C=O), 165.4 (C=O), 165.3 (C=O), 136.5 (Ar),135.5 (Ar), 133.6 ($OCH_2CH{=}CH_2$), 133.20 (Ar), 133.18 (Ar), 131.4 (Ar), 131.3 (Ar), 129.83 (2C, Ar), 129.76 (2C, Ar), 129.70 (2C, Ar), 129.62, (Ar), 129.58 (Ar), 129.5 (Ar), 129.44 (Ar), 129.40 (Ar), 128.45 (2C, Ar), 128.43 (2C, Ar), 128.3 (2C, Ar), 117.5 ($OCH_2CH{=}CH_2$), 105.6 (C-2'), 99.8 (C-1), 83.3 (C-3'), 80.4 (C-4'),

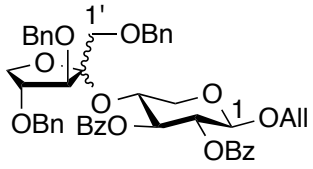
72.8 (C-3), 71.6 (C-2), 70.5 (C-5'), 69.7 (O*C*H$_2$CH=CH$_2$), 69.18 (Ar*C*H$_2$), 69.14 (Ar*C*H$_2$), 68.1 (C-4), 64.9 (C-5), 64.0 (C-1'); HRMS (ESI) calcd. for $C_{42}H_{40}NaO_{12}$ $[M+Na]^+$ 759.2412; found 759.2403.



Methyl 1-*O*-benzoyl-3,4-*O*-xylylidene-α-D-*threo*-pent-2-ulofuranosyl-(2→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (42α) and **Methyl 1-*O*-benzoyl-3,4-*O*-xylylidene-β-D-*threo*-pent-2-ulofuranosyl-(2→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (42β)**. A mixture of **8** (24.0 mg, 0.0519 mmol), **28**[3] (15.5 mg, 0.0432 mmol), and 4Å molecular sieves in CH_2Cl_2 (1.50 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to –78 °C and *N*-iodosuccinimide (14.0 mg, 0.0623 mmol) and silver triflate (1.3 mg, 5.19 μmol) were added. After stirring for 2 h at –78 °C, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (4:1, hexane–EtOAc) to give **42α** (9.0 mg, 30%) as a colorless oil and **42β** (15.8 mg, 52%) as a colorless oil. Data for **42α**: $[\alpha]^{25}_D$ +28.8 (*c* 0.2, $CHCl_3$); R_f 0.58 (2:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.95–7.91 (m, 2H, ArH), 7.57–7.52 (m, 1H, ArH), 7.41–7.21 (m, 16H, ArH), 4.97

(d, 1H, J_{gem} = 11.2 Hz, ArCH_2), 4.90 (d, 1H, J_{gem} = 12.5 Hz, ArCH_2), 4.74 (d, 1H, J_{gem} = 12.5 Hz, ArCH_2), 4.72 (d, 1H, J_{gem} = 11.9 Hz, ArCH_2), 4.70 (d, 1H, J_{gem} = 12.5 Hz, ArCH_2), 4.66 (d, 1H, J_{gem} = 11.2 Hz, ArCH_2), 4.65 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 4.61 (d, 1H, J_{gem} = 12.5 Hz, ArCH_2), 4.59 (d, 1H, J_{gem} = 11.9 Hz, ArCH_2), 4.56 (d, 1H, J_{gem} = 11.7 Hz, H-1'a), 4.32 (dd, 1H, $J_{2,1}$ = 1.8 Hz, $J_{2,3}$ = 3.2 Hz, H-2), 4.35 (d, 1H, J_{gem} = 11.7 Hz, H-1'b), 4.30 (d, 1H, $J_{3',4'}$ = 5.6 Hz, H-3'), 4.10–4.04 (m, 1H, H-4'), 4.00 (app t, 1H, $J_{5'a,4'}$ = J_{gem} = 8.8 Hz, H-5'a), 3.90 (app t, 1H, $J_{5'b,4}$ = J_{gem} = 8.8 Hz, H-5'b), 3.82 (dd, 1H, $J_{3,2}$ = 3.2 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 3.66 (dq, 1H, $J_{5,4}$ = 9.5 Hz, $J_{5,6}$ = 6.3 Hz, H-5), 3.53 (app t, 1H, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, H-4), 3.23 (s, 3H, OCH_3), 1.32 (d, 3H, $J_{6,5}$ = 6.3 Hz, H-6); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 166.0 (C=O), 138.71 (Ar), 138.68 (Ar), 137.1 (Ar), 135.4 (Ar), 132.9 (Ar), 131.6 (Ar), 131.4 (Ar), 130.2 (Ar), 129.7 (2C, Ar), 129.6 (Ar), 129.4 (Ar), 128.4 (3C, Ar), 128.3 (2C, Ar), 128.1 (2C, Ar), 127.7 (2C, Ar), 127.6 (Ar), 127.4 (Ar), 108.8 (C-2'), 100.9 (C-1, $J_{C1,H1}$ = 171.6 Hz), 88.5 (C-3'), 79.9 (C-4'), 79.7 (C-4), 78.9 (C-3), 75.1 (ArCH$_2$), 72.1 (ArCH$_2$), 69.7 (C-2), 69.3 (ArCH$_2$), 69.04 (ArCH$_2$), 69.03 (C-5'), 68.0 (C-5), 64.5 (C-1'), 54.6 (OCH$_3$), 18.0 (C-6); HRMS (ESI) calcd. for $C_{41}H_{44}NaO_{10}$ $[M+Na]^+$ 719.2827; found 719.2830. Data for **42β**: $[\alpha]^{25}_D$ –2.9 (*c* 0.2, $CHCl_3$); R_f 0.40 (2:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.91–7.85 (m, 2H, ArH), 7.55–7.50 (m, 1H, ArH), 7.41–7.22 (m, 16H, ArH), 5.08 (d, 1H, J_{gem} = 12.8 Hz, ArCH_2), 4.89–4.80 (m, 4H, ArCH_2), 4.76 (d, 1H, J_{gem} = 11.4 Hz, ArCH_2), 4.69–4.64 (m, 2H, H-1, H-1'a), 4.60 (d, 1H, J_{gem} = 11.4 Hz, ArCH_2), 4.59 (d, 1H, J_{gem} = 11.4 Hz, ArCH_2), 4.51 (ddd, 1H, $J_{4',3'}$ = 6.4 Hz, $J_{4'5'a}$ = 7.9 Hz, $J_{4',5'b}$ = 5.5 Hz, H-4'), 4.28 (d, 1H, J_{gem} = 11.9 Hz, H-1'b), 4.24 (d, 1H, $J_{5'a,4'}$ = 7.9 Hz, J_{gem} = 9.6 Hz, H-5'a), 4.18–4.14 (m, 2H, H-2, H-3'), 3.84 (dd, 1H, $J_{3,2}$ = 2.9 Hz, $J_{3,4}$ = 9.4 Hz, H-

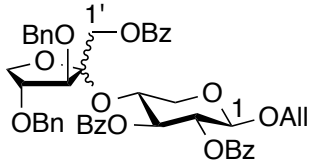
3), 3.74 (dd, 1H, $J_{5'b,4'}$ = 5.5 Hz, J_{gem} = 9.6 Hz, H-5'b), 3.65 (app dq, 1H, $J_{5,4}$ = 9.4 Hz, $J_{5,6}$ = 6.2 Hz, H-5), 3.53 (app t, 1H, $J_{4.3}$ = $J_{4.5}$ = 9.4 Hz, H-4), 3.29 (s, 3H, OCH_3), 1.27 (d, 3H, $J_{6,5}$ = 6.2 Hz, H-6); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 165.8 (C=O), 138.7 (Ar), 138.4 (Ar), 136.7 (Ar), 136.2 (Ar), 132.9 (Ar), 131.4 (Ar), 131.2 (Ar), 129.9 (Ar), 129.7 (2C, Ar), 129.4 (Ar), 129.2 (Ar), 129.0 (2C, Ar), 128.29 (2C, Ar), 128.28 (2C, Ar), 128.1 (2C, Ar), 128.0 (2C, Ar), 127.54 (Ar), 127.47 (Ar), 105.9 (C-2'), 100.2 (C-1, $J_{C1,H1}$ = 172.1 Hz), 82.9 (C-3'), 80.2 (C-4), 80.0 (C-4'), 78.6 (C-3), 74.9 (Ar*C*H_2), 72.6 (Ar*C*H_2), 70.5 (C-5'), 70.0 (C-2), 69.5 (Ar*C*H_2), 69.2 (Ar*C*H_2), 68.0 (C-5), 62.8 (C-1'), 54.7 (O*C*H_3), 18.1 (C-6); HRMS (ESI) calcd. for $C_{41}H_{44}NaO_{10}$ $[M+Na]^+$ 719.2827; found 719.2831.



Allyl 1,3,4-tri-*O*-benzyl-α-D-*threo*-pent-2-ulofuranosyl-(2→4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside (45α) and **Allyl 1,3,4-tri-*O*-benzyl-α-D-*threo*-pent-2-ulofuranosyl-(2→4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside (45β)**. A mixture of the **9** (28.0 mg, 0.0530 mmol), **27** (17.7 mg, 0.0440 mmol), and 4Å molecular sieves in CH_2Cl_2 (1.50 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to –78 °C and *N*-iodosuccinimide (14.3 mg, 0.0636 mmol) and silver triflate (1.4 mg, 5.3 μmol) were added. After stirring for 1 h at –78 °C, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was

concentrated under reduced pressure. The resulting residue was purified by column chromatography (4:1, hexane–EtOAc) to give **45α** (18.9 mg, 53%) as a colorless oil and **45β** (11.8 mg, 33%) as a colorless oil. Data for **45α**: $[\alpha]^{25}_{D}$ +6.6 (*c* 1.0, $CHCl_3$); R_f 0.32 (4:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.99–7.96 (m, 2H, ArH), 7.94–7.91 (m, 2H, ArH), 7.51–7.43 (m, 2H, ArH), 7.37–7.31 (m, 4H, ArH), 7.30–7.26 (m, 5H, ArH), 7.25–7.23 (m, 3H, ArH), 7.22–7.19 (m, 3H, ArH), 7.13–7.08 (m, 4H, ArH), 5.82 (m, 1H, OCH_2CH=CH_2), 5.59 (dd, 1H, $J_{3,2}$ = 8.7 Hz, $J_{3,4}$ = 7.9 Hz, H-3), 5.33 (dd, 1H, $J_{2,1}$ = 6.7 Hz, $J_{2,3}$ = 8.7 Hz, H-2), 5.25 (dq, 1H, *J* = 17.2, 1.6 Hz, OCH_2CH=CH_2), 5.14 (dq, 1H, *J* = 10.4, 1.6 Hz, OCH_2CH=CH_2), 4.70 (d, 1H, $J_{1,2}$ = 6.7 Hz, H-1), 4.54 (d, 1H, J_{gem} = 12.1 Hz, $ArCH_2$), 4.43 (d, 1H, J_{gem} = 12.1 Hz, $ArCH_2$), 4.39 (d, 1H, J_{gem} = 12.1 Hz, $ArCH_2$), 4.36 (d, 1H, J_{gem} = 12.1 Hz, $ArCH_2$), 4.31 (ddt, 1H, *J* = 13.2, 4.9, 1.6 Hz, OCH_2CH=CH_2), 4.27–4.21 (m, 2H, H-4, H-5a), 4.20 (s, 2H, $ArCH_2$), 4.13–4.03 (m, 4H, H-3', H-4', H-5'a, OCH_2CH=CH_2), 3.78 (dd, 1H, $J_{5'b,4'}$ = 9.0 Hz, J_{gem} = 11.7 Hz, H-5'b), 3.51 (s, 2H, H-1'), 3.43 (dd, 1H, $J_{5b,4}$ = 9.9 Hz, J_{gem} = 13.3 Hz, H-5b); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 165.6 (C=O), 165.3 (C=O), 138.8 (Ar), 137.9 (Ar), 137.8 (Ar), 133.7 (OCH_2CH=CH_2), 133.01 (Ar), 132.98 (Ar), 129.9 (2C, Ar), 129.83 (2C, Ar), 129.77 (Ar), 129.7 (Ar), 128.4 (Ar), 128.30 (Ar), 128.29 (Ar), 128.2 (Ar), 127.80 (Ar), 127.77 (Ar), 127.75 (Ar), 127.65 (Ar), 127.5 (Ar), 117.47 (OCH_2CH=CH_2), 108.8 (C-2'), 99.7 (C-1), 88.4 (C-3'), 81.9 (C-4'), 73.4 ($ArCH_2$), 72.8 (C-3), 72.6 ($ArCH_2$), 72.0 (C-2), 71.4 ($ArCH_2$), 70.2 (C-1'), 69.6 (C-5'), 68.9 (OCH_2CH=CH_2), 68.3 (C-4), 64.9 (C-5); HRMS (ESI) calcd. for $C_{48}H_{48}NaO_{11}$ $[M+Na]^+$ 823.3089; found 823.3103. Data for **45β**: $[\alpha]^{25}_{D}$ –18.1 (*c* 1.0, $CHCl_3$); R_f 0.27 (4:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 8.01–7.93 (m, 4H, ArH), 7.51–

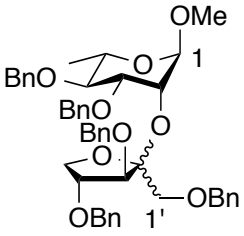
7.44 (m, 2H, ArH), 7.38–7.22 (m, 17H, ArH), 7.11–7.06 (m, 2H, ArH), 5.80 (m, 1H, OCH_2CH=CH_2), 5.62 (app t, 1H, $J_{3,2} = J_{3,4}$ = 8.7 Hz, H-3), 5.34 (dd, 1H, $J_{2,1}$ = 7.0 Hz, $J_{2,3}$ = 8.7 Hz, H-2), 5.24 (dq, 1H, J = 17.3, 1.7 Hz, OCH_2CH=CH_2), 5.13 (dq, 1H, J = 10.4, 1.7 Hz, OCH_2CH=CH_2), 4.70 (d, 1H, $J_{1,2}$ = 7.0 Hz, H-1), 4.69 (d, 1H, J_{gem} = 12.4 Hz, ArCH_2), 4.54 (d, 1H, J_{gem} = 12.4 Hz, ArCH_2), 4.48 (d, 1H, J_{gem} = 12.4 Hz, ArCH_2), 4.47 (d, 1H, J_{gem} = 12.4 Hz, ArCH_2), 4.31 (ddt, 1H, J = 13.3, 5.0, 1.7 Hz, OCH_2CH=CH_2), 4.29–4.24 (m, 1H, H-4), 4.15–4.08 (m, 3H, H-5a, OCH_2CH=CH_2, ArCH_2), 4.07 (d, 1H, $J_{3',4'}$ = 5.7 Hz, H-3'), 4.05–3.98 (m, 2H, H-4', ArCH_2), 3.78 (dd, 1H, $J_{5'a,4'}$ = 6.5 Hz, J_{gem} = 9.2 Hz, H-5'a), 3.53 (d, 1H, J_{gem} = 10.7 Hz, H-1'a), 3.51 (dd, 1H, $J_{5b,4}$ = 12.2 Hz, J_{gem} = 13.7 Hz, H-5b), 3.44 (dd, 1H, $J_{5'b,4'}$ = 5.4 Hz, J_{gem} = 9.2 Hz, H-5'b), 3.40 (d, 1H, J_{gem} = 10.7 Hz, H-1'b); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 165.5 (C=O), 165.4 (C=O), 138.5 (Ar), 137.9 (Ar), 137.5 (Ar), 133.6 (OCH_2CH=CH_2), 133.11 (Ar), 133.06 (Ar), 129.9 (Ar), 129.8 (Ar), 129.6 (Ar), 128.5 (Ar), 128.43 (Ar), 128.39 (Ar), 128.34 (Ar), 128.31 (Ar), 128.2 (Ar), 127.9 (Ar), 127.84 (Ar), 127.82 (Ar), 127.8 (Ar), 127.75 (Ar), 127.7 (Ar), 127.65 (Ar), 127.5 (Ar), 127.5 (Ar), 117.5 (OCH_2CH=CH_2), 105.2 (C-2'), 99.96 (C-1), 83.8 (C-3'), 82.4 (C-4'), 73.6 (ArCH_2), 73.2 (C-3), 72.4 (ArCH_2), 72.0 (ArCH_2), 71.8 (C-2), 70.5 (C-1'), 69.8 (C-5'), 69.4 (OCH_2CH=CH_2), 68.0 (C-4), 65.2 (C-5); HRMS (ESI) calcd. for $C_{48}H_{48}NaO_{11}$ $[M+Na]^+$ 823.3089; found 823.3100.



Allyl 1-*O*-benzoyl-3,4-di-*O*-benzyl-α-D-*threo*-pent-2-ulofuranosyl-(2→4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside (46α) and **Allyl 1-*O*-benzoyl-3,4-di-*O*-benzyl-β-D-*threo*-pent-2-ulofuranosyl-(2→4)-2,3-di-*O*-benzoyl-β-D-xylopyranoside (46β)**. A mixture of **10** (45.1 mg, 0.0830 mmol), **27** (27.7 mg, 0.070 mmol), and 4Å molecular sieves in CH_2Cl_2 (2.3 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to –78 °C and *N*-iodosuccinimide (22.8 mg, 0.0996 mmol) and silver triflate (4.3 mg, 16.6 μmol) were added. After stirring for 1.5 h at –78 °C, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (4:1, hexane–EtOAc) to give an inseparable mixture of **46α** and **46β** (50.2 mg, 88%, α/β = 1:1.4) as a colorless oil. R_f 0.31 (4:1, hexane–EtOAc). ^{1}H NMR ($CDCl_3$, 700 MHz) δ_H 8.02–7.99 (m, 2H, ArH), 7.99–7.96 (m, 2H, ArH), 7.93–7.87 (m, 4H, ArH), 7.72–7.69 (m, 2H, ArH), 7.66–7.63 (m, 2H, ArH), 7.57–7.54 (m, 1H, ArH), 7.52–7.43 (m, 4H, ArH), 7.41–7.23 (m, 21H, ArH), 7.22–7.19 (m, 2H, ArH), 7.18–7.09 (m, 6H, ArH), 7.09–7.05 (m, 2H, ArH), 7.03–7.00 (m, 2H, ArH), 5.84–5.75 (m, 2H, OCH_2CH=CH_2(α), OCH_2CH=CH_2(β)), 5.67 (app t, 1H, $J_{3,2}$ = 8.5 Hz, $J_{3,4}$ = 8.5 Hz, H-3(β)), 5.63 (app t, 1H, $J_{3,2}$ = $J_{3,4}$ = 9.1 Hz, H-3(α)), 5.37 (dd, 1H, $J_{2,1}$ = 6.8 Hz, $J_{2,3}$ = 8.5 Hz, H-2(β)), 5.31 (dd, 1H, $J_{2,1}$ = 7.3 Hz, $J_{2,3}$ = 9.1 Hz, H-2(α)),

5.27–5.20 (m, 2H, $OCH_2CH=CH_2$(α), $OCH_2CH=CH_2$(β)), 5.15–5.10 (m, 2H, $OCH_2CH=CH_2$(α), $OCH_2C=CH_2$(β)), 4.74 (d, 1H, $J_{1,2}$ = 6.8 Hz, H-1(β)), 4.69 (d, 1H, J_{gem} = 12.1 Hz, $ArCH_2$(β)), 4.64 (d, 1H, $J_{1,2}$ = 7.3 Hz, H-1(α)), 4.61 (d, 1H, J_{gem} = 12.1 Hz, $ArCH_2$(β)), 4.55 (d, 1H, J_{gem} = 12.1 Hz, $ArCH_2$(α)), 4.52 (d, 1H, J_{gem} = 12.1 Hz, H-1'a(α)), 4.43–4.39 (m, 2H, $ArCH_2$(α), H-1(β)), 4.37–4.27 (m, 6H, $OCH_2CH=CH_2$(α), $OCH_2CH=CH_2$(β), H-4(α), H-4(β), $ArCH_2$(α), $ArCH_2$(β)), 4.24–4.17 (m, 5H, H-1'b(α), H-1'b(β), H-5a(α), H-5b(β), H-5'a(β)), 4.15–4.07 (m, 6H, H-3'(α), H-3'(β), H-4'(α), $OCH_2CH=CH_2$(α), $OCH_2CH=CH_2$(β), $ArCH_2$(β)), 4.06–4.03 (m, 1H, H-4'(β)), 4.01–3.98 (m, 2H, H-5'b(α), $ArCH_2$(α)), 3.90 (dd, 1H, $J_{5'a,4'}$ = 6.3 Hz, J_{gem} = 8.0 Hz, H-5'a (β)), 3.61 (dd, 1H, $J_{5b,4}$ = 8.8 Hz, J_{gem} = 11.9 Hz, H-5b(β)), 3.51 (dd, 1H, J = 5.3, 8.8 Hz, H-5'b (β)), 3.41 (dd, 1H, $J_{5b,4}$ = 9.0 Hz, J_{gem} = 11.8 Hz, H-5b(α)); ^{13}C NMR ($CDCl_3$, 175 MHz) δ_C 165.7 (C=O), 165.5 (C=O), 165.4 (C=O), 165.3 (C=O), 165.28 (C=O), 165.2 (C=O), 137.9 (Ar), 137.69 (Ar), 137.67 (Ar), 136.9 (Ar), 133.66 ($OCH_2CH=CH_2$), 133.65 ($OCH_2CH=CH_2$), 133.25 (Ar), 133.22 (Ar), 133.1 (Ar), 133.0 (Ar), 132.9 (Ar), 132.7 (Ar), 129.89 (Ar), 129.86 (Ar), 129.8 (Ar), 129.7 (Ar), 129.6 (Ar), 129.57 (Ar), 129.5 (Ar), 129.45 (Ar), 128.8 (Ar), 128.5 (Ar), 128.44 (Ar), 128.4 (Ar), 128.31 (Ar), 128.28 (Ar), 128.24 (Ar), 128.0 (Ar), 127.97 (Ar), 127.89 (Ar), 127.85 (Ar), 127.8 (Ar), 127.79 (Ar), 127.7 (Ar), 127.5 (Ar), 117.51 ($OCH_2CH=CH_2$), 118.43 ($OCH_2CH=CH_2$), 108.9 (C-2'(α)), 104.2 (C-2'(β)), 100.1 (C-1(α)), 99.8 (C-1(β)), 86.5 (C-3'(α)), 83.0 (C-4'(α)), 82.1 (C-3'(β), 81.3 (C-4'(β)), 73.0 ($ArCH_2$), 72.9 (H-3(α)), 72.87 (H-3(β)), 72.79 ($ArCH_2$), 72.5 ($ArCH_2$) 72.3 (H-5'(α)), 72.1 (H-2(α)), 71.7 ($ArCH_2$), 71.6 (H-2(β)), 69.7(H-5'(β)), 69.68 ($OCH_2CH=CH_2$), 69.66 ($OCH_2CH=CH_2$), 68.7 (H-4(α)), 67.9 (H-4(β)), 65.5 (H-5(α)), 64.9 (H-5(β)), 63.8 (H-

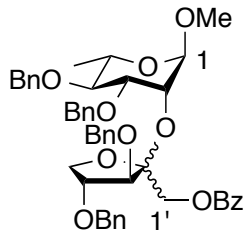
1'(β)), 62.3 (H-1'(α)); HRMS (ESI) calcd. for $C_{29}H_{36}NaO_5Si$ $[M+H]^+$ 837.2887; found 837.2884.



Methyl 1,3,4-tri-*O*-benzyl-α-D-*threo*-pent-2-ulofuranosyl-(2→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (47α) and **Methyl 1,3,4-tri-*O*-benzyl-β-D-*threo*-pent-2-ulofuranosyl-(2→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (47β)**. A mixture of **9** (30.9 mg, 0.0586 mmol), **28**[3] (17.5 mg, 0.0488 mmol), and 4Å molecular sieves in CH_2Cl_2 (1.63 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to –78 °C and *N*-iodosuccinimide (15.8 mg, 0.0703 mmol) and silver triflate (1.5 mg, 5.86 μmol) were added. After stirring for 1 h at –78 °C, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (10:1, hexane–EtOAc) to give **47α** (18.2 mg, 49%) as a colorless oil and **47β** (9.5 mg, 26%) as a colorless oil. Data for **47α**: $[\alpha]^{25}_D$ +21.9 (*c* 0.2, $CHCl_3$); R_f 0.26 (4:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.40–7.24 (m, 25H, ArH), 4.87 (d, 1H, J_{gem} = 11.6 Hz, ArCH_2), 4.81 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 4.78 (d, 1H, J_{gem} = 11.6 Hz, ArCH_2), 4.69 (d, 1H, J_{gem} = 12.0 Hz, ArCH_2), 4.65–4.56 (m, 3H, ArCH_2), 4.55 (d, 1H, J_{gem} = 12.0 Hz, ArCH_2), 4.53 (d, 1H, J_{gem} = 12.0 Hz, ArCH_2), 4.46 (d, 1H,

J_{gem} = 11.6 Hz, ArCH_2), 4.42 (d, 1H, J_{gem} = 12.0 Hz, ArCH_2), 4.35 (dd, 1H, $J_{2,1}$ = 1.7 Hz, $J_{2,3}$ = 3.1 Hz, H-2), 4.25 (d, 1H, $J_{3',4'}$ = 3.7 Hz, H-3'), 4.16–4.09 (m, 2H, H-4', H-5'a), 4.02–3.95 (m, 1H, H-5'b), 3.83 (dd, 1H, $J_{3,2}$ = 3.1 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 3.74 (d, 1H, J_{gem} = 10.8 Hz, H-1'a), 3.68 (d, 1H, J_{gem} = 10.8 Hz, H-1'b), 3.67–3.63 (m, 1H, H-5), 3.55 (app t, 1H, $J_{4,3}$ = $J_{4,5}$ = 9.4 Hz, H-4), 3.28 (s, 3H, OCH_3), 1.32 (d, 3H, $J_{6,5}$ = 6.3 Hz, H-6); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.9 (Ar), 138.8 (Ar), 138.4 (Ar), 138.2 (Ar), 138.0 (Ar), 128.4 (3C, Ar), 128.34 (2C, Ar), 128.29 (2C, Ar), 128.2 (2C, Ar), 127.96 (2C, Ar), 127.93 (2C, Ar), 127.92 (2C, Ar), 127.70 (2C, Ar), 127.69 (2C, Ar), 127.67 (Ar), 127.6 (Ar), 127.5 (Ar), 127.3 (Ar), 108.5 (C-2'), 100.9 (C-1, $J_{C1,H1}$ = 172.8 Hz), 88.2 (C-3'), 82.5 (C-4'), 80.1 (C-4), 79.5 (C-3), 75.2 (Ar*C*H$_2$), 73.9 (Ar*C*H$_2$), 72.6 (Ar*C*H$_2$), 72.0 (Ar*C*H$_2$), 71.9 (Ar*C*H$_2$), 70.0 (C-5'), 69.3 (C-1'), 68.9 (C-2), 68.1 (C-5), 54.5 (O*C*H$_3$), 18.1 (C-6); HRMS (ESI) calcd. for $C_{47}H_{52}NaO_9$ $[M+Na]^+$ 783.3504; found 783.3501. Data for **47β**: $[\alpha]^{25}_D$ –4.7 (*c* 0.3, $CHCl_3$); R_f 0.20 (4:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.36–7.20 (m, 25H, ArH), 4.79 (d, 1H, J_{gem} = 11.5 Hz, ArCH_2), 4.77 (d, 1H, J_{gem} = 10.6 Hz, ArCH_2), 4.72 (d, 1H, $J_{1,2}$ = 1.9 Hz, H-1), 4.65 (d, 1H, J_{gem} = 11.6 Hz, ArCH_2), 4.62 (d, 1H, J_{gem} = 11.6 Hz, ArCH_2), 4.61 (d, 1H, J_{gem} = 11.7 Hz, ArCH_2), 4.53 (d, 1H, J_{gem} = 11.7 Hz, ArCH_2), 4.48 (d, 1H, J_{gem} = 11.5 Hz, ArCH_2), 4.47 (d, 1H, J_{gem} = 12.4 Hz, ArCH_2), 4.44 (d, 1H, J_{gem} = 10.6 Hz, ArCH_2), 4.39–4.34 (m, 2H, H-4', ArCH_2), 4.32 (d, 1H, $J_{3',4'}$ = 5.0 Hz, H-3'), 4.24 (dd, 1H, $J_{2,1}$ = 1.9 Hz, $J_{2,3}$ = 3.0 Hz, H-2), 4.16 (dd, 1H, $J_{5'a,4'}$ = 6.4 Hz, J_{gem} = 9.4 Hz, H-5'a), 3.83 (dd, 1H, $J_{5'b,4'}$ = 7.0 Hz, J_{gem} = 9.4 Hz, H-5'b), 3.81 (dd, 1H, $J_{3,2}$ = 3.0 Hz, $J_{3,4}$ = 9.3 Hz, H-3), 3.69 (d, 1H, J_{gem} = 10.8 Hz, H-1'a), 3.66 (d, 1H, J_{gem} = 10.8 Hz, H-1'b), 3.66–3.61 (m, 1H, H-5), 3.52 (app t, 1H, $J_{4,3}$ = $J_{4,5}$ = 9.3 Hz, H-4), 3.31 (s, 3H, O*C*H$_3$), 1.28

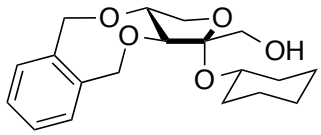
(d, 3H, $J_{6,5}$ = 6.3 Hz, H-6); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 139.0 (Ar), 138.7 (Ar), 138.2 (Ar), 137.9 (Ar), 128.42 (2C, Ar), 128.37 (2C, Ar), 128.35 (2C, Ar), 128.31 (2C, Ar), 128.2 (2C, Ar), 127.89 (2C, Ar), 127.86 (2C, Ar), 127.8 (2C, Ar), 127.71 (Ar), 127.68 (Ar), 127.61 (2C, Ar), 127.55 (Ar), 127.53 (2C, Ar), 127.4 (Ar), 127.3 (Ar), 105.9 (C-2'), 100.3 (C-1, $J_{C1,H1}$ = 171.4 Hz), 84.3 (C-3'), 82.9 (C-4'), 80.6 (C-4), 79.1 (C-3), 75.2 (Ar*C*H$_2$), 73.5 (Ar*C*H$_2$), 72.4 (Ar*C*H$_2$), 71.9 (Ar*C*H$_2$), 71.8 (Ar*C*H$_2$), 70.4 (C-1'), 69.8 (C-2), 69.7 (C-5'), 68.0 (C-5), 54.7 (O*C*H$_3$), 18.0 (C-6); HRMS (ESI) calcd. for $C_{47}H_{52}NaO_9$ $[M+Na]^+$ 783.3504; found 783.3505.



Methyl 1-*O*-benzoyl-3,4-di-*O*-benzyl-α-D-*threo*-pent-2-ulofuranosyl-(2→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (48α) and **Methyl 1-*O*-benzoyl-3,4-di-*O*-benzyl-β-D-*threo*-pent-2-ulofuranosyl-(2→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (48β)**. A mixture of **10** (36.2 mg, 0.0669 mmol), **28**[3] (20.0 mg, 0.0558 mmol), and 4Å molecular sieves in CH_2Cl_2 (1.86 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to –78 ºC and *N*-iodosuccinimide (18.1 mg, 0.0803 mmol) and silver triflate (1.7 mg, 6.69 μmol) were added. After stirring for 2 h at –78 ºC, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting

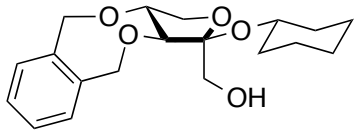
residue was purified by column chromatography (4:1, hexane–EtOAc) to give an inseparable mixture of **48α** and **48β** (34.0 mg, 78%, α/β = 2.4:1) as a colorless oil; R_f 0.28 (4:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 8.09–8.05 (m, 2H, ArH(α)), 8.03–7.99 (m, 2H, ArH(β)), 7.60–7.56 (m, 1H, ArH(α)), 7.56–7.51 (m, 1H, ArH(β)), 7.47–7.42 (m, 3H, ArH), 7.40–7.20 (m, 41H, ArH), 4.94 (d, 1H, J_{gem} = 11.7 Hz, ArCH_2(β)), 4.89 (d, 1H, J_{gem} = 11.2 Hz, ArCH_2(α)), 4.77–4.74 (m, 3H, ArCH_2(α), ArCH_2(β), H-1'a(β)), 4.73–4.71 (m, 1H, H-1a(β)), 4.67–4.62 (m, 3H, ArCH_2(α), ArCH_2(β), H-1a(α)), 4.61 (d, 1H, J_{gem} = 11.6 Hz, H-1'a(α)), 4.60 (d, 1H, J_{gem} = 11.9 Hz, ArCH_2(α)), 4.55–4.38 (m, 12H, 4 x ArCH_2(α), 5 x ArCH_2(β), H-2(α), H-1'b(β), H-4'(β)), 4.33 (d, 1H, $J_{3',4'}$ = 4.5 Hz, H-3'(α)), 4.31–4.29 (m, 2H, H-2(β), H-3'(β)), 4.22–4.18 (m, 1H, H-5'a(β)), 4.14 (app dt, 1H, $J_{4',3'}$ = 4.5 Hz, $J_{4',5'a}$ = $J_{4',5'b}$ = 6.5 Hz, H-4'(α)), 4.08 (dd, 1H, $J_{5'a,4'}$ = 6.5 Hz, J_{gem} = 9.4 Hz, H-5'a(α)), 4.01 (dd, 1H, $J_{5'b,4'}$ = 6.5 Hz, J_{gem} = 9.4 Hz, H-5'b(α)), 3.89–3.83 (m, 3H, H-3(α), H-3(β), H-5'b(β)), 3.67–3.63 (m, 2H, H-5(α), H-5(β)), 3.59–3.52 (m, 2H, H-4(α), H-4(β)), 3.32 (s, 3H, OCH_3(β)), 3.23 (s, 3H, OCH_3(α)), 1.31 (d, 3H, $J_{6,5}$ = 6.2 Hz, H-6(α)), 1.29 (d, 3H, $J_{6,5}$ = 6.2 Hz, H-6(β)); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 166.0 (C=O), 165.9 (C=O), 138.73 (Ar), 138.65 (Ar), 138.4 (Ar), 138.3 (Ar), 137.89 (Ar), 137.88 (Ar), 137.83 (Ar), 133.02 (Ar), 132.99 (Ar), 130.07 (Ar), 129.84 (Ar), 129.80 (Ar), 129.77 (Ar), 128.5 (Ar), 128.4 (Ar), 128.31 (Ar), 128.28 (Ar), 128.2 (Ar), 128.0 (Ar), 127.9 (Ar), 127.83 (Ar), 127.79 (Ar), 127.7 (Ar), 127.6 (Ar), 127.56 (Ar), 127.52 (Ar), 127.49 (Ar), 127.48 (Ar), 127.46 (Ar), 127.4 (Ar), 107.8 (C-2'(α)), 105.0 (C-2'(β)), 100.9 (C-1(α), $J_{C1,H1}$ = 171.6 Hz), 100.3 (C-1(β), $J_{C1,H1}$ = 171.6 Hz), 88.3 (C-3'(α)), 84.5 (C-3'(β)), 83.0 (C-4'(β)), 81.8 (C-4'(α)), 80.7 (C-4(β)), 80.3 (C-4(α)), 79.2 (C-3(α)), 78.7 (C-3(β)), 75.1 (2C, ArCH_2(α),

Ar*C*H$_2$(β)), 72.9 (Ar*C*H$_2$(β)), 72.5 (Ar*C*H$_2$(α)), 72.4 (Ar*C*H$_2$(α)), 72.1 (Ar*C*H$_2$(β)), 72.0 (Ar*C*H$_2$(β)), 71.9 (Ar*C*H$_2$(α)), 70.3 (C-2(β)), 70.2 (C-5'(α)), 70.0 (C-5'(β)), 69.4 (C-2(α)), 68.1 (C-5(α)), 68.0 (C-5(β)), 64.1 (C-1'(β)), 63.6 (C-1'(α)), 54.65 (O*C*H$_3$(β)), 54.60 (O*C*H$_3$(α)), 18.05 (C-6(α)), 18.0 (C-6(β)); HRMS (ESI) calcd. for $C_{47}H_{50}NaO_{10}$ $[M+Na]^+$ 797.3296; found 797.3283.



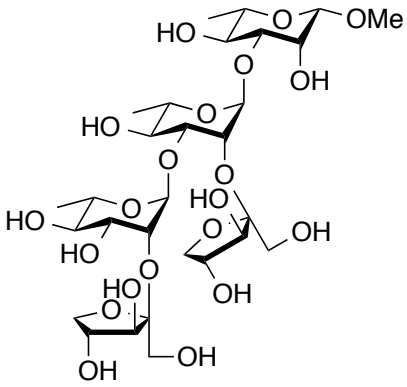
Cyclohexyl 3,4-*O*-xylylidene-α-D-*threo*-pent-2-ulofuranoside (49α). To a solution of **36α** (13.7 mg, 0.0312 mmol) in CH_3OH (1.0 mL) was added sodium methoxide (0.13 mg, 0.00312 mmol) at room temperature. After stirring at room temperature for 30 min, the reaction mixture was neutralized by the addition of Amberlite IR-120 H^+ resin. The mixture was then filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (3:1, hexane–EtOAc) to give **49α** (8.8 mg, 84%) as a colorless oil. $[\alpha]^{25}_D$ +105.1 (*c* 0.9, $CHCl_3$); TLC (2:1, hexane–EtOAc) R_f 0.37; ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.43–7.38 (m, 2H, ArH), 7.37–7.33 (m, 2H, ArH), 4.95 (d, 1H, J_{gem} = 12.7 Hz, ArC*H*$_2$), 4.91 (d, 1H, J_{gem} = 12.7 Hz, ArC*H*$_2$), 4.80 (d, 1H, J_{gem} = 12.7 Hz, ArC*H*$_2$), 4.76 (d, 1H, J_{gem} = 12.7 Hz, ArC*H*$_2$), 4.12 (ddd, 1H, $J_{4,3}$ = 5.0, $J_{4,5a}$ = 7.7 Hz, $J_{4,5b}$ = 9.0 Hz, H-4), 4.08 (d, 1H, $J_{3,4}$ = 5.0 Hz, H-3), 4.03 (dd, 1H, $J_{5a,4}$ = 7.7 Hz, J_{gem} = 8.4 Hz, H-5a), 3.76 (dd, 1H, $J_{5b,4}$ = 9.0 Hz, J_{gem} = 8.4 Hz, H-5b), 3.70–3.57 (m, 3H, cyclohexyl OC*H*, H-1a, H-1b), 2.66 (app t, 1H, $J_{OH,H1a}$ = $J_{OH,H1b}$ = 7.0 Hz, OH), 1.84–1.64 (m, 4H, cyclohexyl C*H*$_2$), 1.54–1.46 (m, 1H, cyclohexyl C*H*$_2$), 1.35–1.17 (m, 4H, cyclohexyl C*H*$_2$), 1.16–1.06 (m, 1H, cyclohexyl

C*H*$_2$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 136.2 (Ar), 135.8 (Ar), 132.0 (Ar), 131.8 (Ar), 130.1 (Ar), 130.0 (Ar), 109.6 (C-2), 89.9 (C-3), 81.7 (C-4), 70.7 (cyclohexyl O*C*H), 69.8 (Ar*C*H$_2$), 68.9 (Ar*C*H$_2$), 68.1 (C-5), 62.3 (C-1), 35.1 (cyclohexyl *C*H$_2$), 34.5 (cyclohexyl *C*H$_2$), 25.5 (cyclohexyl *C*H$_2$), 24.8 (2C, cyclohexyl *C*H$_2$); HRMS (ESI) calcd. for $C_{19}H_{26}NaO_5$ $[M+Na]^+$ 357.1672; found 357.1667.



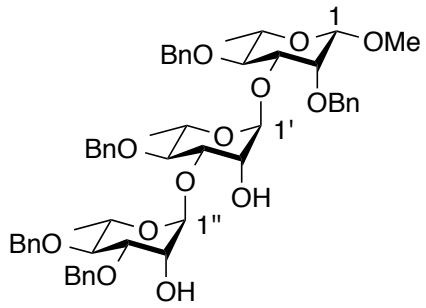
Cyclohexyl 3,4-*O*-xylylidene-β-D-*threo*-pent-2-ulofuranoside (49β). To a solution of **36β** (27.3 mg, 0.0623 mmol) in CH_3OH (1.0 mL) was added sodium methoxide (0.25 mg, 0.00623 mmol) at room temperature. After stirring at room temperature for 30 min, the reaction mixture was neutralized by the addition of Amberlite IR-120 H^+ resin. The mixture was then filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (2:1, hexane–EtOAc) to give **49β** (19.8 mg, 95%) as a colorless oil. **49β** was dissolved with minimal EtOAc, then slowly diffused with hexanes to obtain colorless crystal for X-ray crystallography. $[\alpha]^{25}_D$ –7.3 (*c* 0.3, $CHCl_3$); R_f 0.27 (2:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.40–7.32 (m, 4H, ArH), 5.05 (d, 1H, J_{gem} = 12.9 Hz, ArC*H*$_2$), 4.88 (d, 1H, J_{gem} = 12.9 Hz, ArC*H*$_2$), 4.86 (d, 1H, J_{gem} = 12.9 Hz, 1H, ArC*H*$_2$), 4.77 (d, 1H, J_{gem} = 12.9 Hz, ArC*H*$_2$), 4.39 (ddd, $J_{4,3}$ = 5.1 Hz, $J_{4,5a}$ = 7.7 Hz, $J_{4,5b}$ = 4.0 Hz, H-4), 4.23 (dd, 1H, $J_{5a,4}$ = 7.7 Hz, J_{gem} = 9.3 Hz, H-5a), 4.13 (d, 1H, $J_{3,4}$ = 5.1 Hz, H-3), 3.75 (dd, 1H, $J_{5b,4}$ = 4.0 Hz, J_{gem} = 9.3 Hz, H-5b), 3.67–3.60 (m, 3H, cyclohexyl OC*H*, H-1a, H-1b), 1.85–1.80 (m, 1H, cyclohexyl C*H*$_2$), 1.78–1.67 (m, 4H, cyclohexyl C*H*$_2$), 1.56–1.49 (m, 1H,

cyclohexyl C*H*$_2$), 1.47–1.31 (m, 2H, cyclohexyl C*H*$_2$), 1.29–1.16 (m, 1H, C*H*$_2$), 1.14–1.03 (m, 1H, cyclohexyl C*H*$_2$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 136.4 (Ar), 136.1 (Ar), 131.6 (2C, Ar), 129.53 (Ar), 129.51 (Ar), 106.8 (C-2), 84.0 (C-3), 80.9 (C-4), 71.0 (C-5), 70.8 (cyclohexyl O*C*H), 70.1 (Ar*C*H$_2$), 68.8 (Ar*C*H$_2$), 62.5 (C-1), 34.8 (cyclohexyl *C*H$_2$), 34.4 (cyclohexyl *C*H$_2$), 25.4 (cyclohexyl *C*H$_2$), 25.1 (cyclohexyl *C*H$_2$), 25.0 (cyclohexyl *C*H$_2$); HRMS (ESI) calcd. for $C_{19}H_{26}NaO_5$ $[M+Na]^+$ 357.1672; found 357.1669.



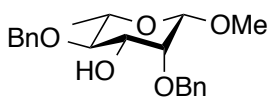
Methyl β-D-*threo*-pent-2-ulofuranosyl-(2→2)-α-L-rhamnopyranosyl-(1→3)-[β-D-*threo*-pent-2-ulofuranosyl-(2→2)]-α-L-rhamnopyranosyl-(1→3)-β-L-rhamnopyranoside (**50**). To a solution of **59β** (10.3 mg, 6.56 μmol) in EtOAc–CH_3OH (1:1, 1.0 mL) was added $Pd(OH)_2$/C (20 mg) at roomt. The reaction mixture was stirred under an H_2 atmosphere by exchange of three cycles of vacuum/H_2. After stirring for 1 h, the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by gel filtration chromatography (Sephadex, LH-20) with 1:1 CH_3OH–H_2O as the eluent to give **50** (4.3 mg, 89%) as a colorless oil. $[\alpha]^{25}_D$ –9.7 (*c* 0.4, H_2O); R_f 0.21 (10:2:1:0.5, EtOAc–CH_3OH–H_2O–AcOH); ^{1}H NMR (D_2O, 500 MHz) δ 5.32 (br s, 1H), 5.15 (m, 1H), 4.62 (br s, 1H),

4.49–4.43 (m, 2H), 4.36–4.33 (m, 1H), 4.30–4.27 (m, 1H), 4.21–4.08 (m, 5H), 3.94–3.68 (m, 12H), 3.64–3.52 (m, 2H), 3.58 (s, 3H, OCH_3), 3.51–3.45 (m), 1.40 (d, 3H, J = 6.4 Hz), 1.38 (d, 3H, J = 6.4 Hz), 1.36 (d, 3H, J = 6.4 Hz); ^{13}C NMR (D_2O, 125 MHz) δ 106.07, 106.01, 101.9, 101.83, 101.75, 80.2, 79.5, 78.3, 75.6, 75.0, 73.5, 73.0, 72.9, 72.8, 71.90, 71.87, 71.27, 71.23, 71.19, 70.4, 70.33, 70.25, 61.5, 57.8, 17.7, 17.5, 17.3; HRMS (ESI) calcd. for $C_{29}H_{50}NaO_{21}$ $[M+Na]^+$ 757.2737; found 757.2740.



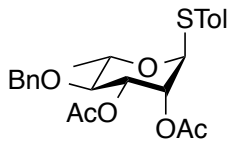
Methyl 3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-4-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-β-L-rhamnopyranoside (51). To a solution of **58** (23.0 mg, 0.0277 mmol) in toluene (10.0 mL) was added di-*n*-butyltin oxide (10.3 mg, 0.0415 mmol) and the reaction mixture was stirred at reflux for 3 h. The mixture was then cooled to room temperature before tetrabutylammonium bromide (13.4 mg, 0.0415 mmol) and benzyl bromide (7.1 mg, 4.9 μL, 0.0415 mmol) were added. After stirring for 1 h at reflux, the solution was then cooled to room temperature and concentrated under reduced pressure. The resulting residue was purified by column chromatography (2:1, hexane–EtOAc) to give **51** (24.4 mg, 96%) as a colorless oil. $[\alpha]^{25}_D$ +1.2 (*c* 1.0, $CHCl_3$); R_f 0.67 (1:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 700 MHz) δ_H 7.46–7.42 (m, 2H, ArH), 7.39–7.27 (m, 22H, ArH), 7.21–7.16 (m, 1H, ArH), 5.11–5.08 (m, 2H, H-1', H-1''), 5.04 (d, 1H, J_{gem} = 12.8 Hz, ArCH_2), 4.88 (d, 1H, J_{gem} = 11.0

Hz, ArCH_2), 4.76 (d, 1H, J_{gem} = 11.0 Hz, ArCH_2), 4.72 (d, 1H, J_{gem} = 12.8 Hz, ArCH_2), 4.67–4.60 (m, 5H, ArCH_2), 4.55 (d, 1H, J_{gem} = 11.0 Hz, ArCH_2), 4.36 (br s, 1H, H-1), 4.02–3.99 (m, 1H, H-2''), 3.95 (dd, 1H, $J_{3'',2''}$ = 3.6 Hz, $J_{3'',4''}$ = 9.2 Hz, H-3''), 3.94-3.92 (m, 1H, H-2'), 3.85–3.78 (m, 3H, H-2, H-3', H-5'), 3.69–3.61 (m, 3H, H-3, H-4, H-5''), 3.54 (s, 3H, OCH_3), 3.49 (app t, 1H, $J_{4',3'}$ = $J_{4',5'}$ = 9.2 Hz, H-4'), 3.39 (app t, 1H, $J_{4'',3''}$ = $J_{4'',5''}$ = 9.2 Hz, H-4''), 3.34 (app dq, 1H, $J_{5,6}$ = 6.2 Hz, $J_{5,4}$ = 8.8 Hz, H-5), 2.39 (d, 1H, $J_{OH,2'}$ = 1.9 Hz, 2'-OH), 2.03 (d, 1H, $J_{OH,2''}$ = 3.0 Hz, 2''-OH),1.39 (d, 3H, $J_{6,5}$ = 6.2 Hz, H-6), 1.27 (d, 3H, $J_{6'',5''}$ = 6.2 Hz, H-6''), 1.19 (d, 3H, $J_{6',5'}$ = 6.2 Hz, H-6'); ^{13}C NMR ($CDCl_3$, 175 MHz) δ_C 138.8 (Ar), 138.5 (Ar), 138.3 (Ar), 138.1 (Ar), 138.0 (Ar), 128.72 (2C, Ar), 128.70 (2C, Ar), 128.61 (2C, Ar), 128.56 (2C, Ar), 128.4 (2C, Ar), 128.2 (2C, Ar), 128.1 (2C, Ar), 128.04 (Ar), 128.0 (Ar), 127.97 (2C,Ar), 127.89 (2C, Ar), 127.84 (Ar), 127.7 (2C, Ar), 127.6 (Ar), 102.7 (C-1, $J_{C1,H1}$ = 153.5 Hz), 101.6 (C-1', $J_{C1',H1'}$ = 171.8 Hz), 101.0 (C-1'', $J_{C1'',H1''}$ = 171.8 Hz), 81.0 (C-4), 80.6 (C-3), 80.3 (C-4''), 79.90 (C-4'), 79.89 (C-3''), 79.5 (C-3'), 78.4 (C-2), 75.7 (ArCH$_2$), 75.6 (ArCH$_2$), 75.2 (ArCH$_2$), 74.6 (ArCH$_2$), 72.3 (ArCH$_2$), 72.1 (C-5), 71.3 (C-2''), 69.0 (C-2'), 68.5 (C-5'), 68.2 (C-5''), 57.3 (OCH_3), 18.12 (C-6'), 18.08 (C-6), 17.98 (C-6''); HRMS (ESI) calcd. for $C_{54}H_{64}NaO_{13}$ $[M+Na]^+$ 943.4239; found 943.4228.

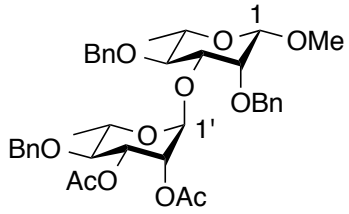


Methyl 2,4-di-*O*-benzyl-β-L-rhamnopyranoside (52). To a solution of **S2**[4] (430 mg, 1.44 mmol) in DMF (14.4 mL) was added benzyl bromide (590 mg, 410 μL, 3.46 mmol) and 60% NaH (173 mg, 4.32 mmol) at room temperature. After 1 h, CH_3OH was added.

The mixture was concentrated and then diluted with CH_2Cl_2, and then washed with brine and water. The organic layers were dried with $MgSO_4$ and then filtered. The filtrate was concentrated and dried *in vacuo*. To a solution of resulting residue in CH_2Cl_2–H_2O (9:1, 15 mL) was added DDQ (489 mg, 2.16 mmol) at room temperature and the reaction mixture was stirred for 30 min. After the completion of reaction, the reaction mixture was diluted with EtOAc and washed with satd aq $NaHCO_3$ and brine. The organic layer was then dried with $MgSO_4$, filtered and the filtrate was concentrated. The resulting residue was purified by column chromatography (4:1, hexane–EtOAc) to give **52** (454 mg, 88%) as a colorless oil. $[\alpha]^{25}_D$ +95.4 (*c* 0.7, $CHCl_3$); R_f 0.31 (4:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.43–7.27 (m, 10H, ArH), 5.08 (d, 1H, J_{gem} = 11.9 Hz, ArCH_2), 4.93 (d, 1H, J_{gem} = 11.0 Hz, ArCH_2), 4.64 (d, 1H, J_{gem} = 11.0 Hz, ArCH_2), 4.63 (d, 1H, J_{gem} = 11.9 Hz, ArCH_2), 4.37 (d, 1H, $J_{1,2}$ = 0.8 Hz, H-1), 3.83 (dd, 1H, $J_{2,1}$ = 0.8 Hz, $J_{2,3}$ = 3.7 Hz, H-2), 3.64 (ddd, 1H, $J_{3,2}$ = 3.7 Hz, $J_{3,4}$ = 8.9 Hz, $J_{3,OH}$ = 9.8 Hz, H-3), 3.56 (s, 3H, OCH_3), 3.32 (app dq, 1H, $J_{5,6}$ = 6.1 Hz, $J_{5,4}$ = 8.9 Hz, H-5), 3.28 (app t, 1H, $J_{4,3}$ = $J_{4,5}$ = 8.9 Hz, H-4), 2.41 (d, 1H, $J_{OH,3}$ = 9.8 Hz, OH), 1.41 (d, 3H, $J_{6,5}$ = 6.1 Hz, H-6); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.48 (Ar), 138.46 (Ar), 128.5 (2C, Ar), 128.4 (2C, Ar), 128.2 (2C, Ar), 128.0 (2C, Ar), 127.9 (Ar), 127.7 (Ar), 102.7 (C-1, $J_{C1,\ H1}$ = 153.1 Hz), 82.2 (C-4), 78.1 (C-2), 75.1 (ArCH$_2$), 75.0 (ArCH$_2$), 74.0 (C-3), 71.4 (C-5), 57.1 (OCH_3), 18.0 (C-6); HRMS (ESI) calcd. for $C_{21}H_{26}NaO_5$ $[M+Na]^+$ 381.1672; found 381.1680.

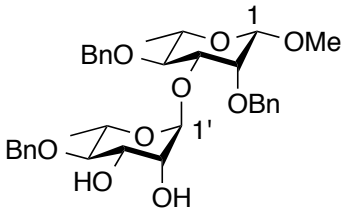


***p*-Tolyl 2,3-di-*O*-acetyl-4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (53)**. To a solution of **S3**[5] (70 mg, 0.175 mmol) in CH_2Cl_2 (2 mL) was added triethylamine (44.2 mg, 60.6 μL, 0.437 mmol), acetic anhydride (44.6 mg, 41.3 μL, 0.437 mmol) and 4-dimethylaminopyridine (2.1 mg, 0.0175 mmol) and the reaction mixture was stirred for 30 min. Excess acetic anhydride was quenched by the addition of CH_3OH and the solution was then concentrated under reduced pressure. The resulting residue was purified by column chromatography (4:1, hexane–EtOAc) to give **53** (71.5 mg, 92%) as a colorless syrup. $[\alpha]^{25}_D$ –111.3 (*c* 1.0, $CHCl_3$); R_f 0.63 (2:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 700 MHz) δ_H 7.37–7.33 (m, 4H, ArH), 7.32–7.27 (m, 3H, ArH), 7.12 (d, 1H, J = 8.1 Hz, ArH), 5.49 (dd, 1H, $J_{2,1}$ = 1.7 Hz, $J_{2,3}$ = 3.4 Hz, H-2), 5.32 (dd, 1H, $J_{3,2}$ = 3.4 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 5.29 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 4.72 (d, 1H, J_{gem} = 11.3 Hz, ArCH_2), 4.66 (d, 1H, J_{gem} = 11.3 Hz, ArCH_2), , 4.31 (app dq, 1H, $J_{5,4}$ = 9.6 Hz, $J_{5,6}$ = 6.3 Hz, H-5), 3.57 (app t, 1H, $J_{4,3}$ = $J_{4,5}$ = 9.6 Hz, H-4), 2.32 (s, 3H, ArCH_3), 2.12 (s, 3H, CH_3CO), 1.99 (s, 3H, CH_3CO), 1.36 (d, 3H, $J_{6,5}$ = 6.3 Hz, H-6); ^{13}C NMR ($CDCl_3$, 175 MHz) δ_C 170.0 (C=O), 169.8 (C=O), 138.06 (Ar), 138.05 (Ar), 132.6 (2C, Ar), 129.9 (2C, Ar), 129.8 (Ar), 128.5 (2C, Ar), 127.9 (Ar), 127.7 (2C, Ar), 86.1 (C-1, $J_{C1,H1}$ = 172.3 Hz), 79.0 (C-4), 75.1 (ArCH$_2$), 71.9 (C-3), 71.9 (C-2), 69.1 (C-5), 21.1 (ArCH$_3$), 21.0 (CH$_3$CO), 20.9 (CH$_3$CO), 17.9 (C-6); HRMS (ESI) calcd. for $C_{24}H_{28}NaO_6S$ $[M+Na]^+$ 467.1499; found 467.1496.



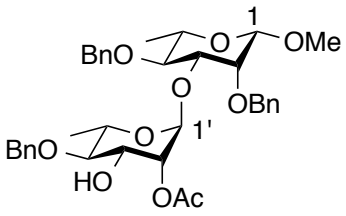
Methyl 2,3-di-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-β-L-rhamnopyranoside (54). A mixture of the **53** (45.4 mg, 0.102 mmol) and **52** (33.3 mg, 0.093 mmol) and 4Å molecular sieves in CH_2Cl_2 (1.0 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to 0 °C and *N*-iodosuccinimide (27.5 mg, 0.122 mmol) and silver triflate (2.6 mg, 0.0102 mmol) were added. After stirring for 15 min, triethylamine was added. The reaction mixture was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (4:1, hexane–EtOAc) to give **54** (55.5 mg, 88%) as a colorless oil. $[\alpha]^{25}_D$ +4.6 (*c* 0.9, $CHCl_3$); R_f 0.27 (4:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 700 MHz) δ_H 7.50–7.47 (m, 2H, ArH), 7.36–7.28 (m, 9H, ArH), 7.27–7.24 (m, 3H, ArH), 7.19–7.15 (m, 1H, ArH), 5.41 (dd, 1H, $J_{2',1'}$ = 1.9 Hz, $J_{2',3'}$ = 3.5 Hz, H-2'), 5.39 (dd, 1H, $J_{3',2'}$ = 3.5 Hz, $J_{3',4'}$ = 9.7 Hz, H-3'), 5.05 (d, 1H, J_{gem} = 12.2 Hz, ArCH_2), 5.04 (d, 1H, $J_{1',2'}$ = 1.9 Hz, H-1'), 4.83 (d, 1H, J_{gem} = 11.0 Hz, ArCH_2), 4.78 (d, 1H, J_{gem} = 12.2 Hz, ArCH_2), 4.66 (d, 2H, J_{gem} = 11.0 Hz, ArCH_2), 4.58 (d, 1H, J_{gem} = 11.0 Hz, ArCH_2) 4.34 (br s, 1H, H-1), 3.81 (d, 1H, $J_{2,3}$ = 1.8 Hz, H-2), 3.75 (app dq, 1H, $J_{5',6'}$ = 6.2 Hz, $J_{5',4'}$ = 9.7 Hz, H-5'), 3.68–3.66 (m, 2H, H-3, H-4), 3.53 (s, 3H, OCH_3), 3.44 (app t, $J_{4',3'} = J_{4',5'}$ = 9.7 Hz, H-4'), 3.33 (app dq,

1H, $J_{5,6}$ = 6.3 Hz, $J_{5,4}$ = 9.3 Hz, H-5), 2.05 (s, 3H, CH_3CO), 1.97 (s, 3H, CH_3CO), 1.38 (d, 3H, $J_{6,5}$ = 6.3 Hz, H-6), 1.21 (d, 3H, $J_{6',5'}$ = 6.3 Hz, H-6'); ^{13}C NMR ($CDCl_3$, 175 MHz) δ_C 169.74 (C=O), 169.65 (C=O), 138.5 (Ar), 138.3 (Ar), 138.1 (Ar), 128.33 (2C, Ar), 128.31 (2C, Ar), 128.25 (2C, Ar), 128.0 (2C, Ar), 127.9 (2C, Ar), 127.6 (2C, Ar), 127.4 (2C, Ar), 102.6 (C-1, $J_{C1,H1}$ = 153.5 Hz), 99.5 (C-1', $J_{C1',H1'}$ = 175.6 Hz), 80.6 (C-3), 80.5 (C-4), 78.6 (C-4'), 77.6 (C-2), 75.4 (Ar*C*H$_2$), 74.6 (Ar*C*H$_2$), 74.2 (Ar*C*H$_2$), 72.0 (C-5), 71.5 (C-3'), 70.3 (C-2'), 68.2 (C-5'), 57.1 (OCH$_3$), 20.9 (*C*H$_3$CO), 20.8 (*C*H$_3$CO), 17.93 (C-6), 17.90 (C-6'); HRMS (ESI) calcd. for $C_{38}H_{46}NaO_{11}$ $[M+Na]^+$ 701.2932; found 701.2932.



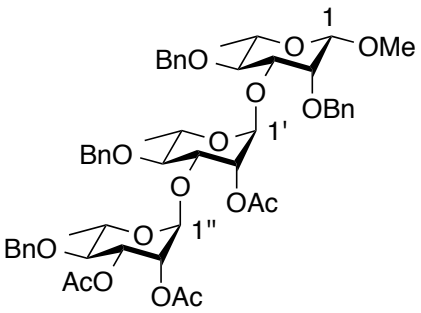
Methyl 4-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-β-L-rhamnopyranoside (55). To a solution of **54** (48 mg, 0.076 mmol) in CH_3OH (1 mL) was added sodium methoxide (0.3 mg, 7.6 μmol) and the reaction mixture was stirred at room temperature for 1 h. The reaction mixture was then neutralized by the addition of Amberlite IR-120 H^+ resin. The reaction mixture was filtered and then concentrated under reduced pressure. The resulting residue was purified by column chromatography (1:1, hexane–EtOAc) to give **55** (39 mg, 87%) as a colorless oil. $[\alpha]^{25}_D$ +31.9 (*c* 0.3, $CHCl_3$); R_f 0.23 (1:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.44–7.40 (m, 2H, ArH), 7.38–7.27 (m, 12H, ArH), 7.23–7.18 (m, 1H, ArH), 5.06 (d, 1H, $J_{1',2'}$ = 1.4 Hz, H-1'), 5.00 (d, 1H, J_{gem} = 12.3 Hz, ArCH_2), 4.74–4.65 (m, 5H, ArCH_2), 4.35 (s, 1H,

H-1), 3.87 (app dt, 1H, $J_{2',1'}$ = 1.4 Hz, $J_{2',3'} = J_{2',OH}$ = 3.6 Hz, H-2'), 3.83 (ddd, 1H, $J_{3',2'}$ = 3.6 Hz, $J_{3',4'}$ = 9.4 Hz, $J_{3',OH'}$ = 4.9 Hz, H-3'), 3.78 (d, 1H, $J_{2,3}$ = 2.5 Hz, H-2), 3.69–3.64 (m, 2H, H-3, H-5'), 3.61 (app t, 1H, $J_{4,3} = J_{4,5}$ = 9.6 Hz, H-4), 3.52 (s, 3H, OCH_3), 3.33 (app dq, 1H, $J_{5,4}$ = 9.6 Hz, $J_{5,6}$ = 6.2 Hz, H-5), 3.29 (app t, $J_{4',3'} = J_{4',5'}$ = 9.4 Hz, H-4'), 2.22 (d, 1H, $J_{OH,3'}$ = 4.9 Hz, OH), 2.02 (d, 1H, $J_{OH,2'}$ = 3.6 Hz, OH), 1.39 (d, 3H, $J_{6,5}$ = 6.2 Hz, H-6), 1.22 (d, 3H, $J_{6',5'}$ = 6.2 Hz, H-6'); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.8 (Ar), 138.5 (Ar), 138.2 (Ar), 128.6 (4C, Ar), 128.2 (2C, Ar), 127.9 (4C, Ar), 127.8 (2C, Ar), 127.75 (2C, Ar), 127.4 (Ar), 102.6 (C-1, $J_{C1,H1}$ = 153.1 Hz), 101.5 (C-1', $J_{C1',H1'}$ = 172.3 Hz), 81.5 (C-4'), 81.3 (C-4), 80.2 (C-3), 78.0 (C-2), 75.6 (ArCH$_2$), 74.7 (ArCH$_2$), 74.3 (ArCH$_2$), 72.1 (C-5), 71.3 (C-2'), 71.2 (C-3'), 67.9 (C-5'), 57.2 (OCH$_3$), 18.0 (2C, C-6, C-6'); HRMS (ESI) calcd. for $C_{34}H_{42}NaO_9$ $[M+Na]^+$ 617.2721; found 617.2734.



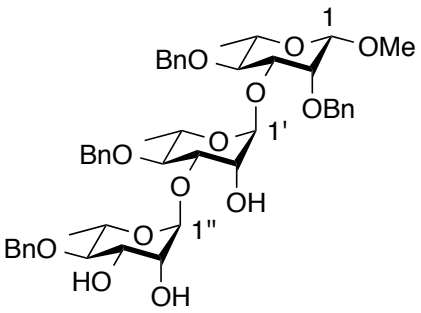
Methyl 2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-β-L-rhamnopyranoside (56). To a solution of **55** (35.5 mg, 0.060 mmol) in acetonitrile (1.0 mL) was added triethyl orthoacetate (8.6 mg, 9.2 mL, 0.072 mmol) and *p*-toluenesulfonic acid (1.0 mg, 6.0 μmol) at room temperature. After stirring for 1 h, triethylamine was added and the solution was concentrated. The residue was then dried *in vacuo* for 30 min. The residue was then dissolved in 80% aq AcOH and stirred for 30 min at room temperature. The reaction mixture was then diluted with EtOAc and

washed with water, satd aq $NaHCO_3$ and brine. The organic layer was then dried with $MgSO_4$, filtered and the filtrate was concentrated. The resulting residue was purified by column chromatography (4:1, hexane–EtOAc) to give **56** (31.3 mg, 88% over two steps) as a colorless oil. $[\alpha]^{25}_D$ +18.1 (*c* 1.7, $CHCl_3$); R_f 0.21 (4:1, hexane–EtOAc); ^1H NMR ($CDCl_3$, 700 MHz) δ_H 7.44–7.41 (m, 2H, ArH), 7.37–7.26 (m, 12H, ArH), 7.22–7.18 (m, 1H, ArH), 5.23 (dd, 1H, $J_{2',1'}$ = 1.7 Hz, $J_{2',3'}$ = 3.6 Hz, H-2'), 5.05 (d, 1H, $J_{1',2'}$ = 1.7 Hz, H-1'), 5.02 (d, 1H, J_{gem} = 12.2 Hz, ArCH_2), 4.83 (d, 1H, J_{gem} = 11.1 Hz, ArCH_2), 4.77 (d, 1H, J_{gem} = 11.3 Hz, ArCH_2), 4.70 (d, 1H, J_{gem} = 12.3 Hz, ArCH_2), 4.65 (d, 1H, J_{gem} = 11.3 Hz, ArCH_2), 4.63 (d, 1H, J_{gem} = 11.1 Hz, ArCH_2), 4.33 (d, 1H, $J_{1,2}$ = 0.5 Hz, H-1), 4.02 (app dt, 1H, $J_{3',2'} = J_{3',OH}$ = 3.9 Hz, $J_{3',4'}$ = 8.9 Hz, H-3'), 3.78 (dd, 1H, $J_{2,1}$ = 0.5 Hz, $J_{2,3}$ = 2.9 Hz, H-2), 3.70 (app dq, 1H, $J_{5',6'}$ = 6.3 Hz, $J_{5',4'}$ = 9.5 Hz, H-5'), 3.67 (dd, 1H, $J_{3,2}$ = 2.8 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 3.63 (app t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4), 3.51 (s, 3H, OCH_3), 3.31 (app dq, $J_{5,6}$ = 6.3 Hz, $J_{5,4}$ = 9.1 Hz, H-5), 3.30 (app t, $J_{4',3'} = J_{4',5'}$ = 9.4 Hz, H-4'), 2.07 (s, 3H, CH_3CO), 2.02 (d, 1H, $J_{OH,\,3'}$ = 3.9 Hz, OH), 1.35 (d, 3H, $J_{6,5}$ = 6.2 Hz, H-6), 1.24 (d, 3H, $J_{6',5'}$ = 6.2 Hz, H-6'); ^{13}C NMR ($CDCl_3$, 175 MHz) δ_C 170.6 (C=O), 138.7 (Ar), 138.5 (Ar), 138.1 (Ar), 128.5 (2C, Ar), 128.4 (2C, Ar), 128.2 (2C, Ar), 128.1 (2C, Ar), 127.8 (Ar), 127.7 (2C, Ar), 127.3 (Ar), 102.5 (C-1), 99.3 (C-1'), 81.4 (C-4'), 80.8 (C'4), 80.1 (C-3), 78.0 (C-2), 75.4 (ArCH_2), 74.8 (ArCH_2), 74.4 (ArCH_2), 72.6 (C-2'), 72.1 (C-5), 70.2 (C-3'), 68.1 (C-5'), 57.1 (OCH_3), 21.0 (CH_3CO), 18.01 (C-6), 17.96 (C-6)'; HRMS (ESI) calcd. for $C_{36}H_{44}NaO_{10}$ $[M+Na]^+$ 659.2827; found 659.2826.



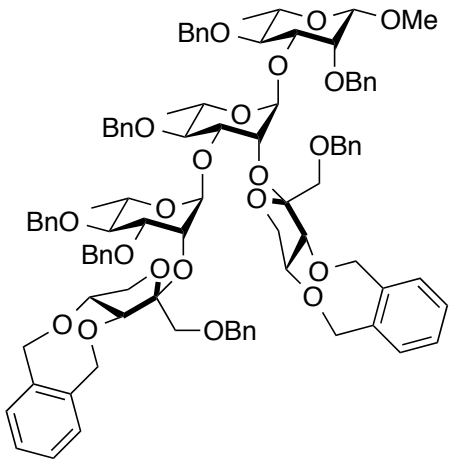
Methyl 2,3-di-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-β-L-rhamnopyranoside (57). A mixture of **53** (34.1 mg, 0.0767 mmol), **56** (40.7 mg, 0.0639 mmol) and 4Å molecular sieves in CH_2Cl_2 (2.0 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to 0 °C and and then *N*-iodosuccinimide (20.7 mg, 0.0920 mmol) and silver triflate (2.0 mg, 7.7 μmol) were added. After stirring for 30 min, triethylamine was added. The solution was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (4:1, hexane–EtOAc) to give **57** (58.1 mg, 95%) as a colorless syrup. $[\alpha]^{25}_D$ –8.0 (*c* 0.9, $CHCl_3$); R_f 0.37 (4:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 700 MHz) δ_H 7.44–7.41 (m, 2H, ArH), 7.38–7.35 (m, 2H, ArH), 7.34–7.30 (m, 6H, ArH), 7.30–7.26 (m, 9H, ArH), 7.18–7.15 (m, 1H, ArH), 5.34 (dd, 1H, $J_{2',1'}$ = 1.7 Hz, $J_{2',3'}$ = 3.3 Hz, H-2'), 5.31 (dd, 1H, $J_{2'',1''}$ = 2.0 Hz, $J_{2'',3''}$ = 3.2 Hz, H-2''), 5.27 (dd, 1H, $J_{3'',2''}$ = 3.2 Hz, $J_{3'',4''}$ = 9.6 Hz, H-3''), 5.07 (d, 1H, $J_{1',2'}$ = 1.5 Hz, H-1'), 5.04 (d, 1H, J_{gem} = 12.1 Hz, ArCH_2), 4.93 (d, 1H, $J_{1'',2''}$ = 1.8 Hz, H-1''), 4.90 (d, 1H, J_{gem} = 10.8 Hz, ArCH_2), 4.80 (d, 1H, J_{gem} = 11.2 Hz, ArCH_2), 4.68 (d, 1H, J_{gem} = 12.1 Hz, ArCH_2), 4.67 (d, 1H, J_{gem} = 11.6 Hz, ArCH_2), 4.62 (d, 1H, J_{gem} = 11.6 Hz, ArCH_2), 4.61 (d, 1H,

J_{gem} = 11.2 Hz, ArCH_2), 4.57 (d, 1H, J_{gem} = 10.8 Hz, ArCH_2), 4.33 (br s, 1H, H-1), 4.08 (dd, 1H, $J_{3',2'}$ = 3.4 Hz, $J_{3',4'}$ = 9.6 Hz, H-3'), 3.90 (app dq, 1H, $J_{5'',6''}$ = 6.4 Hz, $J_{5'',4''}$ = 9.6 Hz, H-5''), 3.79 (d, 1H, $J_{2,3}$ = 2.8 Hz, H-2), 3.70 (app dq, 1H, $J_{5',6'}$ = 6.4 Hz, $J_{5',4'}$ = 9.7 Hz, H-5'), 3.67 (dd, 1H, $J_{3,2}$ = 2.8 Hz, $J_{3,4}$ = 9.4 Hz, H-3), 3.63 (app t, 1H, $J_{4,3}$ = $J_{4,5}$ = 9.4 Hz, H-4), 3.52 (s, 3H, OCH_3), 3.46 (app t, 1H, $J_{4'',3''}$ = $J_{4'',5''}$ = 9.4 Hz, H-4''), 3.45 (app t, $J_{4',3'}$ = $J_{4',5'}$ = 9.4 Hz, H-4'), 3.30 (app dq, 1H, $J_{5,6}$ = 6.2 Hz, $J_{5,4}$ = 9.4 Hz, H-5), 2.14 (s, 3H, CH_3CO), 2.06 (s, 3H, CH_3CO), 1.95 (s, 3H, CH_3CO), 1.32 (d, 3H, $J_{6,5}$ = 6.2 Hz, H-6), 1.24 (d, 3H, $J_{6'',5''}$ = 6.4 Hz, H-6''), 1.21 (d, 3H, $J_{6',5'}$ = 6.4 Hz, H-6'); ^{13}C NMR ($CDCl_3$, 175 MHz) δ_C 170.1 (C=O), 169.9 (C=O), 169.8 (C=O), 138.7 (Ar), 138.24 (Ar), 138.23 (Ar), 138.0 (Ar), 128.5 (2C, Ar), 128.39 (2C, Ar), 128.36 (2C, Ar), 128.25 (2C, Ar), 128.2 (2C, Ar), 127.81 (Ar), 127.76 (2C, Ar), 127.75 (2C, Ar), 127.72 (Ar), 127.70 (2C, Ar), 127.5 (Ar), 127.3 (Ar), 102.6 (C-1, $J_{C1,H1}$ = 155.3 Hz), 99.4 (C-1'', $J_{C1'',H1''}$ = 174.9 Hz), 99.2 (C-1', $J_{C1',H1'}$ = 174.9 Hz), 80.6 (C-3), 80.5 (C-4), 80.3 (C-4'), 78.4 (C-4''), 78.1 (C-2), 76.8 (C-3'), 75.5 (ArCH$_2$), 75.2 (ArCH$_2$), 74.41 (ArCH$_2$), 74.39 (ArCH$_2$), 72.1 (C-2'), 72.0 (C-5), 71.4 (C-3''), 70.4 (C-2''), 68.5 (C-5''), 68.4 (C-5'), 57.1 (OCH_3), 21.0 (CH$_3$CO), 20.9 (CH$_3$CO), 20.8 (CH$_3$CO), 17.93 (C-6), 17.91 (2C, C-6', C-6''); HRMS (ESI) calcd. for $C_{53}H_{64}NaO_{16}$ $[M+Na]^+$ 979.4087; found 979.4094.



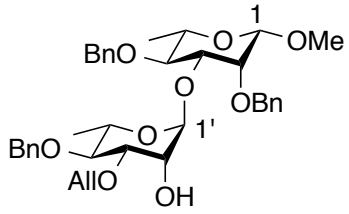
Methyl 4-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-4-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-β-L-rhamnopyranoside (58). To a solution of **57** (58.1 mg, 0.0607 mmol) in CH_3OH (2.0 mL) was added sodium methoxide (1 mg, 0.0243 mmol) and the reaction mixture was stirred for 1 day. The reaction mixture was then neutralized by the addition of Amberlite IR-120 H^+ resin. The mixture was then filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (4:1, hexane–EtOAc) to give **58** (46.0 mg, 89%) as a colorless oil. $[\alpha]^{25}_D$ +0.8 (*c* 1.0, $CHCl_3$); R_f 0.33 (2:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 700 MHz) δ_H 7.45–7.42 (m, 2H, ArH), 7.38–7.26 (m, 17H, ArH), 7.20–7.17 (m, 1H, ArH), 5.08 (d, 1H, $J_{1',2'}$ = 1.4 Hz, H-1'), 5.03 (d, 1H, J_{gem} = 12.1 Hz, ArCH_2), 5.02 (d, 1H, $J_{1'',2''}$ = 1.8 Hz, H-1''), 4.75 (d, 1H, J_{gem} = 11.0 Hz, ArCH_2), 4.72 (s, 2H, ArCH_2), 4.70 (d, 1H, J_{gem} = 12.1 Hz, ArCH_2), 4.64 (d, 1H, J_{gem} = 11.0 Hz, ArCH_2), 4.63 (d, 1H, J_{gem} = 11.0 Hz, ArCH_2), 4.59 (d, 1H, J_{gem} = 11.0 Hz, ArCH_2), 4.35 (br s, 1H, H-1), 3.98–3.96 (m, 1H, H-2'), 3.94 (dd, 1H, $J_{3',2'}$ = 3.5 Hz, $J_{3',4'}$ = 9.4 Hz, H-3'), 3.88–3.84 (m, 1H, H-3''), 3.83–3.81 (m, 1H, H-2''), 3.79 (d, 1H, $J_{2,3}$ = 2.6 Hz, H-2), 3.78 (app dq, 1H, $J_{5'',6''}$ = 6.4 Hz, $J_{5'',4''}$ = 9.3 Hz, H-5''), 3.67 (dd, 1H, $J_{3,2}$ = 2.6 Hz, $J_{3,4}$ = 9.6 Hz, H-3), 3.66 (app dq, 1H, $J_{5',6'}$ = 6.3 Hz, $J_{5',4'}$ = 9.5 Hz, H-5'), 3.62 (app t, 1H, $J_{4,3}$ = $J_{4,5}$ = 9.6 Hz, H-4), 3.52 (s, 3H, OCH_3), 3.39 (app t, 1H, $J_{4',3'}$ = $J_{4',5'}$ = 9.5 Hz, H-4'), 3.34 (app t, $J_{4'',3''}$ = $J_{4'',5''}$ = 9.3 Hz, H-4''), 3.33 (app

dq, 1H, $J_{5,6}$ = 6.2 Hz, $J_{5,4}$ = 9.4 Hz, H-5), 2.29 (d, 1H, $J_{OH,3''}$ = 5.2 Hz, 3''-OH), 2.11 (d, 1H, $J_{OH,2''}$ = 3.8 Hz, 2''-OH), 2.06 (d, 1H, $J_{OH,2'}$ = 3.0 Hz, 2'-OH), 1.37 (d, 3H, $J_{6,5}$ = 6.2 Hz, H-6), 1.27 (d, 3H, $J_{6'',5''}$ = 6.4 Hz, H-6''), 1.19 (d, 3H, $J_{6',5'}$ = 6.3 Hz, H-6'); ^{13}C NMR ($CDCl_3$, 175 MHz) δ_C 138.7 (Ar), 138.4 (Ar), 138.1 (Ar), 138.0 (Ar), 128.7 (2C, Ar), 128.6 (2C, Ar), 128.4 (2C, Ar), 128.2 (2C, Ar), 128.1 (Ar), 128.04 (2C, Ar), 127.96 (2C, Ar), 127.94 (Ar), 127.8 (2C, Ar), 127.7 (Ar), 127.6 (2C, Ar), 127.4 (Ar), 102.6 (C-1, $J_{C1,H1}$ = 154.5 Hz), 101.5 (C-1', $J_{C1',H1'}$ = 172.5 Hz), 101.1 (C-1'', $J_{C1'',H1''}$ = 172.5 Hz), 81.4 (C-4''), 80.8 (C-4), 80.6 (C-4'), 80.5 (C-3), 78.9 (C-3'), 78.3 (C-2), 75.5 (ArCH_2), 75.20 (ArCH_2), 75.18 (ArCH_2), 74.4 (ArCH_2), 72.0 (C-5), 71.4 (C-2''), 71.3 (C-3''), 71.2 (C-2'), 68.2 (C-5''), 68.1 (C-5'), 57.2 (OCH_3), 18.1 (C-6), 17.94 (C-6''), 17.87 (C-6'); HRMS (ESI) calcd. for $C_{47}H_{58}NaO_{13}$ $[M+Na]^+$ 853.3770; found 853.3761.



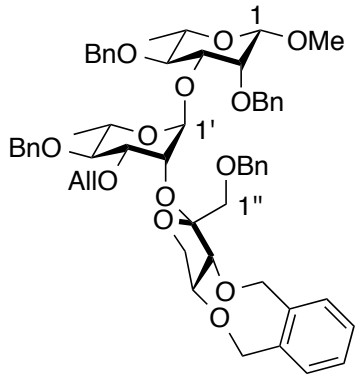
Methyl 1-*O*-benzyl-3,4-*O*-xylylidene-β-D-*threo*-pent-2-ulofuranosyl-(2→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-[1-*O*-benzyl-3,4-*O*-xylylidene-β-D-*threo*-pent-2-ulofuranosyl-(2→2)]-4-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-β-L-rhamnopyranoside (59β). A mixture of **7** (7.0 mg, 0.0155 mmol), **65** (16.1

mg, 0.0129 mmol) and 4 Å molecular sieves in CH_2Cl_2 (0.43 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to –78 °C and then *N*-iodosuccinimide (4.2 mg, 0.0186 mmol) and silver triflate (0.8 mg, 3.1 μmol) were added. After stirring for 1 h at – 78 ºC, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (4:1, hexane–EtOAc) to give **59β** (11.7 mg, 58%) as a colorless oil. $[\alpha]^{25}_D$ +22.0 (*c* 1.1, $CHCl_3$); R_f 0.32 (2:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 700 MHz) δ_H 7.46–7.41 (m, 2H, ArH), 7.36–7.10 (m, 37H, ArH), 7.07–7.05 (m, 2H, ArH), 6.94–6.91 (m, 2H, ArH), 5.15 (br s, 1H), 5.09 (d, 1H, J_{gem} 11.7 Hz, ArCH_2), 5.01 (br s, 1H), 4.91 (d, 1H, J_{gem} = 11.7 Hz, ArCH_2), 4.87 (d, 1H, J_{gem} = 11.7 Hz, ArCH_2), 4.81–4.69 (m, 7H, ArCH_2), 4.63–4.55 (m, 5H), 4.47–4.31 (m, 9H), 4.21–4.10 (m, 7H), 3.91–3.82 (m, 3H), 3.74–3.70 (m, 1H), 3.63–3.47 (m, 14H), 3.31–3.26 (m, 1H), 1.28 (d, 3H, *J* = 6.7 Hz), 1.13 (d, 3H, *J* = 6.7 Hz), 1.04 (d, 3H, *J* = 6.7 Hz); ^{13}C NMR ($CDCl_3$, 175 MHz) δ_C 139.2, 138.9, 138.6, 138.5, 138.4, 137.0, 136.9, 136.8, 131.62, 131.60, 131.3, 131.1, 129.3, 129.2, 128.7, 128.6, 128.5, 128.4, 128.3, 128.15, 128.07, 128.0, 127.9, 127.7, 127.68, 127.58 ,127.5, 127.46, 127.43, 127.4, 127.3, 107.2, 107.1, 102.9, 101.8, 100.8, 82.1, 80.5, 80.1, 80.0, 79.1, 79.06, 75.6, 74.6, 74.5, 73.4, 73.3, 73.0, 72.8, 721, 70.4, 70.1, 69.5, 69.46, 69.43, 69.2, 68.9, 57.3, 18.7, 18.2, 18.1; HRMS (ESI) calcd. for $C_{94}H_{104}NaO_{21}$ $[M+Na]^+$ 1591.6962; found 1591.6966.



Methyl 3-*O*-allyl-4-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-β-L-rhamnopyranoside (60). To a solution of the **55** (158 mg, 0.266 mmol) in toluene (30.0 mL) was added di-*n*-butyltin oxide (99 mg, 0.399 mmol) and the mixture was heated at reflux for 3 h. The mixture was then cooled to room temperature before tetrabutylammonium bromide (128 mg, 0.399 mmol) and allyl bromide (38.5 mg, 34.5 μL, 0.399 mmol) were added. After stirring for 2 h at reflux, the reaction mixture was concentrated and the resulting residue was purified by column chromatography (4:1, hexane–EtOAc) to give **60** (103 mg, 77%) as a colorless oil. $[\alpha]^{25}_{D}$ +20.2 (*c* 1.0, $CHCl_3$); R_f 0.36 (2:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.47–7.43 (m, 2H, ArH), 7.39–7.27 (m, 12H, ArH), 7.22–7.18 (m, 1H, ArH), 5.92 (ddt, 1H, *J* = 5.7, 10.5, 17.1 Hz, OCH_2CH=CH_2), 5.28 (dq, 1H, *J* = 1.7, 17.1 Hz, OCH_2CH=CH_2), 5.19–5.15 (m, 2H, OCH_2CH=CH_2, H-1'), 5.02 (d, 1H, J_{gem} = 12.4 Hz, ArCH_2), 4.86 (d, 1H, J_{gem} = 11.4 Hz, ArCH_2), 4.78 (d, 1H, J_{gem} = 10.9 Hz, ArCH_2), 4.74 (d, 1H, J_{gem} = 12.4 Hz, ArCH_2), 4.65 (d, 1H, J_{gem} = 10.9 Hz, ArCH_2), 4.61 (d, 1H, J_{gem} = 11.4 Hz, ArCH_2), 4.36 (br s, 1H, H-1), 4.14 (ddt, 1H *J* = 1.7, 5.7, 12.8 Hz, OCH_2CH=CH_2), 4.09 (ddt, 1H, *J* = 1.7, 5.7, 12.8 Hz, OCH_2CH=CH_2), 4.01–3.99 (m, 1H, H-2'), 3.82 (d, 1H, $J_{2,3}$ = 2.7 Hz, H-2), 3.74–3.67 (m, 3H, H-3, H-3', H-5'), 3.64 (app t, 1H, $J_{4,3}$ = $J_{4,5}$ = 9.6 Hz, H-4), 3.53 (s, 3H, OCH_3), 3.40 (app t, 1H, $J_{4',3'}$ = $J_{4',5'}$ = 9.1 Hz, H-4'), 3.35 (app dq, $J_{5,6}$ = 6.1 Hz, $J_{5,4}$ = 9.6 Hz, H-5), 2.40 (d, 1H, $J_{OH,\,2'}$ = 1.5 Hz, 2'-OH), 1.40 (d, 3H, $J_{6,5}$ =

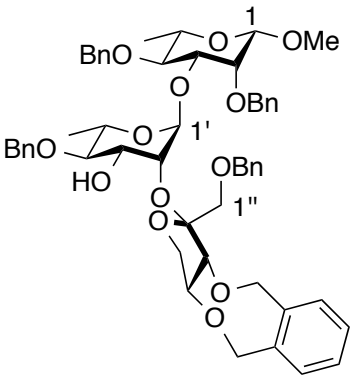
6.1 Hz, H-6), 1.22 (d, 3H, $J_{6',5'}$ = 6.4 Hz, H-6'); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.8 (Ar), 138.7 (Ar), 138.0 (Ar), 134.6 ($OCH_2CH{=}CH_2$), 128.5 (2C, Ar), 128.3 (2C, Ar), 128.1 (2C, Ar), 128.0 (2C, Ar), 127.9 (Ar), 127.8 (2C, Ar), 127.7 (Ar), 127.5 (Ar), 127.3 (Ar), 117.3 ($OCH_2CH{=}CH_2$), 102.6 (C-1, $J_{C1,H1}$ = 154.0 Hz), 101.1 (C-1', $J_{C1',H1'}$ = 172.2 Hz), 81.0 (C-4), 80.0 (C-3), 79.8 (C-3'), 79.4 (C-4'), 78.1 (C-5'), 75.5 ($ArCH_2$), 75.0 ($ArCH_2$), 74.4 ($ArCH_2$), 72.0 (C-5), 71.0 ($OCH_2CH{=}CH_2$), 69.1 (C-2'), 68.0 (C-2), 57.1 (OCH_3), 17.9 (C-6), 17.84 (C-6'); HRMS (ESI) calcd. for $C_{37}H_{46}NaO_9$ $[M+Na]^+$ 657.3034; found 657.3034.



Methyl 1-*O*-benzyl-3,4-*O*-xylylidene-β-D-*threo*-pent-2-ulofuranosyl-(2→2)-3-*O*-allyl-4-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-β-L-rhamnopyranoside (61β). A mixture of **7** (32.2 mg, 0.072 mmol), **60** (38.0 mg, 0.060 mmol), and 4Å molecular sieves in CH_2Cl_2 (2.0 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to –78 °C and *N*-iodosuccinimide (19.4 mg, 0.0864 mmol) and silver triflate (1.9 mg, 7.2 μmol) were added. After stirring for 1 h at –78 °C, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3{\cdot}5H_2O$ until the solution was colorless. The solution was then dried over

$MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (4:1, hexane–EtOAc) to give **61α** (15.3 mg, 26%) and **61β** (30.6 mg, 52%) both as colorless oils. Data for **61β**: $[\alpha]^{25}_D$ +14.1 (*c* 0.4, $CHCl_3$); R_f 0.30 (2:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 700 MHz) δ_H 7.44–7.41 (m, 2H, ArH), 7.38–7.23 (m, 19H, ArH), 7.20–7.16 (m, 3H, ArH), 5.77–5.73 (m, 1H, OCH_2CH=CH_2), 5.17 (dq, 1H, *J* = 17.3, 1.7 Hz, OCH_2CH=CH_2), 5.06–5.00 (m, 3H, OCH_2CH=CH_2, 2 x ArCH_2), 4.96 (br s, 1H, H-1'), 4.88–4.81 (m, 3H, ArCH_2), 4.79 (d, 1H, J_{gem} = 12.9 Hz, ArCH_2), 4.76 (d, 1H, J_{gem} = 12.9 Hz, ArCH_2), 4.66 (d, 1H, J_{gem} = 12.0 Hz, ArCH_2), 4.57 (d, 1H, J_{gem} = 11.5 Hz, ArCH_2), 4.53 (d, 1H, J_{gem} = 11.5 Hz, ArCH_2), 4.51 (d, 1H, J_{gem} = 12.5 Hz, ArCH_2), 4.41–4.37 (m, 2H, ArCH_2, H-4''), 4.31 (s, 1H, H-1), 4.25 (d, 1H, $J_{3'',4''}$ = 6.4 Hz, H-3''), 4.11 (app t, 1H, $J_{2',1'} = J_{2',3'}$ = 2.4 Hz, H-2'), 4.01–3.92 (m, 3H, H-5''a, 2 x OCH_2CH=CH_2), 3.79 (d, 1H, $J_{2,3}$ = 2.8 Hz, H-2), 3.69 (dq, 1H, $J_{5',4'}$ = 9.3 Hz, $J_{5',6'}$ = 6.4 Hz, H-5'), 3.66 (dd, 1H, $J_{3',2'}$ = 2.4 Hz, $J_{3',4'}$ = 9.3 Hz, H-3'), 3.63 (dd, 1H, $J_{3,2}$ = 2.8 Hz, $J_{3,4}$ = 9.7 Hz, H-3), 3.58–3.50 (m, 4H, H-4, H-1''a, H-1''b, H-5''b), 3.49 (s, 3H, OCH_3), 3.45 (app t, $J_{4',3'} = J_{4',5'}$ = 9.3 Hz, H-4'), 3.30 (app dq, $J_{5,6}$ = 6.2 Hz, $J_{5,4}$ = 9.1 Hz, H-5), 1.27 (d, 3H, $J_{6,5}$ = 6.2 Hz, H-6), 1.18 (d, 3H, $J_{6',5'}$ = 6.4 Hz, H-6'); ^{13}C NMR ($CDCl_3$, 175 MHz) δ_C 139.1 (Ar), 138.8 (Ar), 138.30 (Ar), 138.26 (Ar), 136.7 (Ar), 136.1 (Ar), 134.9 (OCH_2CH=CH_2), 131.5 (Ar), 131.0 (Ar), 129.2 (Ar), 129.1 (Ar), 128.4 (2C, Ar), 128.3 (2C, Ar), 128.2 (2C, Ar), 128.1 (2C, Ar), 127.8 (2C, Ar), 127.72 (2C, Ar), 127.71 (Ar), 127.6 (2C, Ar), 127.54 (2C, Ar), 127.50 (Ar), 127.3 (Ar), 127.2 (Ar), 116.7 (OCH_2CH=CH_2), 107.1 (C-2''), 102.6 (C-1, $J_{C1,H1}$ = 154.6 Hz), 101.6 (C-1', $J_{C1,H1}$ = 173.6 Hz), 82.0 (C-3''), 80.9 (C-3), 80.5 (C-4), 80.1 (C-4'), 79.7 (C-4''), 78.5 (C-2), 78.2 (C-3'), 75.3 (ArCH_2), 74.6

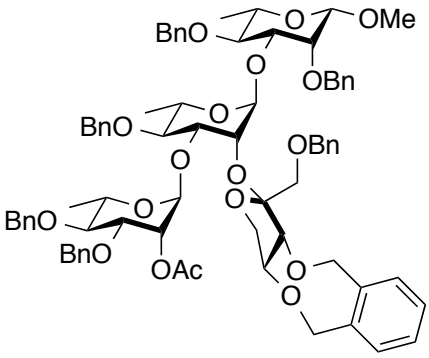
(Ar*C*H$_2$), 74.5 (Ar*C*H$_2$), 73.3 (Ar*C*H$_2$), 72.0 (C-5), 71.7 (O*C*H$_2$CH=CH$_2$), 70.4 (C-5''), 69.9 (C-2'), 69.5 (Ar*C*H$_2$), 69.3 (Ar*C*H$_2$), 68.9 (C-5'), 68.5 (C-1''), 57.1 (O*C*H$_3$), 18.1 (C-6), 17.9 (C-6'); HRMS (ESI) calcd. for $C_{57}H_{66}NaO_{13}$ $[M+Na]^+$ 981.4396; found 981.4385.



Methyl 1-*O*-benzyl-3,4-*O*-xylylidene-β-D-*threo*-pent-2-ulofuranosyl-(2→2)-4-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-β-L-rhamnopyranoside (62). To a solution of **61β** (30.6 mg, 0.0319 mmol) in THF (1.0 mL), degassed under vaccum, and stirred under an Ar atmosphere, (1,5-cyclooctadiene) bis-(methyldiphenylphosphine)iridium I hexafluorophosphate catalyst (1.3 mg, 1.6 μmol) was added, followed by further degassing of the mixture. The suspension was stirred for 30 min at 0 ºC, and the catalyst was then activated with hydrogen. At this point, the solution became nearly colorless. The excess of hydrogen gas was removed by exchange of Ar gas. The reaction mixture was then stirred for 24 h at room temperature under an Ar atmosphere. The solvent was then evaporated, and the residue was dissolved in acetone–water (9:1, 2.0 mL). To the solution was then added HgO (10.4 mg, 0.0479 mmol) and $HgCl_2$ (13.0 mg, 0.0479 mmol). After stirring for 24 h at room temperature, the solvent was evaporated and the residue was dissolved in EtOAc and

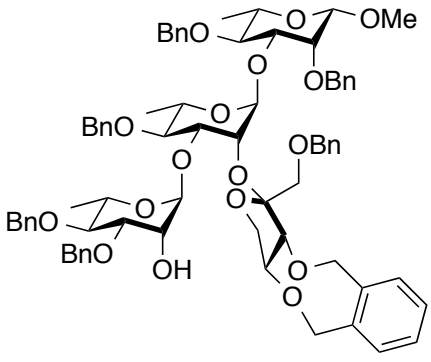
washed with 10% KI solution, satd aq $Na_2S_2O_3$, and then water. The organic layer was then dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (4:1, hexane–EtOAc) to give **62** (23.5 mg, 80%) as a colorless oil. $[\alpha]^{25}_D$ +15.5 (*c* 1.5, $CHCl_3$); R_f 0.30 (2:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.45–7.39 (m, 4H, ArH), 7.35–7.24 (m, 17H, ArH), 7.21–7.17 (m, 3H, ArH), 5.10 (d, 1H, $J_{1',2'}$ = 1.2 Hz, H-1'), 5.04 (d, 1H, J_{gem} = 11.7 Hz, ArCH_2), 4.96 (d, 1H, J_{gem} = 13.2 Hz, ArCH_2), 4.93 (d, 1H, J_{gem} = 11.7 Hz, ArCH_2), 4.83 (d, 1H, J_{gem} = 11.4 Hz, ArCH_2), 4.78 (d, 1H, J_{gem} = 12.3 Hz, ArCH_2), 4.75 (d, 1H, J_{gem} = 12.3 Hz, ArCH_2), 4.69 (d, 1H, J_{gem} = 11.4 Hz, ArCH_2), 4.68 (d, 1H, J_{gem} = 13.2 Hz, ArCH_2), 4.61 (d, 1H, J_{gem} = 11.4 Hz, ArCH_2), 4.55 (d, 1H, J_{gem} = 11.4 Hz, ArCH_2), 4.47 (d, 1H, J_{gem} = 12.4 Hz, ArCH_2), 4.40 (d, 1H, J_{gem} = 12.4 Hz, ArCH_2), 4.32 (s, 1H, H-1), 4.28 (app dt, $J_{4'',3''}$ = $J_{4'',5''b}$ = 5.3 Hz, $J_{4'',5''a}$ = 8.0 Hz, H-4''), 4.10 (dd, 1H, $J_{5''a,4''}$ = 8.0 Hz, J_{gem} = 9.6 Hz, H-5''), 4.04 (dd, 1H, $J_{2',1'}$ = 1.2 Hz, $J_{2',3'}$ = 3.3 Hz, H-2'), 4.00–3.97 (m, 1H, H-3'), 3.97 (d, 1H, $J_{3'',4''}$ = 5.3 Hz, H-3''), 3.85 (d, 1H, $J_{2,3}$ = 2.6 Hz, H-2), 3.75 (dq, 1H, $J_{5',4'}$ = 9.4 Hz, $J_{5',6'}$ = 6.1 Hz, H-5'), 3.63 (dd, 1H, $J_{3,2}$ = 2.6 Hz, $J_{3,4}$ = 9.5 Hz, H-3), 3.58 (dd, 1H, $J_{4,3}$ = 9.5 Hz, $J_{4,5}$ = 8.8 Hz, H-4), 3.57 (d, 1H, J_{gem} = 10.9 Hz, H-1''a), 3.51 (s, 3H, OCH_3), 3.53–3.47 (m, 1H, H-5''), 3.34 (d, 1H, J_{gem} = 10.9 Hz, H-1''b), 3.31 (app dq, $J_{5,6}$ = 6.4 Hz, $J_{5,4}$ = 8.8 Hz, H-5), 3.25 (app t, 1H, $J_{4',3'}$ = $J_{4',5'}$ = 9.3 Hz, H-4'), 1.32 (d, 3H, $J_{6,5}$ = 6.4 Hz, H-6), 1.17 (d, 3H, $J_{6',5'}$ = 6.1 Hz, H-6'); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 139.2 (Ar), 138.8 (Ar), 138.5 (Ar), 137.6 (Ar), 136.8 (Ar), 135.9 (Ar), 131.6 (Ar), 131.3 (Ar), 129.5 (Ar), 128.41 (2C, Ar), 128.39 (2C, Ar), 128.15 (2C, Ar), 128.11 (2C, Ar), 127.8 (2C, Ar), 127.7 (2C, Ar), 127.62 (2C, Ar), 127.61 (2C, Ar), 127.57 (2C, Ar), 127.3 (Ar), 127.2 (Ar), 106.5 (C-

2''), 102.6 (C-1, $J_{C1,H1}$ = 152.9 Hz), 101.4 (C-1', $J_{C1',H1'}$ = 173.9 Hz), 84.3 (C-3''), 81.8 (C-4'), 81.7 (C-4), 80.9 (C-4''), 80.3 (C-3), 78.3 (C-2), 75.2 (Ar*C*H_2), 74.4 (Ar*C*H_2), 74.2 (Ar*C*H_2), 73.33 (C-2'), 73.26 (Ar*C*H_2), 72.1 (C-5), 71.0 (C-3'), 70.4 (C-5''), 69.7 (C-1''), 69.5 (Ar*C*H_2), 69.0 (Ar*C*H_2), 67.8 (C-5'), 57.1 (OCH_3), 18.1 (C-6), 17.9 (C-6'); HRMS (ESI) calcd. for $C_{54}H_{62}NaO_{13}$ $[M+Na]^+$ 941.4083; found 941.4080.



Methyl 2-*O*-acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-[1-*O*-benzyl-3,4-*O*-xylylidene-β-D-*threo*-pent-2-ulofuranosyl-(2→2)]-4-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-β-L-rhamnopyranoside (64). A mixture of **63**[6] (8.8 mg, 0.0179 mmol), **62** (13.7 mg, 0.0149 mmol), and 4Å molecular sieves in CH_2Cl_2 (1.0 mL) was stirred under an Ar atmosphere at room temperature for 30 min. The mixture was then cooled to 0 ºC and *N*-iodosuccinimide (4.8 mg, 0.0215 mmol) and silver triflate (0.9 mg, 3.6 μmol) were added. After stirring for 2 h at 0 ºC, triethylamine was added. The reaction was warmed to room temperature and then a small amount of water was added, followed by solid $Na_2S_2O_3 \cdot 5H_2O$ until the solution was colorless. The solution was then dried over $MgSO_4$, filtered and the filtrate concentrated under reduced pressure. The resulting residue was purified by column chromatography (4:1, hexane–EtOAc) to give **64** (17.5 mg, 91%) as a colorless oil. $[\alpha]^{25}_D$ +25.0 (*c* 1.3, $CHCl_3$); R_f 0.36 (2:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 700 MHz)

δ_H 7.47–7.44 (m, 3H, ArH), 7.38–7.15 (m, 29H, ArH), 6.98–6.94 (m, 2H, ArH), 5.51 (br s, 1H), 5.15–5.07 (m, 3H), 4.96 (d, 1H, J_{gem} = 13.0 Hz, ArCH_2), 4.97 (d, 1H, J_{gem} = 11.1 Hz, ArCH_2), 4.87 (d, 1H, J_{gem} = 11.1 Hz, ArCH_2), 4.84 (d, 1H, J_{gem} = 11.1 Hz, ArCH_2), 4.77–4.72 (m, 3H, ArCH_2), 4.66–4.54 (m, 5H, ArCH_2), 4.41–4.32 (m, 4H), 4.20–4.11 (m, 5H), 4.02–3.94 (m, 2H), 3.86–3.84 (m, 1H), 3.75–3.71 (m 1H), 3.64–3.55 (m, 5H) 3.53–3.50 (m, 4H, OCH_3), 3.40 (app t, 1H, J = 9.2 Hz), 3.33–3.28 (m, 1H), 2.06 (s, 3H, CH_3CO), 1.28 (d, 3H, $J_{6,5}$ = 6.1 Hz), 1.18 (d, 3H, J = 6.1 Hz), 1.12 (d, 3H, J = 6.1 Hz); ^{13}C NMR ($CDCl_3$, 175 MHz) δ_C 170.3 (C=O), 139.0 (Ar), 138.9 (Ar), 138.49 (Ar), 138.44 (Ar), 138.34 (Ar), 138.25 (Ar), 136.9 (Ar), 136.8 (Ar), 131.6 (Ar), 131.3 (Ar), 129.4 (Ar), 129.2 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.36 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.9 (Ar), 127.84 (Ar), 127.79 (Ar), 127.7 (Ar), 127.6 (Ar), 127.6 (Ar), 127.4 (Ar), 127.33 (Ar), 107.1, 102.8, 101.6, 99.3, 82.8, 82.2, 80.6, 80.5, 80.1, 80.0, 78.8, 78.4, 75.7, 75.6, 75.5, 74.7, 74.4, 73.4, 72.5, 72.2, 71.9, 70.4, 69.4, 69.3, 69.2, 69.1, 68.8, 68.5, 57.3, 21.2 (*C*H_3CO), 18.5, 18.2, 18.1; HRMS (ESI) calcd. for $C_{76}H_{86}NaO_{18}$ $[M+Na]^+$ 1309.5706; found 1309.5706.



Methyl 2-*O*-benzyl-3,4-*O*-xylylidene-α-D-*threo*-pent-2-ulofuranosyl-(2→2)-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-4-*O*-benzyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-β-L-rhamnopyranoside (65). To a solution of the **64** (17.5

mg, 0.013 mmol) in CH_3OH (1.0 mL) was added sodium methoxide (0.06 mg, 1.3 μmol) and the reaction mixture was stirred at room temperature. After stirring for 24 h, the reaction mixture was neutralized by the addition of Amberlite IR-120 H^+ resin. The solution was filtered and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography (2:1, hexane–EtOAc) to give **65** (15.2 mg, 93%) as a colorless oil. $[\alpha]^{25}_D$ +11.4 (*c* 1.0, $CHCl_3$); R_f 0.41 (1:1, hexane–EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.45–7.41 (m, 2H, ArH), 7.37–7.22 (m, 28H, ArH), 7.20–7.16 (m, 1H, ArH), 7.15–7.10 (m, 1H, ArH), 7.09–7.07 (m, 2H, ArH), 5.09 (d, 1H, J = 1.3 Hz), 5.06–4.98 (m, 3H), 4.88 (d, 1H, J_{gem} = 11.0 Hz, ArCH_2), 4.83–4.67 (m, 6H, ArCH_2), 4.65–4.58 (m, 3H, ArCH_2), 4.55 (d, 1H, J_{gem} = 11.0 Hz, ArCH_2), 4.46 (d, 1H, J_{gem} = 11.0 Hz, ArCH_2), 4.42–4.36 (m, 2H), 4.35 (s, 1H), 4.26–4.19 (m, 2H), 4.13–4.10 (m, 1H), 4.04–3.96 (m, 3H), 3.80 (d, 1H, J = 2.7 Hz), 3.76 (dd, 1H, J = 2.7, 9.2 Hz), 3.72–3.65 (m, 3H), 3.62 (app t, 1H, J = 9.2 Hz), 3.58–3.50 (m, 6H), 3.46 (d, 1H, J = 11.2 Hz), 3.38–3.29 (m, 2H), 1.37 (d, 3H, J = 6.2 Hz), 1.18 (d, 3H, J = 6.2 Hz), 1.15 (d, 3H, J = 6.2 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 138.9 (Ar), 138.64 (Ar), 138.55 (Ar), 138.53 (Ar), 138.4 (Ar), 138.1 (Ar), 136.9 (Ar), 136.7 (Ar), 131.7 (Ar), 131.2 (Ar), 129.4 (Ar), 129.3 (Ar), 129.3 (Ar), 128.7 (Ar), 128.6 (Ar), 128.5 (Ar), 128.43 (Ar), 128.37 (Ar), 128.26 (Ar), 128.15 (Ar), 128.09 (Ar), 127.88 (Ar), 127.85 (Ar), 127.77 (Ar), 127.73 (Ar), 127.61 (Ar), 127.58 (Ar), 127.54 (Ar), 107.3, 102.8, 101.7, 101.6, 82.1, 81.0, 80.9, 80.3, 80.02, 80.00, 78.6, 78.4, 75.8, 75.3, 75.1, 74.5, 73.3, 73.3, 72.8, 72.2, 71.6, 70.5, 70.1, 69.52, 69.50, 69.41, 68.9, 68.3, 57.3, 18.4, 18.1, 18.0; HRMS (ESI) calcd. for $C_{74}H_{84}NaO_{17}$ $[M+Na]^+$ 1267.5601 found 1267.5608.

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Recorded on:	u500, Jan 25 2018	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
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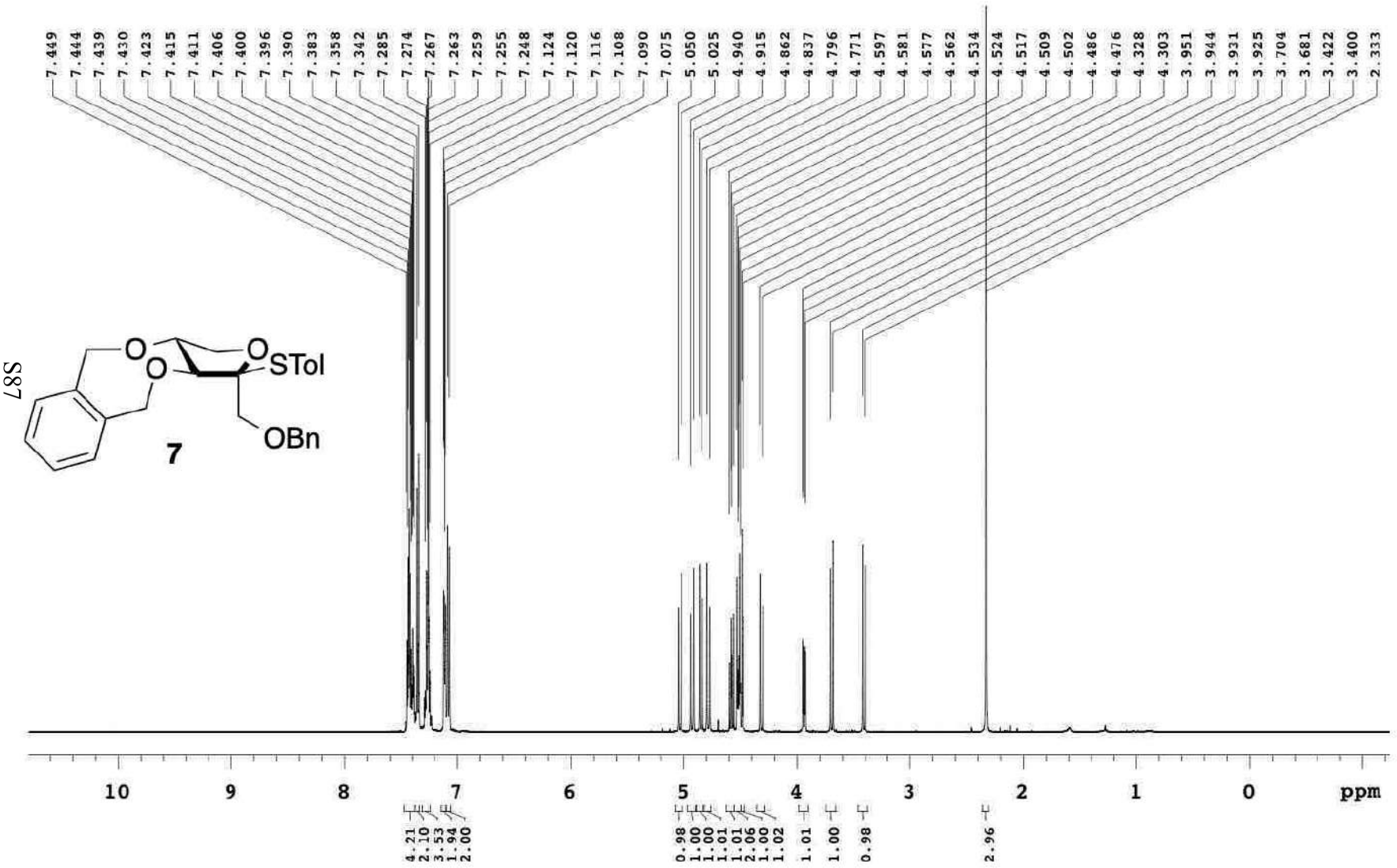

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Recorded on:	u500, Jan 25 2018	Sweep Width(Hz):	33783.8	Acquisiton Time(s):	1	Relaxation Delay(s):	1
Pulse Sequence:	s2pul	Digital Res.(Hz/pt):	0.26	Hz per mm(Hz/mm):	109.99	Completed Scans	32

Bo-Shun, Ball-XYL-042-Bn
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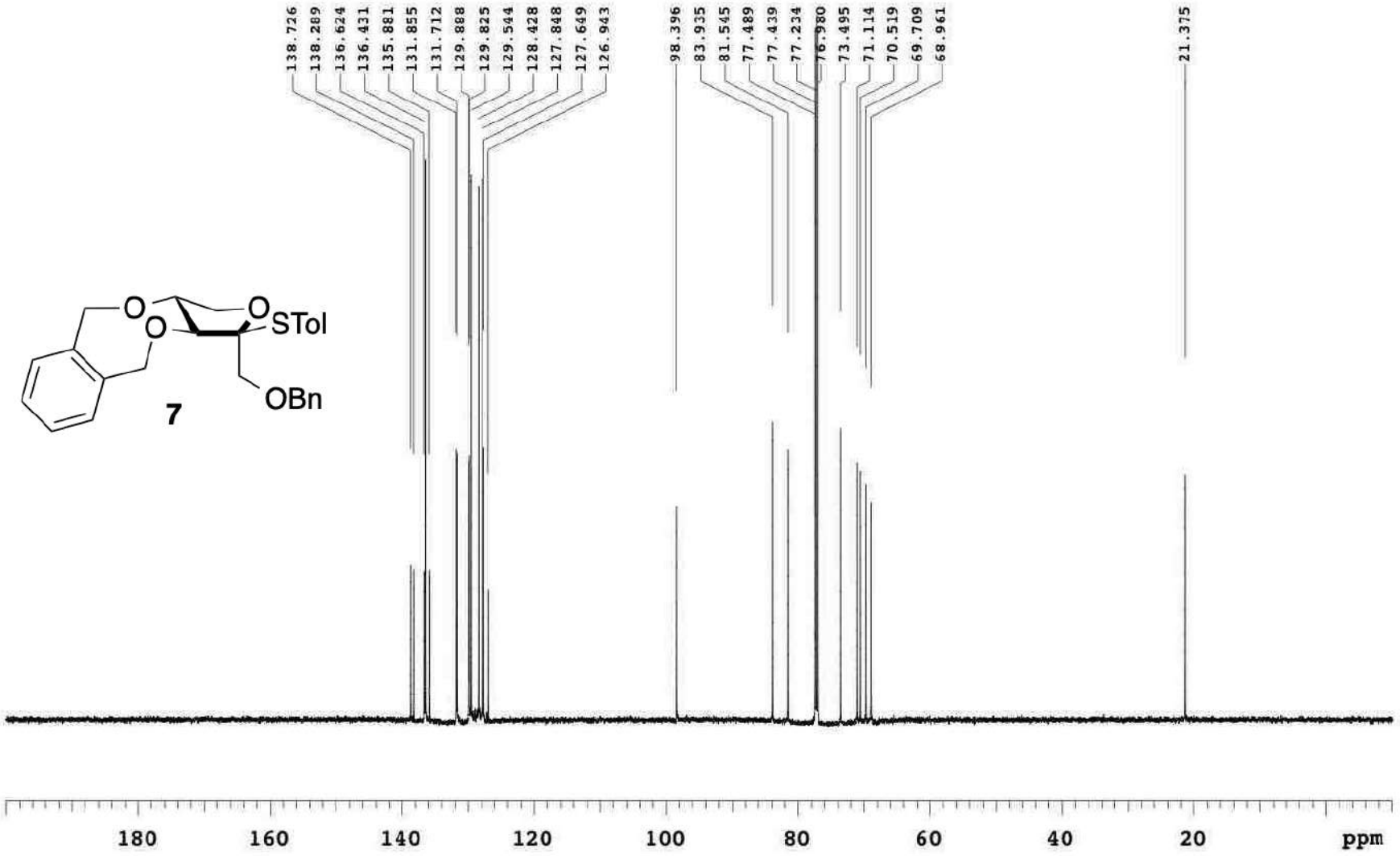

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Recorded on:	u500, Jun 24 2016	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	25.04	Completed Scans	16

Bo-Shun, Ball-XYL-042

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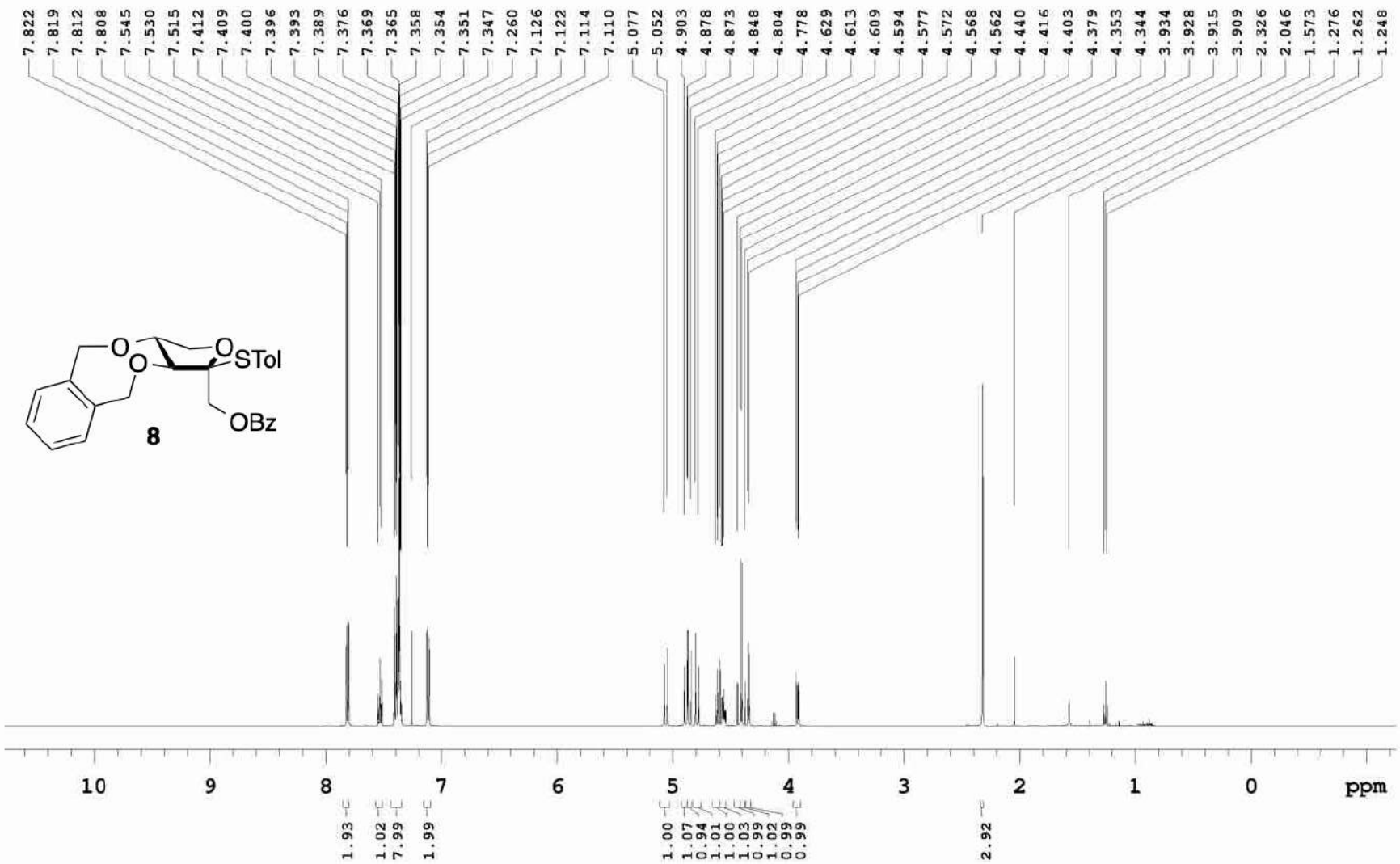

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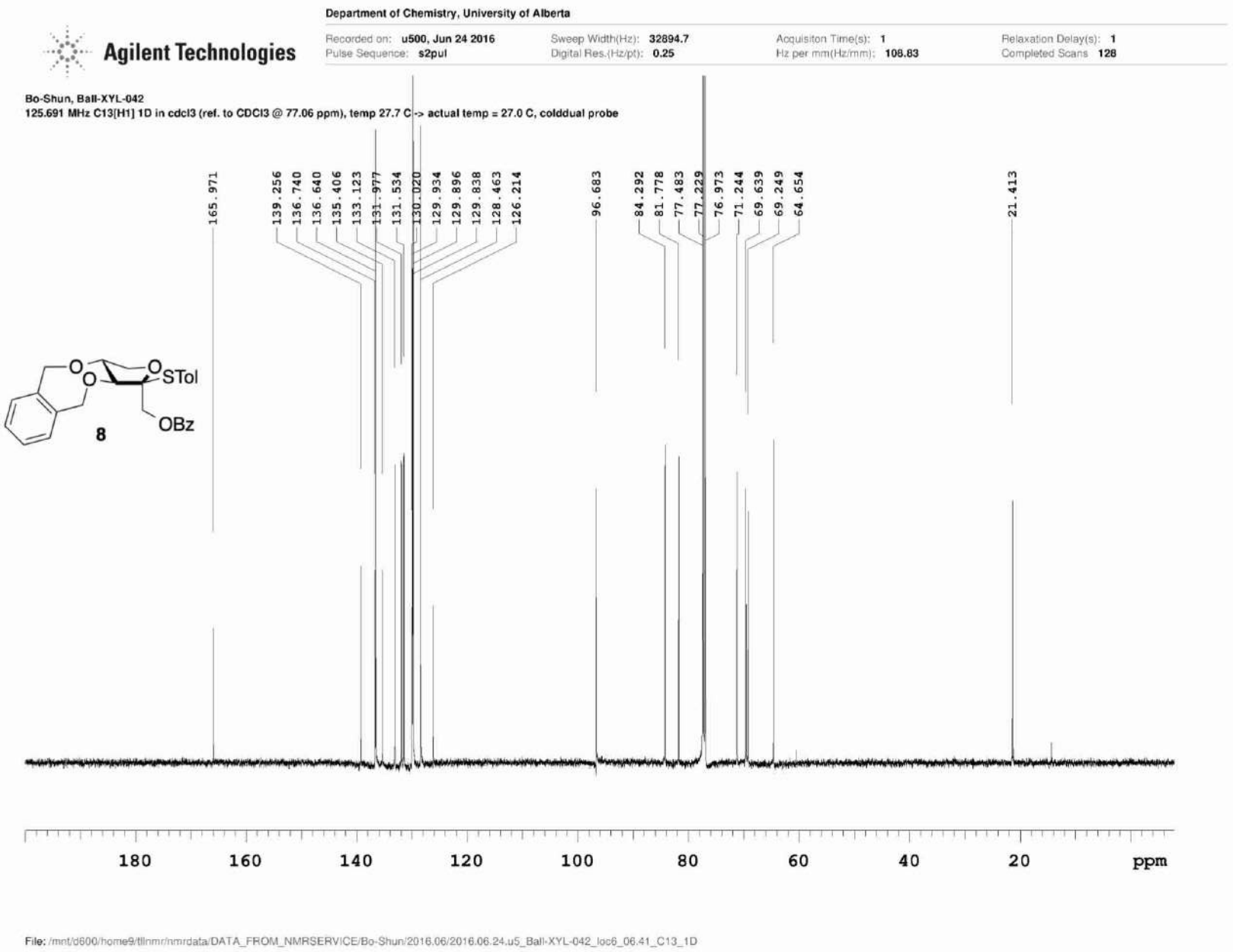
Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Jun 24 2016
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Hz per mm(Hz/mm): 108.83
Relaxation Delay(s): 1
Completed Scans 128
Bo-Shun, Ball-XYL-042
125.691 MHz C13[H1] 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
165.971
139.256
136.740
136.640
135.406
133.123
131.977
131.534
130.020
129.934
129.896
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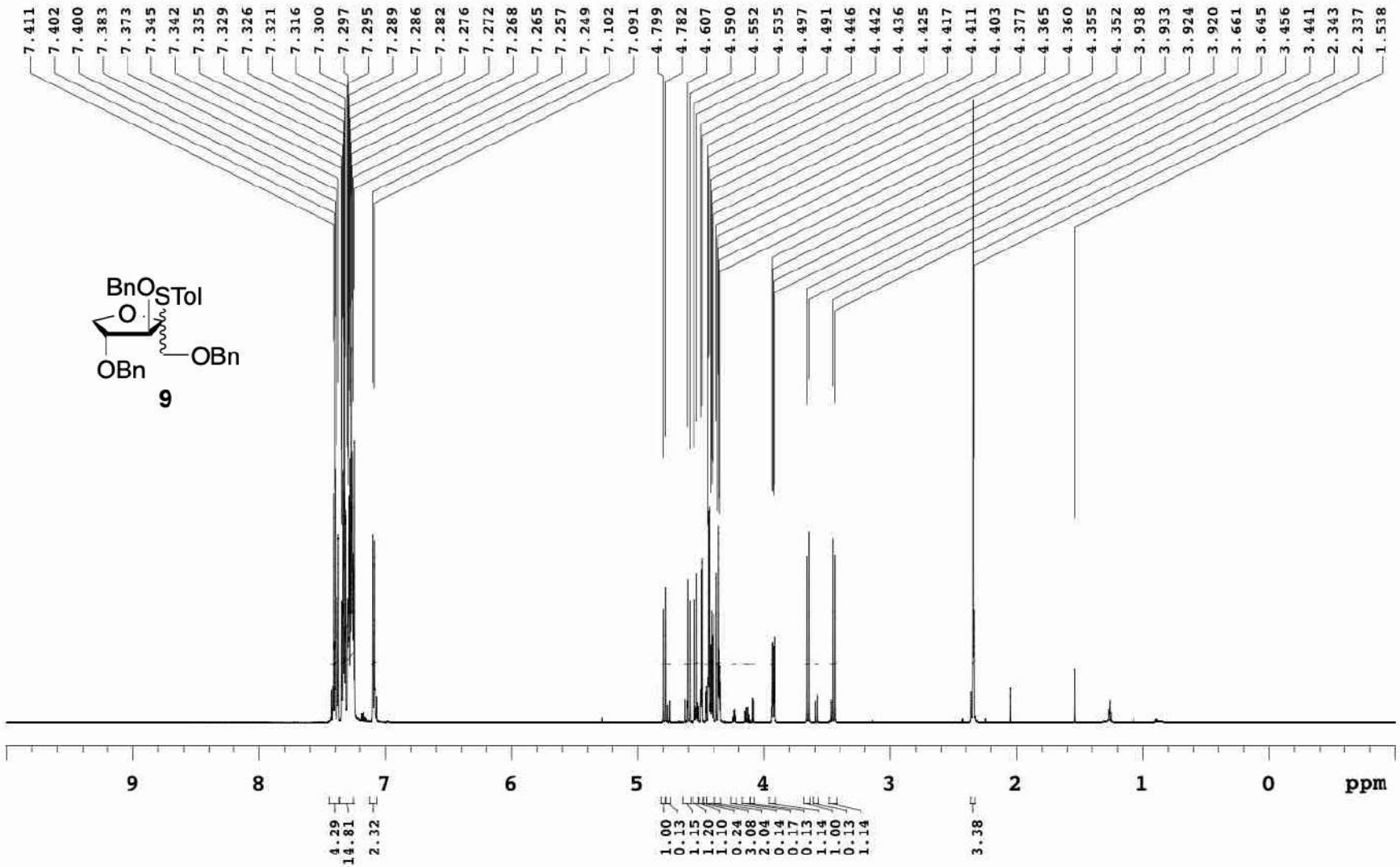
126.214
96.683
84.292
81.778
77.483
77.229
76.973
71.244
69.639
69.249
64.654
21.413
STol
OBz
8
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tllnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.06/2016.06.24.u5_Ball-XYL-042_loc6_06.41_C13_1D

Department of Chemistry, University of Alberta

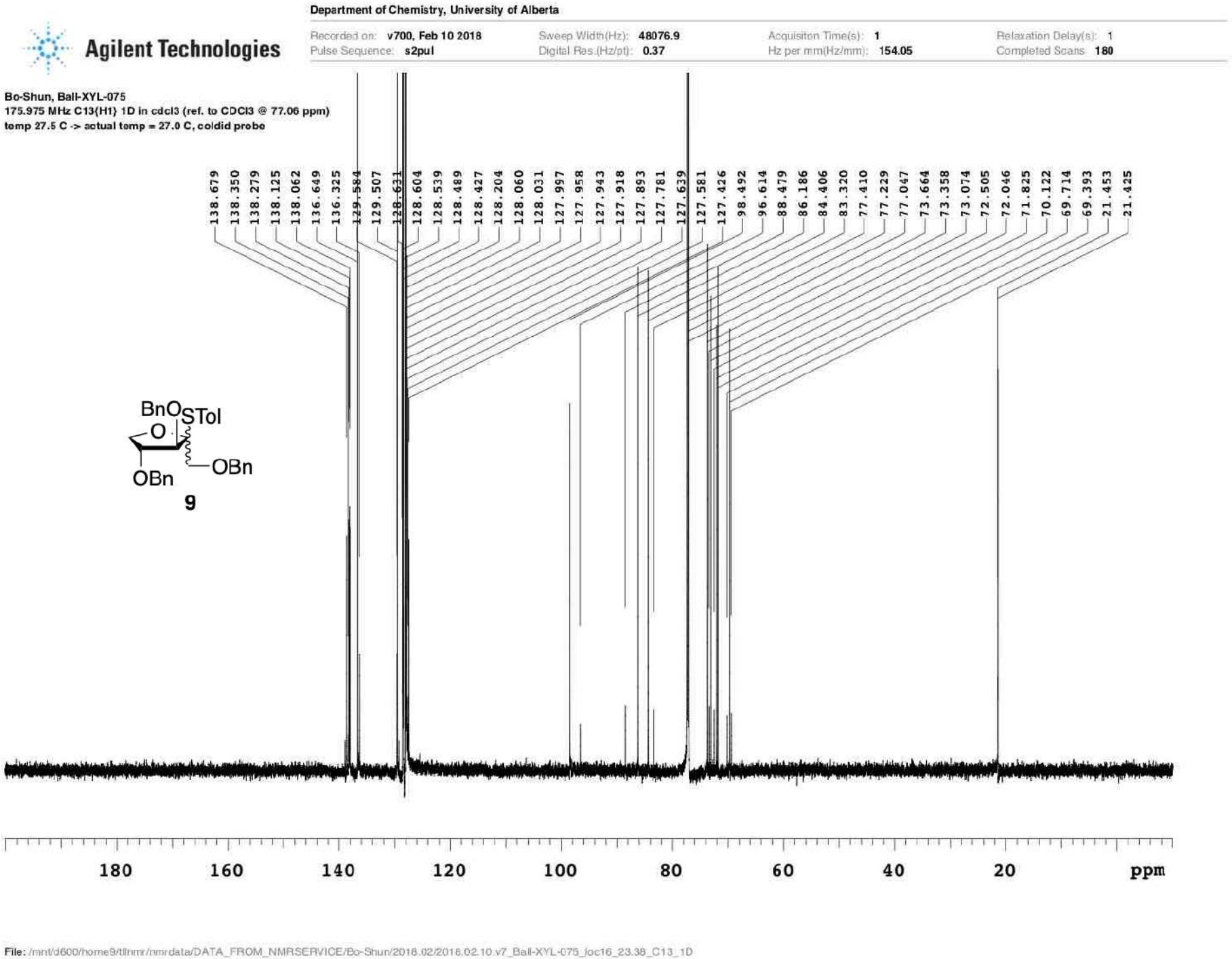
Agilent Technologies

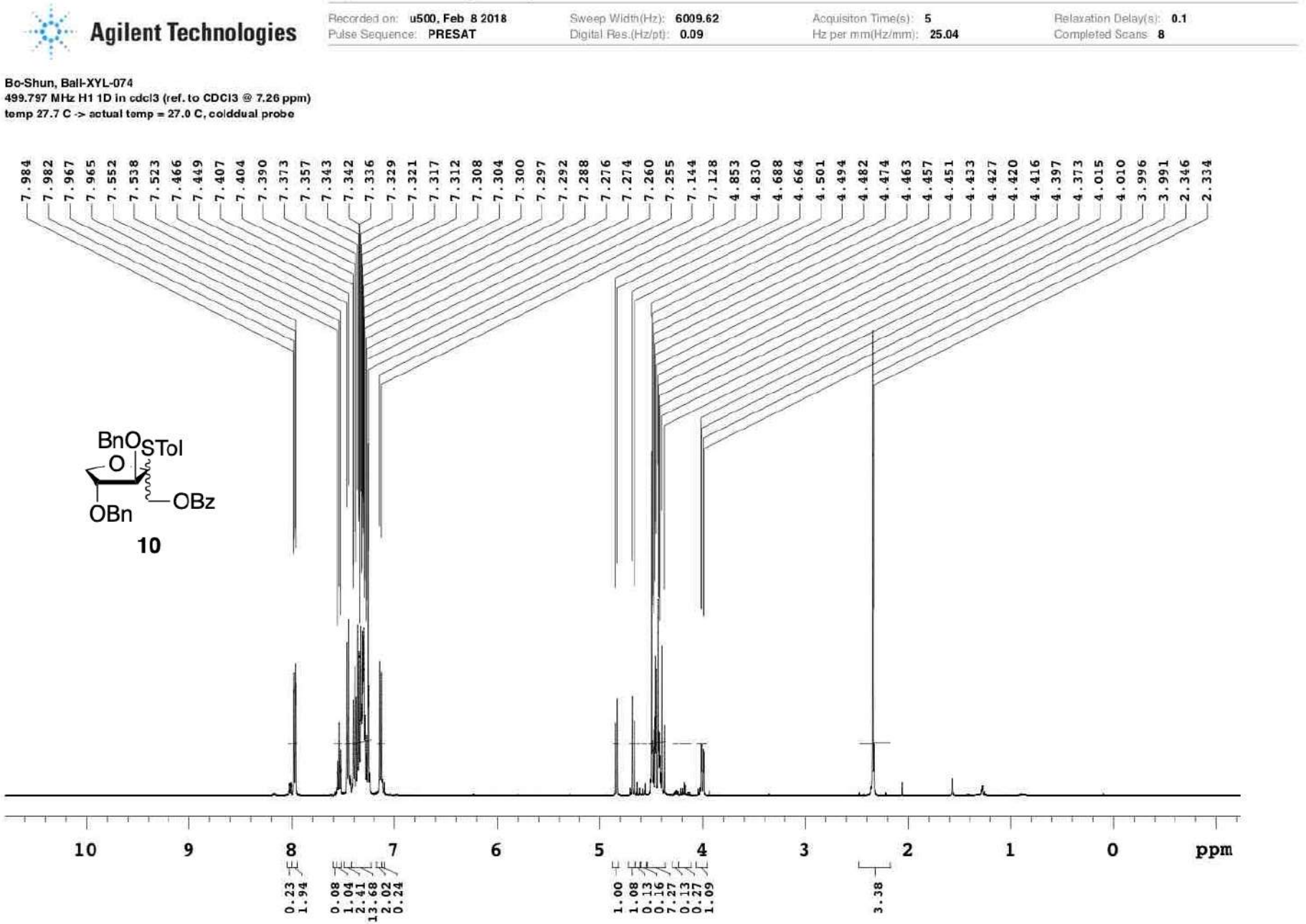
Recorded on:	v700, Feb 10 2018	Sweep Width(Hz):	8389.26	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.13	Hz per mm(Hz/mm):	32.09	Completed Scans	8

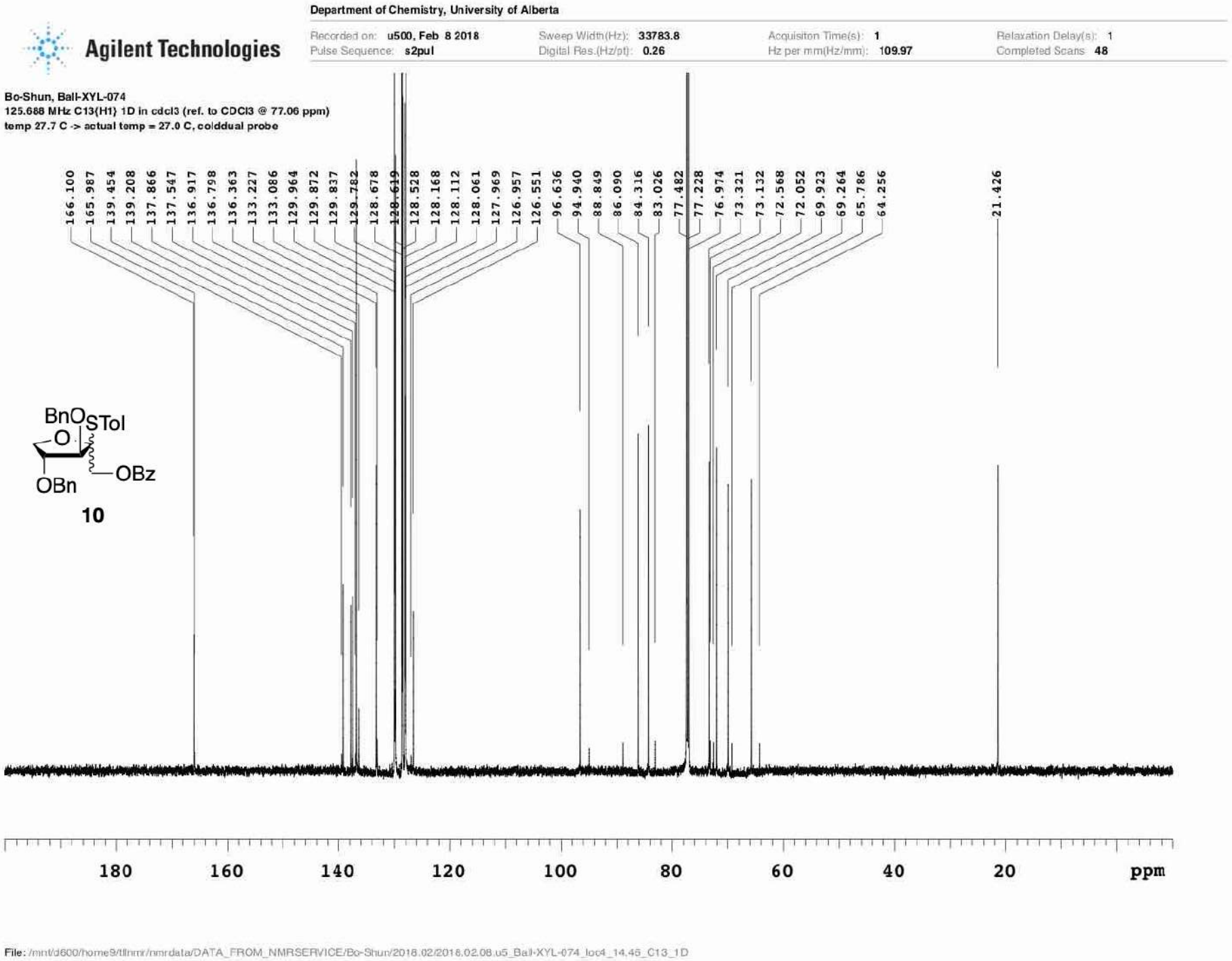
Bo-Shun, Ball-XYL-075
699.762 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe



File: /mnt/d600/home9/tlhnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2018.02/2018.02.10.v7_Ball-XYL-075_loc16_23.37_H1_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: v700, Feb 10 2018
Pulse Sequence: s2pul
Sweep Width(Hz): 48076.9
Digital Res.(Hz/pt): 0.37
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 154.05
Relaxation Delay(s): 1
Completed Scans 180
Bo-Shun, Ball-XYL-075
175.975 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe
138.679
138.350
138.279
138.125
138.062
136.649
136.325
129.584
129.507
128.631
128.604
128.539
128.489
128.427
128.204
128.060
128.031
127.997
127.958
127.943
127.918
127.893
127.781
127.639
127.581
127.426
98.492
96.614
88.479
86.186
84.406
83.320
77.410
77.229
77.047
73.664
73.358
73.074
72.505
72.046
71.825
70.122
69.714
69.393
21.453
21.425
BnO
STol
O
OBn
OBn
9
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2018.02/2018.02.10.v7_Ball-XYL-075_loc16_23.38_C13_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Feb 8 2018
Pulse Sequence: PRESAT
Sweep Width(Hz): 6009.62
Digital Res.(Hz/pt): 0.09
Acquisiton Time(s): 5
Hz per mm(Hz/mm): 25.04
Relaxation Delay(s): 0.1
Completed Scans 8
Bo-Shun, Ball-XYL-074
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, coilddual probe
7.984 7.982 7.967 7.965 7.552 7.538 7.523 7.466 7.449 7.407 7.404 7.390 7.373 7.357 7.343 7.342 7.336 7.329 7.321 7.317 7.312 7.308 7.304 7.300 7.297 7.292 7.288 7.276 7.274 7.260 7.255 7.144 7.128 4.853 4.830 4.688 4.664 4.501 4.494 4.482 4.474 4.463 4.457 4.451 4.433 4.427 4.420 4.416 4.397 4.373 4.015 4.010 3.996 3.991 2.346 2.334
BnO
STol
O
OBz
OBn
10
10 9 8 7 6 5 4 3 2 1 0 ppm
0.23 1.94
0.08 1.04 2.41 13.68 2.02 0.24
1.00 1.08 0.13 0.16 7.27 0.13 0.27 1.09
3.38
File: /mnt/d600/home9/tlhnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2018.02/2018.02.08.u5_Ball-XYL-074_loc4_14.45_H1_1D

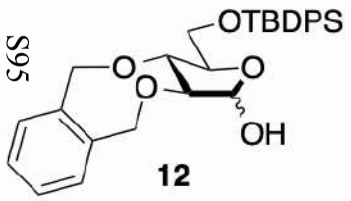

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Feb 8 2018
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.97
Relaxation Delay(s): 1
Completed Scans 48
Bo-Shun, Ball-XYL-074
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
166.100
165.987
139.454
139.208
137.866
137.547
136.917
136.798
136.363
133.227
133.086
129.964
129.872
129.837
129.782
128.678
128.619
128.528
128.168
128.112
128.061
127.969
126.957
126.551
96.636
94.940
88.849
86.090
84.316
83.026
77.482
77.228
76.974
73.321
73.132
72.568
72.052
69.923
69.264
65.786
64.256
21.426
BnO
STol
O
OBz
OBn
10
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2018.02/2018.02.08.u5_Ball-XYL-074_loc4_14.45_C13_1D

Department of Chemistry, University of Alberta

Agilent Technologies

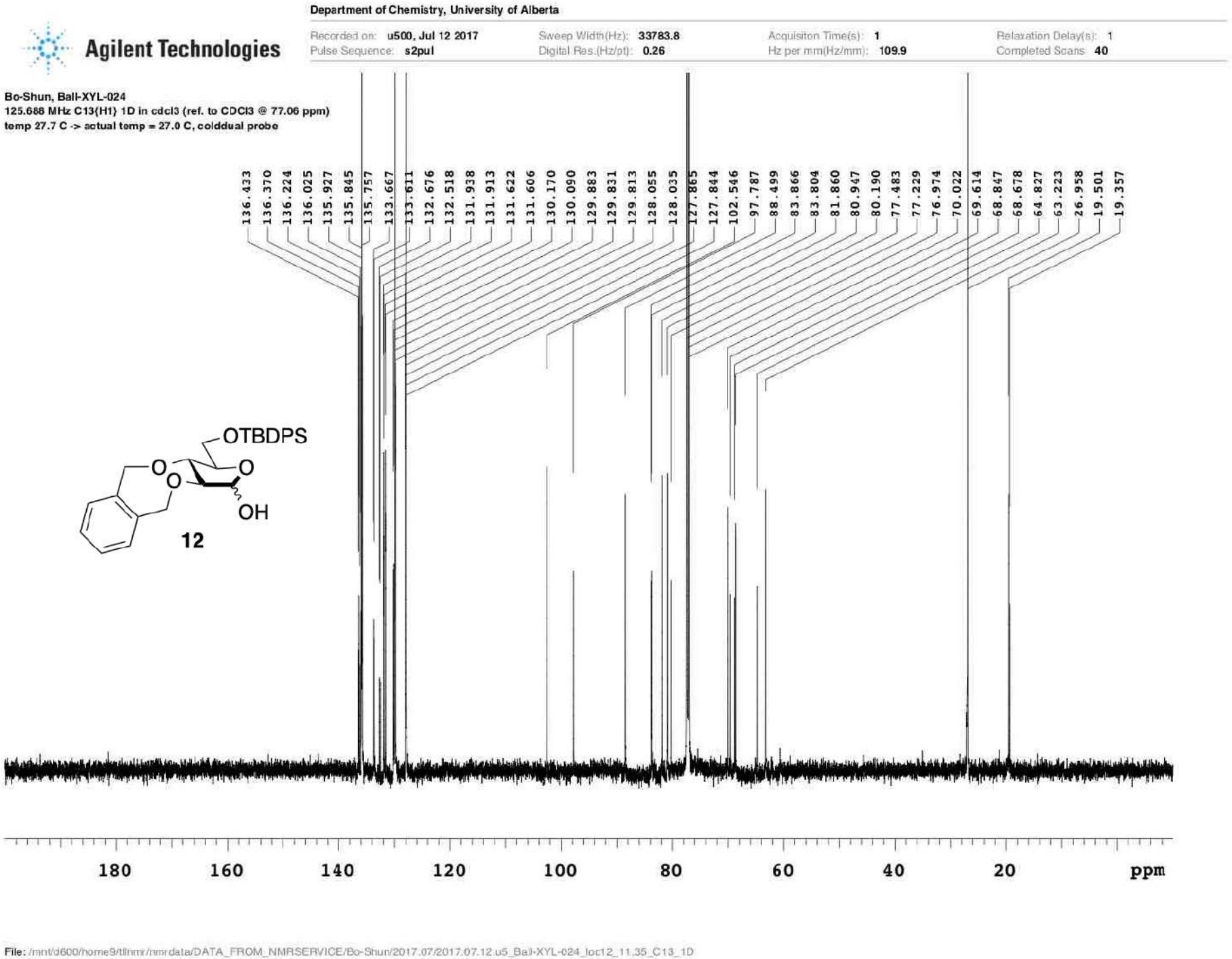
Recorded on:	u500, Jul 12 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.91	Completed Scans	8

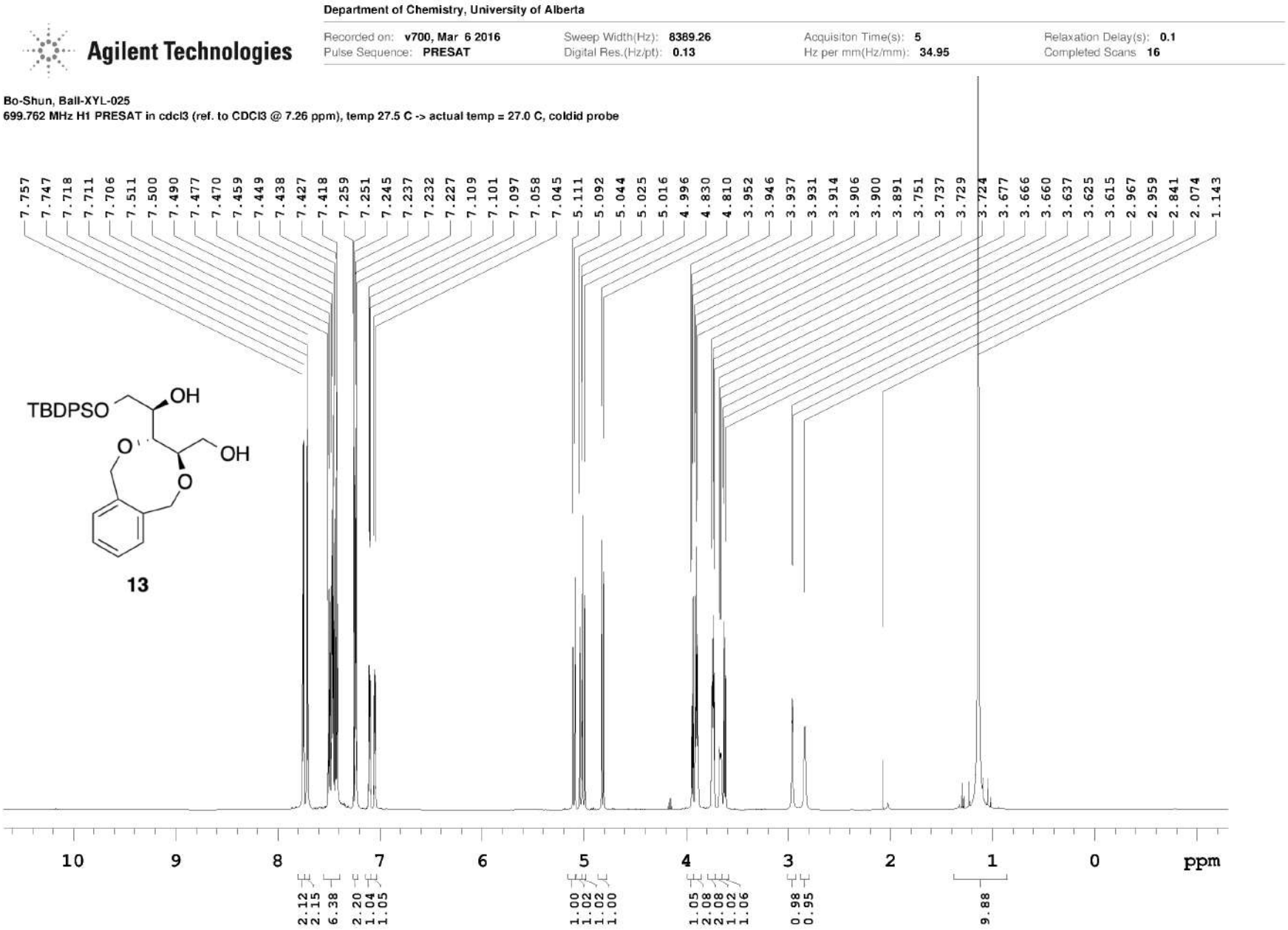
Bo-Shun, Ball-XYL-024
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, coilddual probe



12

File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.07/2017.07.12.u5_Ball-XYL-024_loc12_11.34_H1_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Jul 12 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.9
Relaxation Delay(s): 1
Completed Scans 40
Bo-Shun, Ball-XYL-024
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, coilddual probe
136.433
136.370
136.224
136.025
135.927
135.845
135.757
133.667
133.611
132.676
132.518
131.938
131.913
131.622
131.606
130.170
130.090
129.883
129.831
129.813
128.055
128.035
127.865
127.844
102.546
97.787
88.499
83.866
83.804
81.860
80.947
80.190
77.483
77.229
76.974
70.022
69.614
68.847
68.678
64.827
63.223
26.958
19.501
19.357
OTBDPS
O
O
O
OH
12
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlhnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.07/2017.07.12.u5_Ball-XYL-024_loc12_11.35_C13_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: v700, Mar 6 2016
Pulse Sequence: PRESAT
Sweep Width(Hz): 8389.26
Digital Res.(Hz/pt): 0.13
Acquisiton Time(s): 5
Hz per mm(Hz/mm): 34.95
Relaxation Delay(s): 0.1
Completed Scans 16
Bo-Shun, Ball-XYL-025
699.762 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.5 C -> actual temp = 27.0 C, coldid probe
7.757 7.747 7.718 7.711 7.706 7.511 7.500 7.490 7.477 7.470 7.459 7.449 7.438 7.427 7.418 7.259 7.251 7.245 7.237 7.232 7.227 7.109 7.101 7.097 7.058 7.045 5.111 5.092 5.044 5.025 5.016 4.996 4.830 4.810 3.952 3.946 3.937 3.931 3.914 3.906 3.900 3.891 3.751 3.737 3.729 3.724 3.677 3.666 3.660 3.637 3.625 3.615 2.967 2.959 2.841 2.074 1.143
TBDPSO
OH
OH
O
O
13
10 9 8 7 6 5 4 3 2 1 0 ppm
2.12 2.15 6.38 2.20 1.04 1.05 1.00 1.02 1.02 1.00 1.05 2.08 2.08 1.02 1.06 0.98 0.95 9.88
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.03/2016.03.6.v7_Ball-XYL-025_loc17_20.03_H1_1D

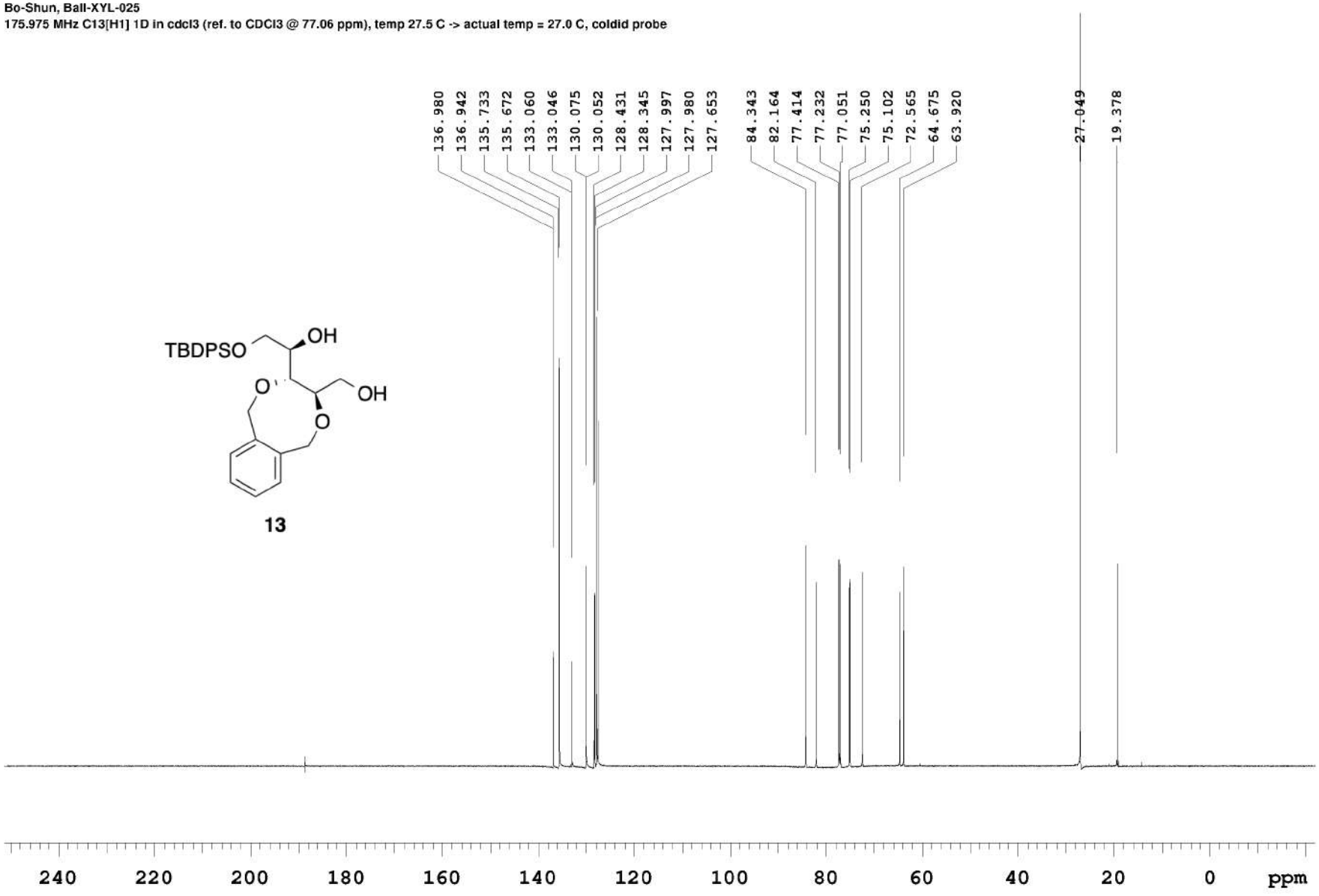
Agilent Technologies

Department of Chemistry, University of Alberta

Recorded on: v700, Mar 6 2016	Sweep Width(Hz): 48076.9	Acquisiton Time(s): 2	Relaxation Delay(s): 0.5
Pulse Sequence: s2pul	Digital Res.(Hz/pt): 0.37	Hz per mm(Hz/mm): 200.32	Completed Scans 256

Bo-Shun, Ball-XYL-025

175.975 MHz C13[H1] 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.5 C -> actual temp = 27.0 C, coldid probe



13

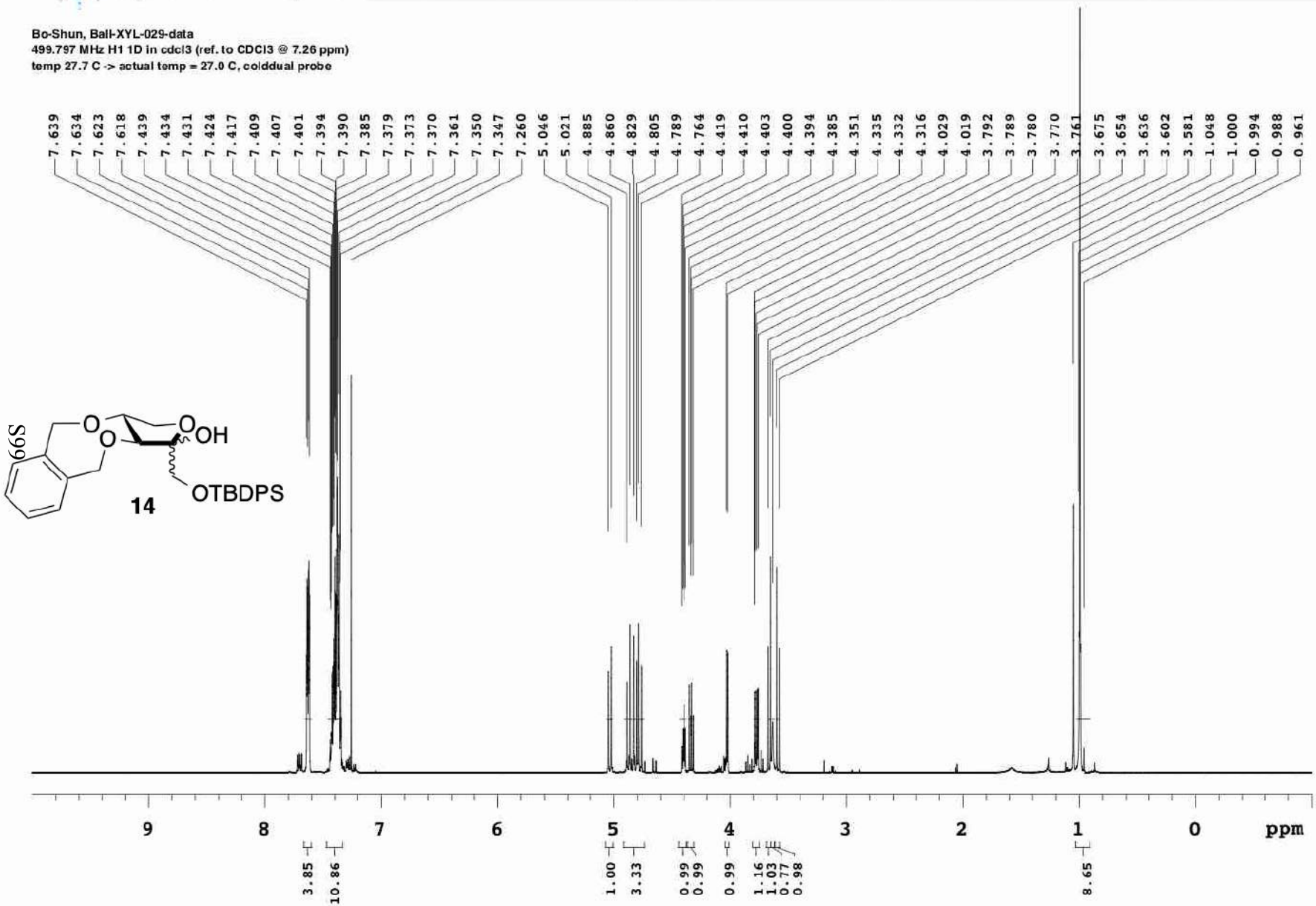
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.03/2016.03.6.v7_Ball-XYL-025_loc17_20.04_C13_1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	u500, Jan 10 2018	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.91	Completed Scans	8

Bo-Shun, Ball-XYL-029-data
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, coilddual probe



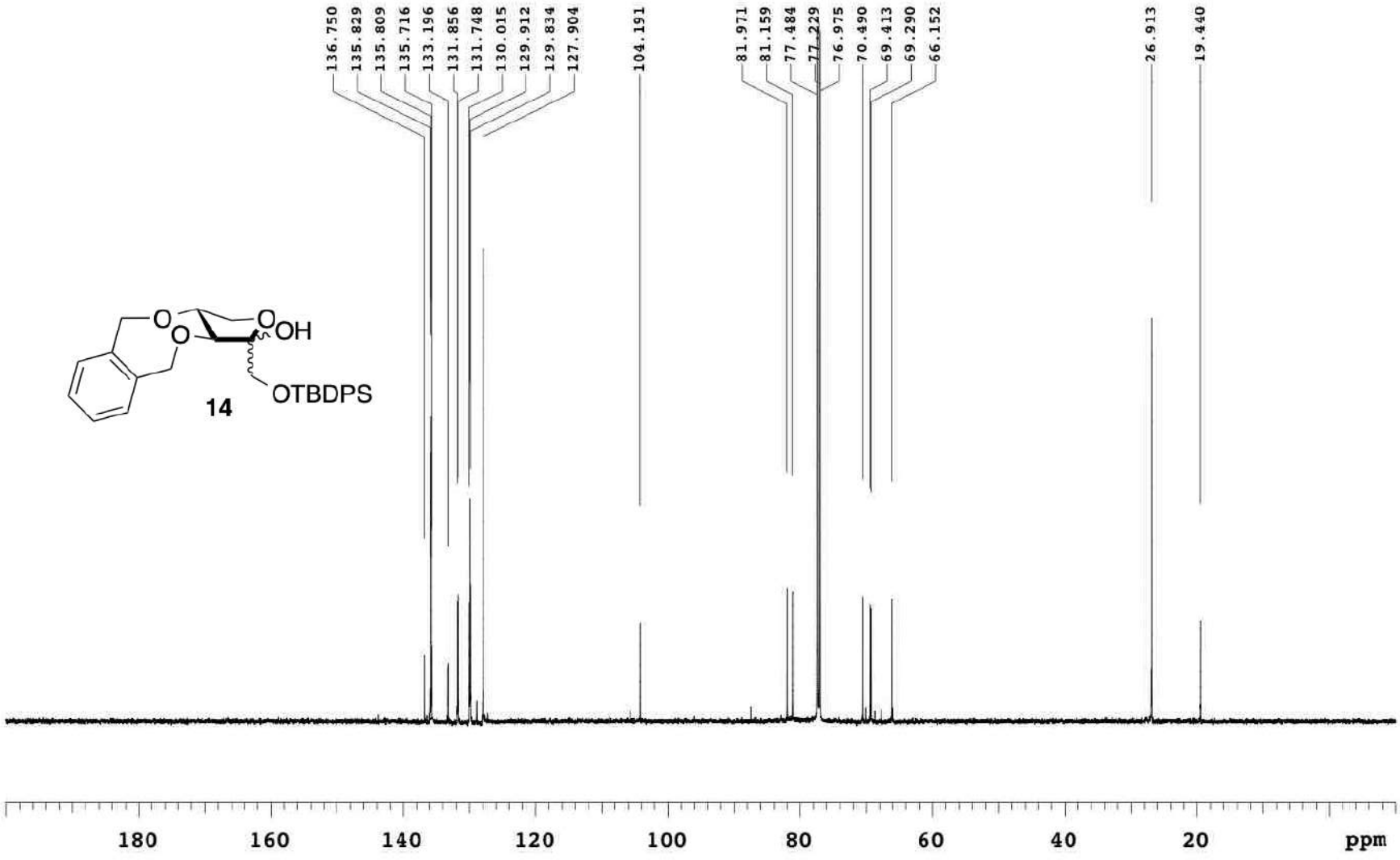
File: /mnt/d600/home9/tlinmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2018.01/2018.01.10.u5_Ball-XYL-029-data_loc1_11.42_H1_1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	u500, Jan 10 2018	Sweep Width(Hz):	33783.8	Acquisiton Time(s):	1	Relaxation Delay(s):	1
Pulse Sequence:	s2pul	Digital Res.(Hz/pt):	0.26	Hz per mm(Hz/mm):	109.97	Completed Scans	76

Bo-Shun, Ball-XYL-029-data
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe

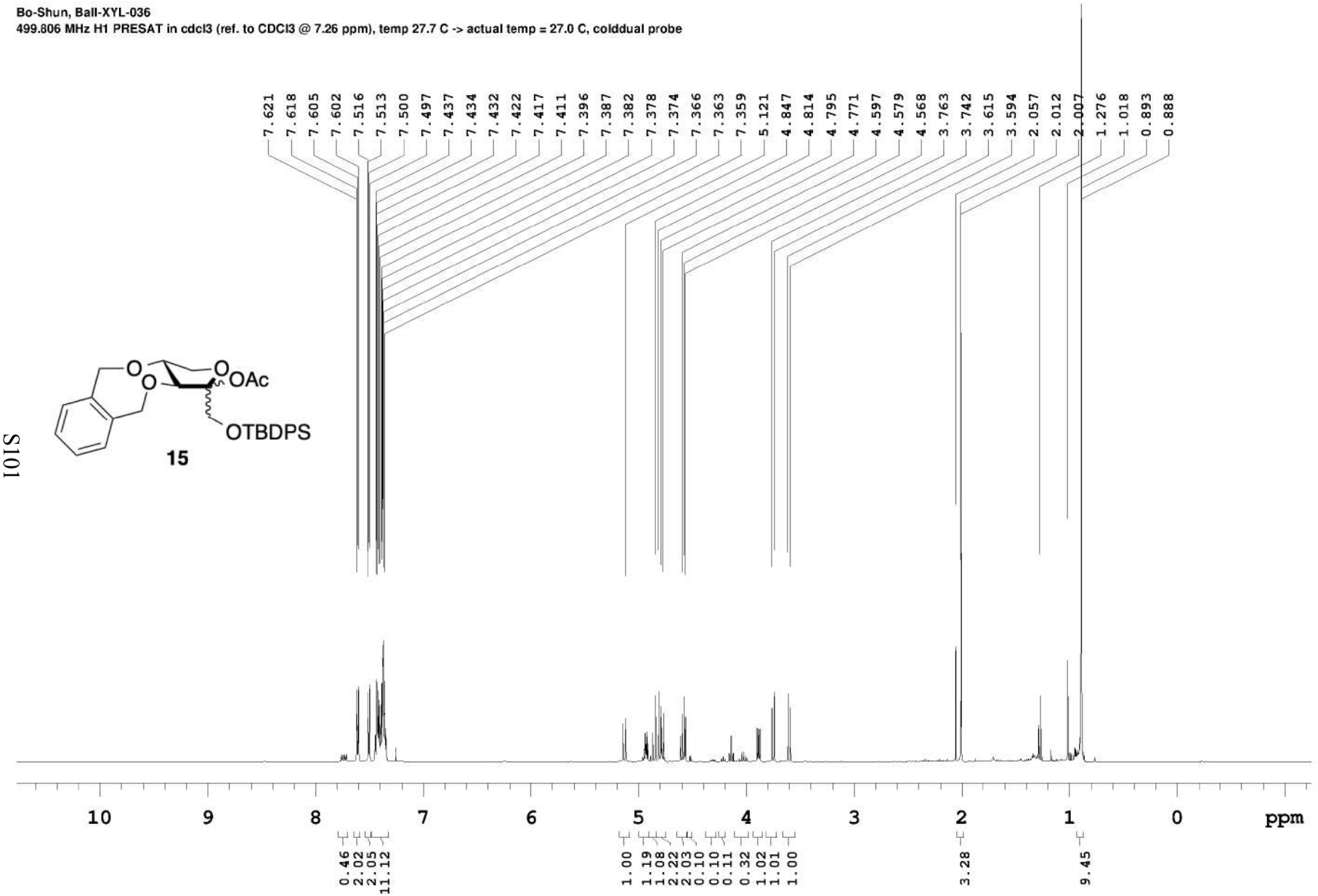


File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2018.01/2018.01.10.u5_Ball-XYL-029-data_loc1_11.43_C13_1D

Agilent Technologies

Recorded on: u500, May 28 2016 | Sweep Width(Hz): 6009.62 | Acquisiton Time(s): 5 | Relaxation Delay(s): 0.1
Pulse Sequence: PRESAT | Digital Res.(Hz/pt): 0.09 | Hz per mm(Hz/mm): 25.04 | Completed Scans 16

Bo-Shun, Ball-XYL-036
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe



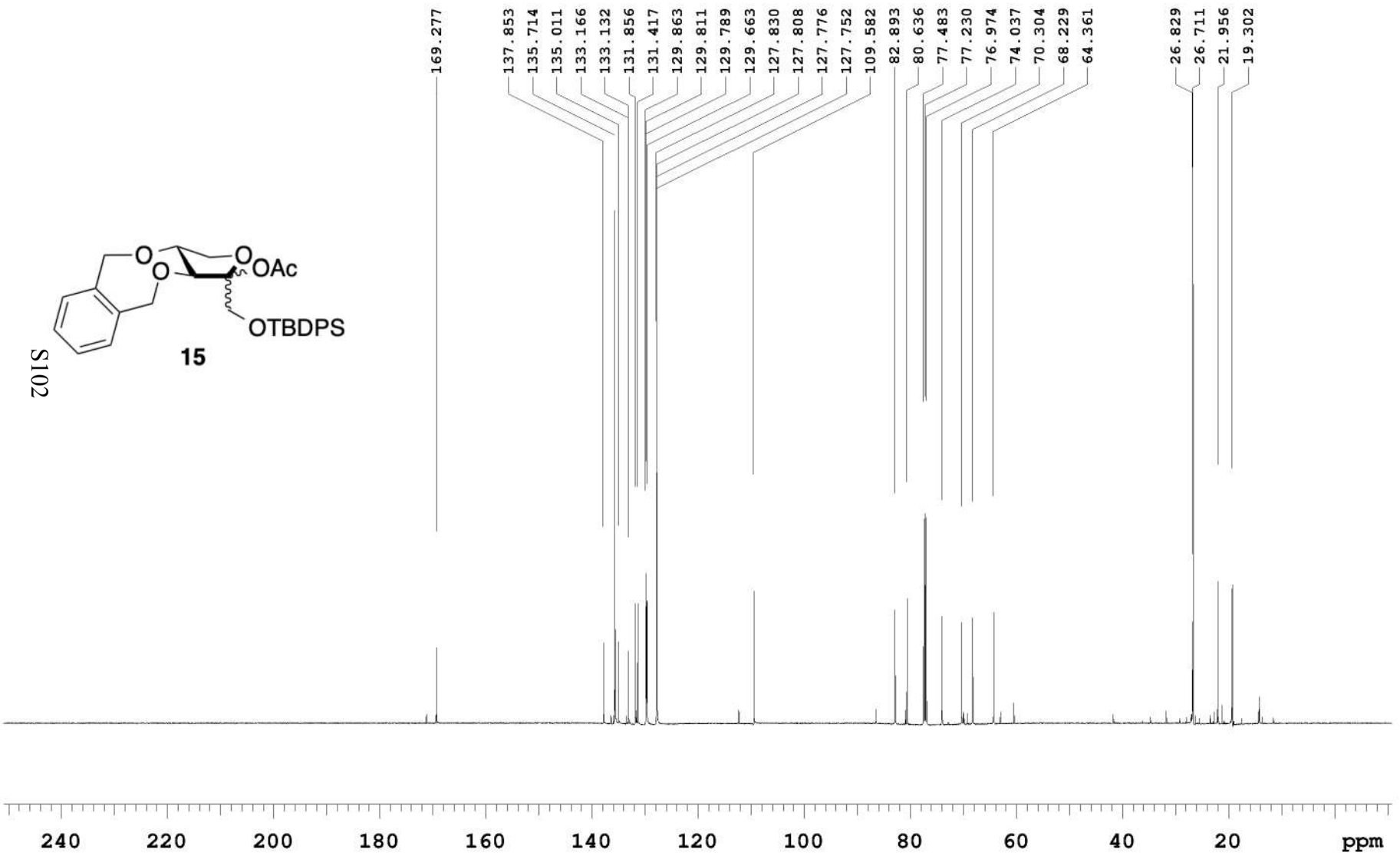
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.05/2016.05.28.u5_Ball-XYL-036_loc6_02.52_H1_1D

Agilent Technologies

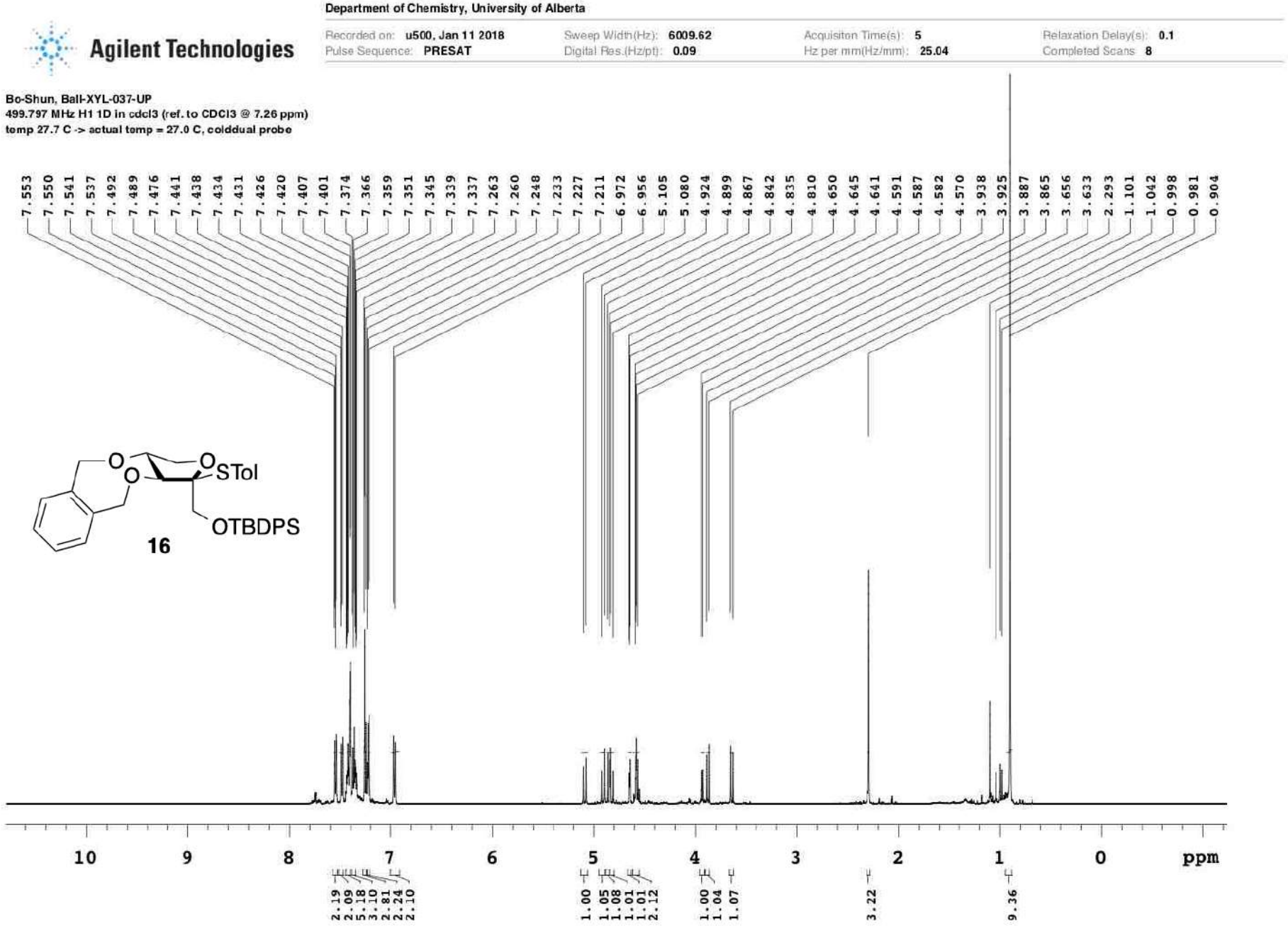
Department of Chemistry, University of Alberta

Recorded on: **u500, May 28 2016**	Sweep Width(Hz): **32894.7**	Acquisiton Time(s): **2.5**	Relaxation Delay(s): **0.1**
Pulse Sequence: **s2pul**	Digital Res.(Hz/pt): **0.25**	Hz per mm(Hz/mm): **137.06**	Completed Scans **128**

Bo-Shun, Ball-XYL-036
125.691 MHz C13[H1] 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016/2016-05-28-u5_Ball-XYL-036_loc6_02-53_C13_1D

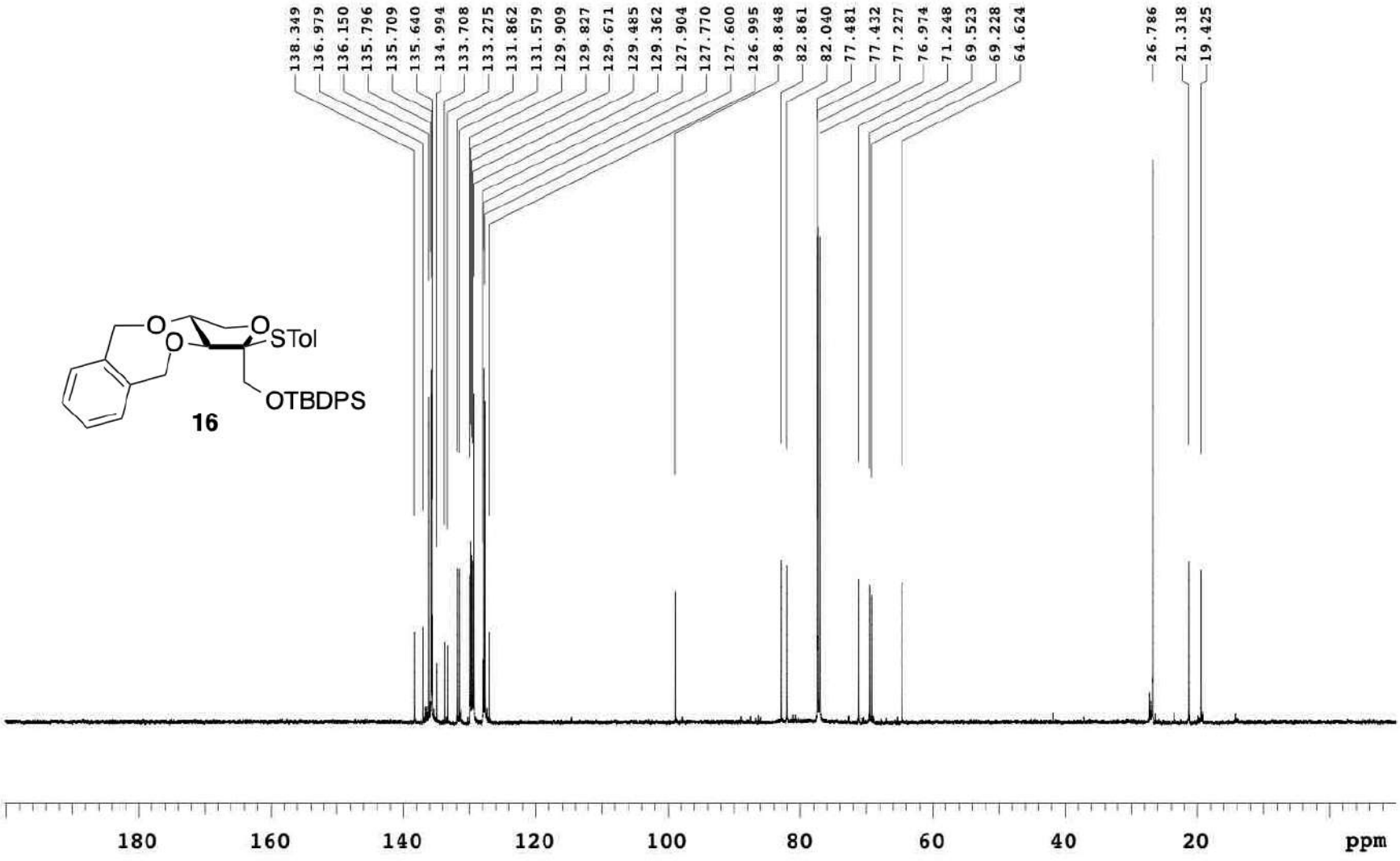

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Jan 11 2018
Pulse Sequence: PRESAT
Sweep Width(Hz): 6009.62
Digital Res.(Hz/pt): 0.09
Acquisiton Time(s): 5
Hz per mm(Hz/mm): 25.04
Relaxation Delay(s): 0.1
Completed Scans 8
Bo-Shun, Ball-XYL-037-UP
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
7.553 7.550 7.541 7.537 7.492 7.489 7.476 7.441 7.438 7.434 7.431 7.426 7.420 7.407 7.401 7.374 7.366 7.359 7.351 7.345 7.339 7.337 7.263 7.260 7.248 7.233 7.227 7.211 6.972 6.956 5.105 5.080 4.924 4.899 4.867 4.842 4.835 4.810 4.650 4.645 4.641 4.591 4.587 4.582 4.570 3.938 3.925 3.887 3.865 3.656 3.633 2.293 1.101 1.042 0.998 0.981 0.904
STol
OTBDPS
16
10 9 8 7 6 5 4 3 2 1 0 ppm
2.19 2.09 5.18 3.10 2.81 2.24 2.10
1.00 1.05 1.08 1.01 1.01 2.12
1.00 1.04 1.07
3.22
9.36
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2018.01/2018.01.11.u5_Ball-XYL-037-UP_loc1_15.34_H1_1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	u500, Jan 11 2018	Sweep Width(Hz):	33783.8	Acquisiton Time(s):	1	Relaxation Delay(s):	1
Pulse Sequence:	s2pul	Digital Res.(Hz/pt):	0.26	Hz per mm(Hz/mm):	109.99	Completed Scans	44

Bo-Shun, Ball-XYL-037-UP
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



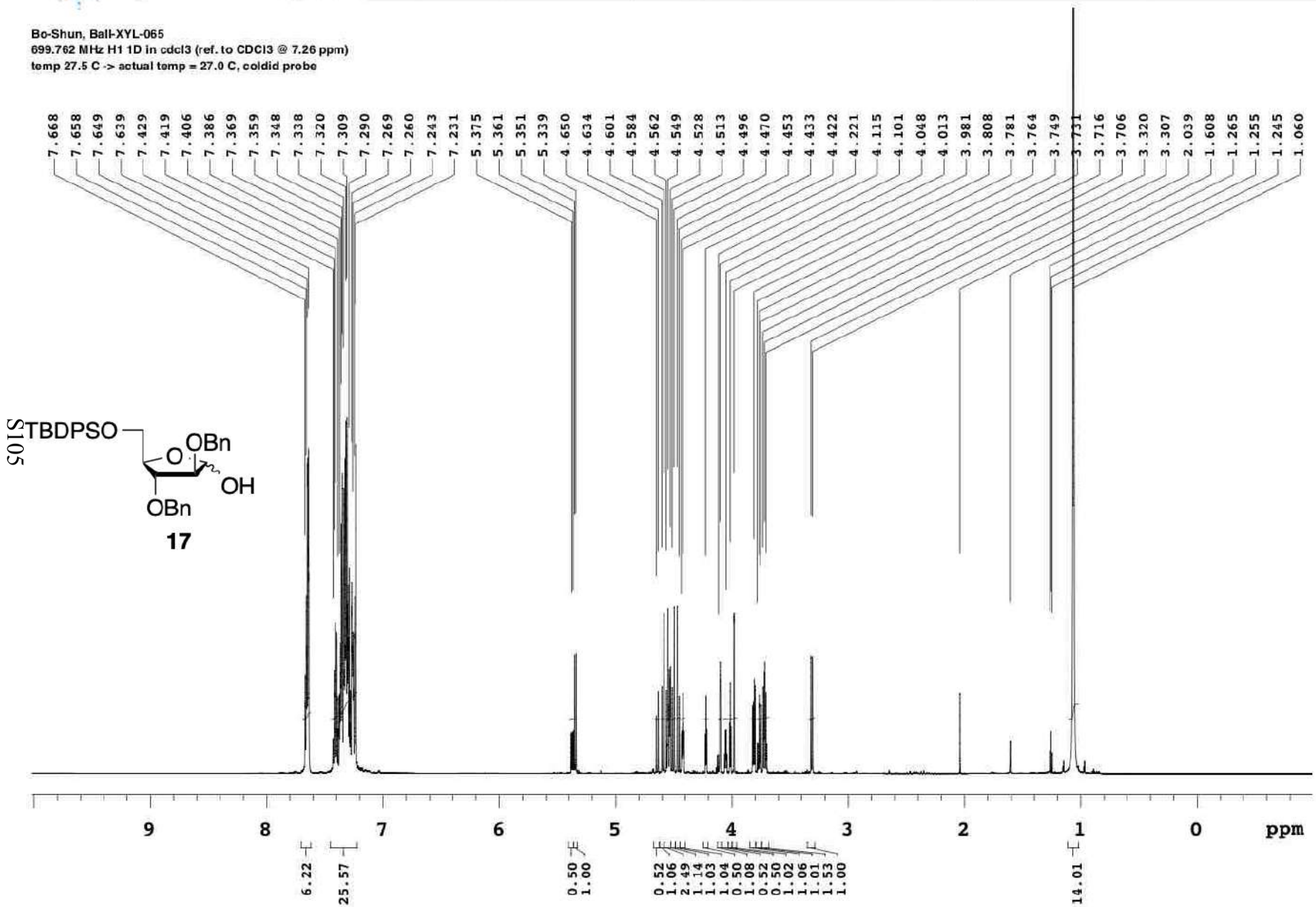
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2018.01/2018.01.11.u5_Ball-XYL-037-UP_loc1_15.35_C13_1D

Department of Chemistry, University of Alberta

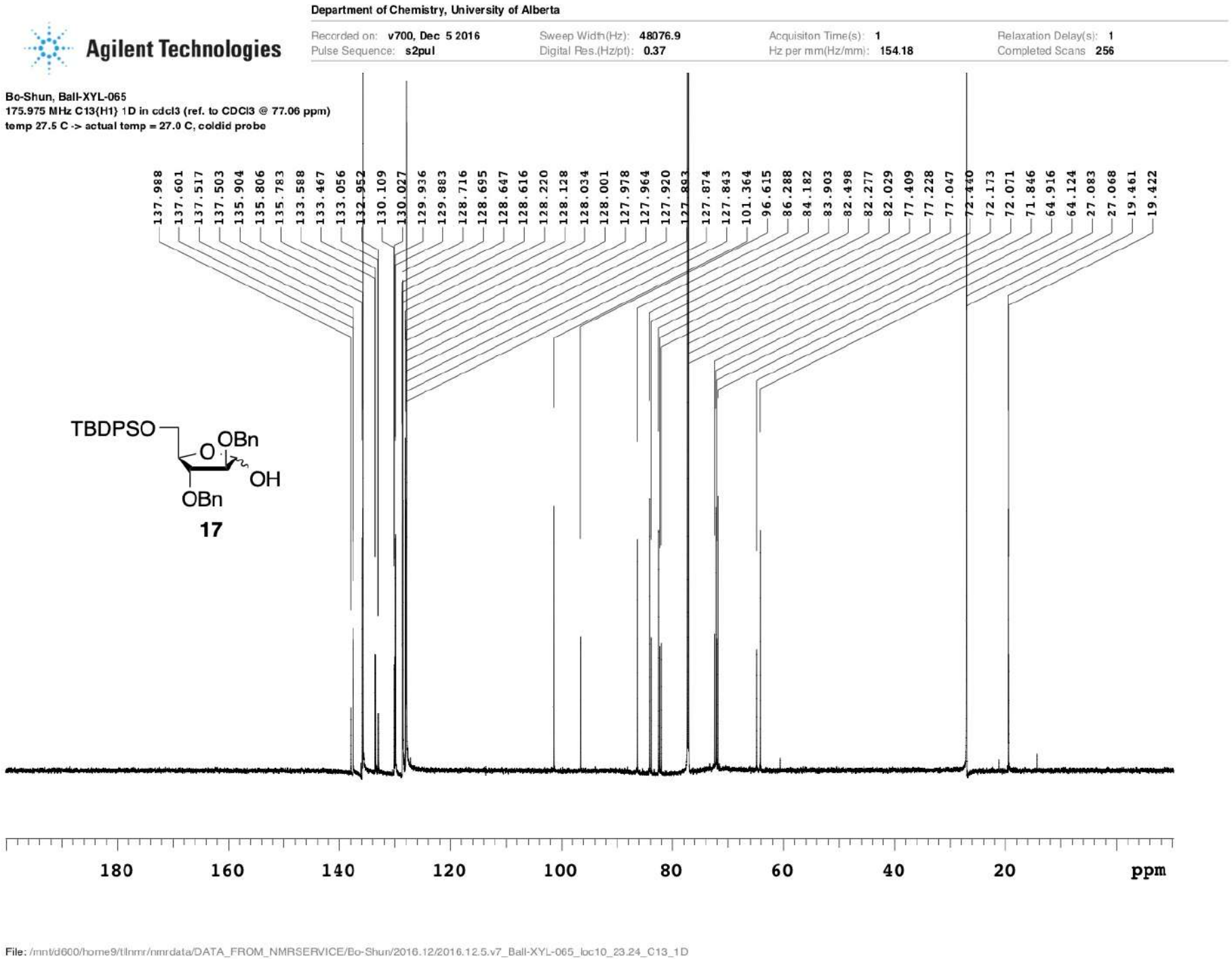
Agilent Technologies

Recorded on:	v700, Dec 5 2016	Sweep Width(Hz):	8389.26	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.13	Hz per mm(Hz/mm):	32.09	Completed Scans	16

Bo-Shun, Ball-XYL-065
699.762 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.12/2016.12.5.v7_Ball-XYL-065_loc10_23.22_H1_1D



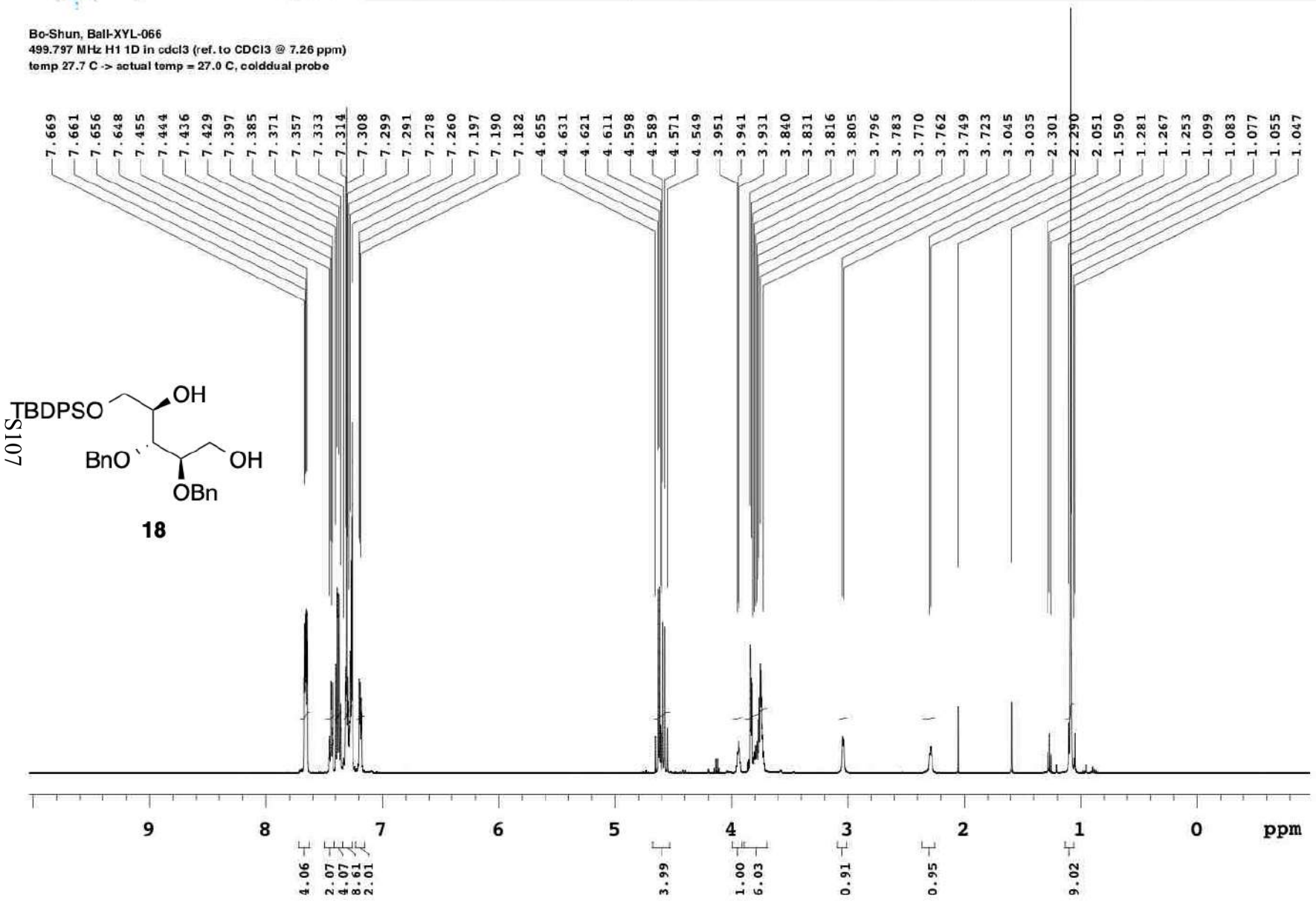
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.12/2016.12.5.v7_Ball-XYL-065_loc10_23.24_C13_1D

Department of Chemistry, University of Alberta

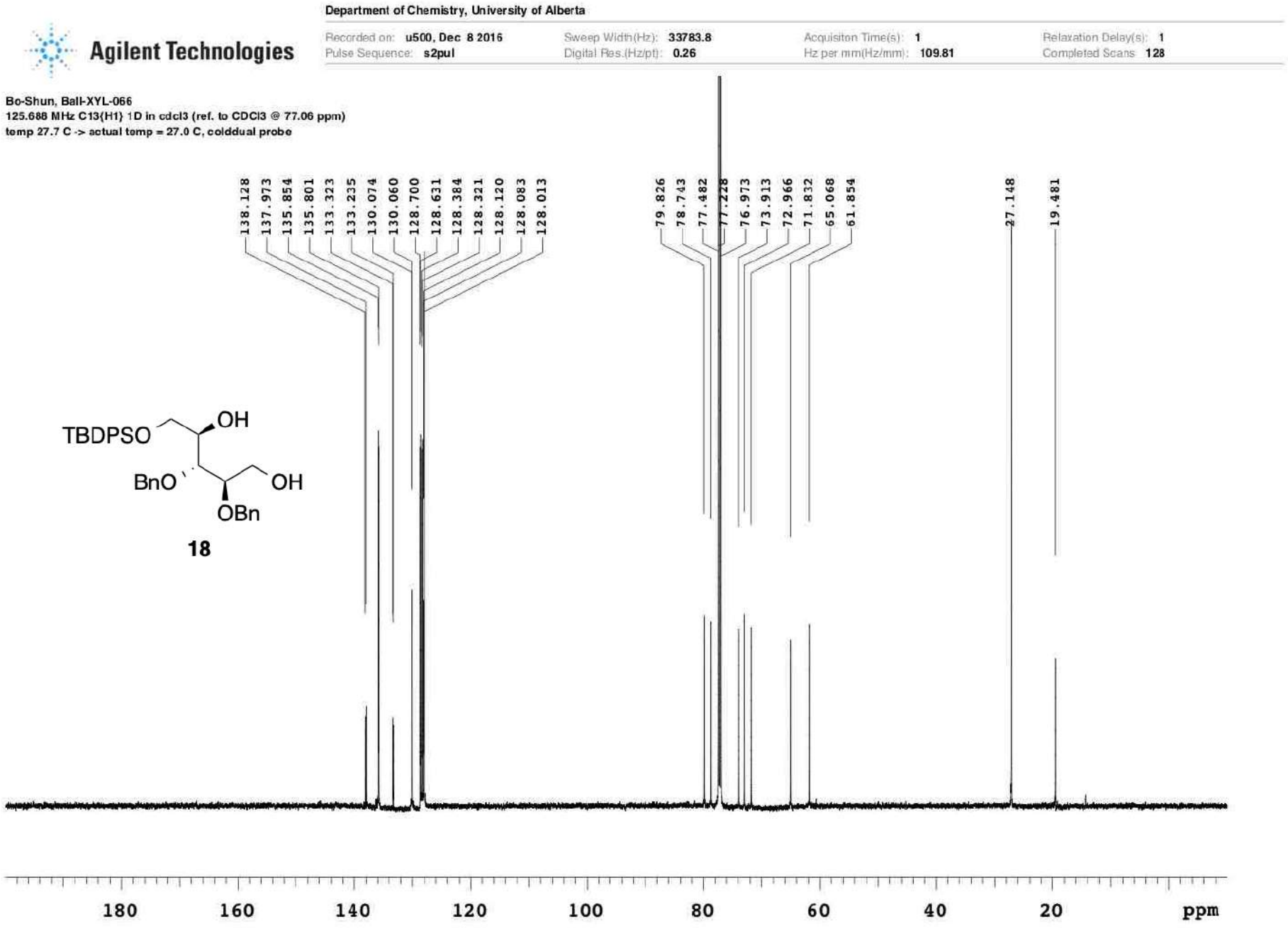
Agilent Technologies

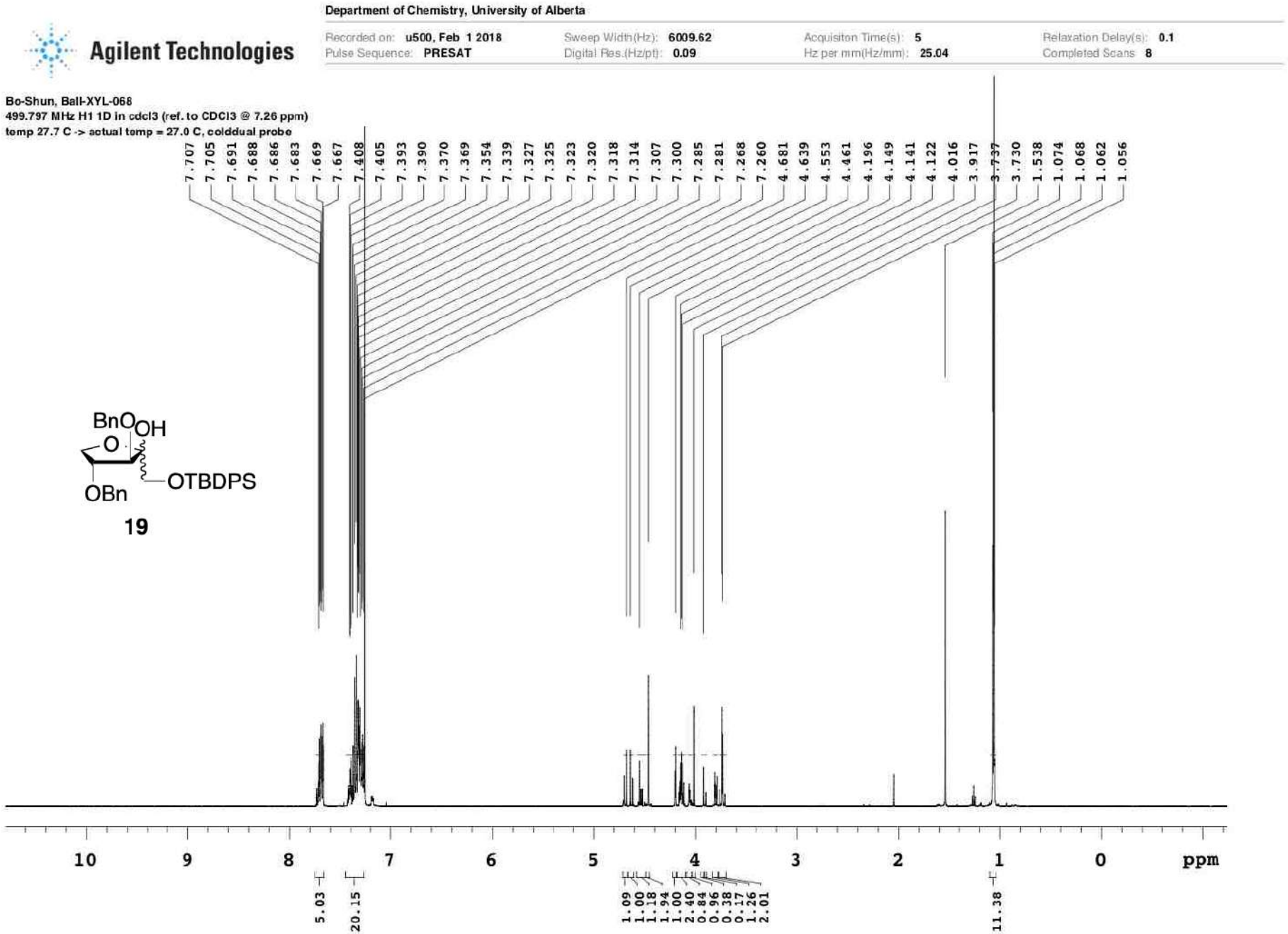
Recorded on:	u500, Dec 8 2016	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.91	Completed Scans	16

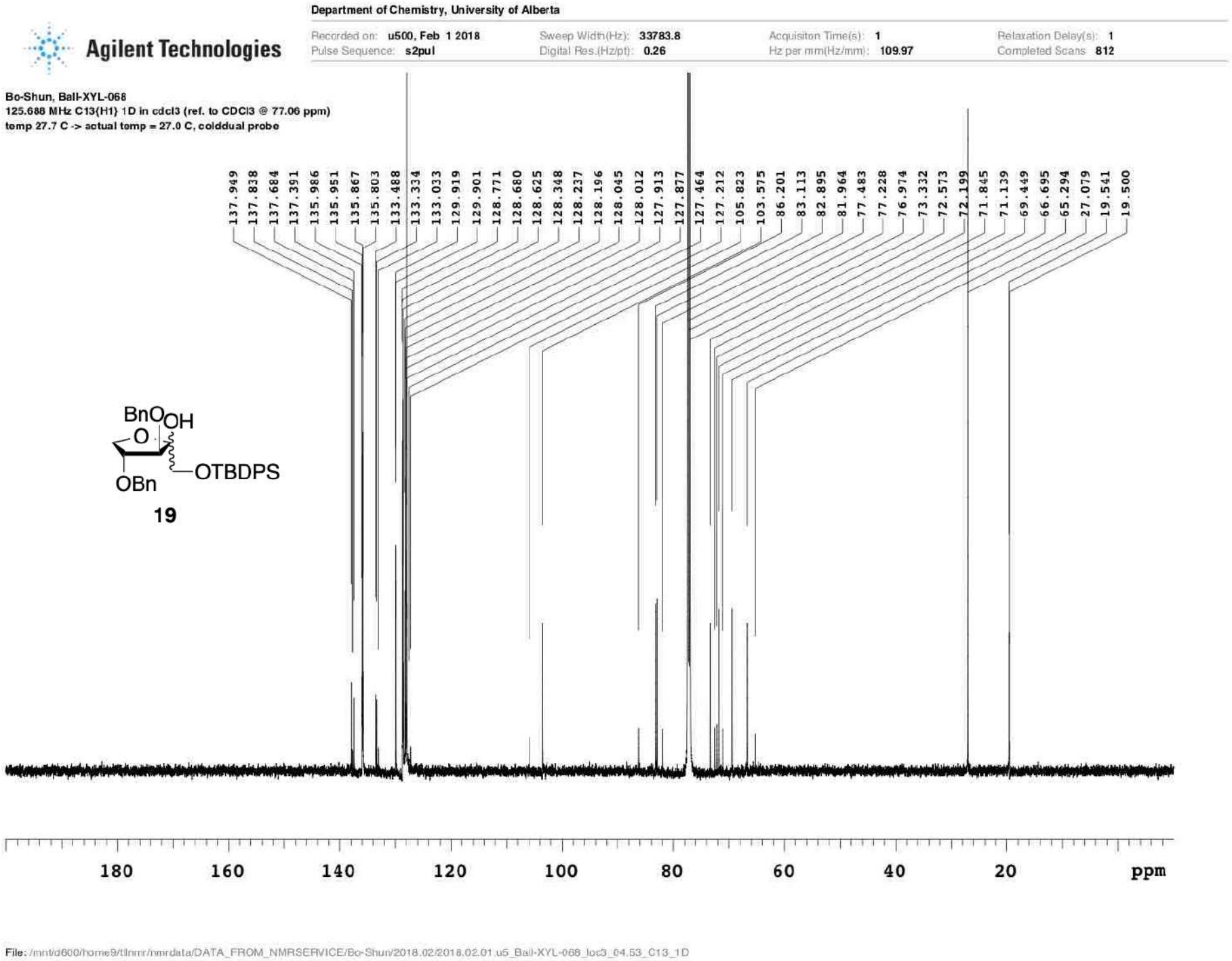
Bo-Shun, Ball-XYL-066
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.12/2016.12.8.u5_Ball-XYL-066_loc6_06.06_H1_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Dec 8 2016
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.81
Relaxation Delay(s): 1
Completed Scans 128
Bo-Shun, Ball-XYL-066
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
138.128
137.973
135.854
135.801
133.323
133.235
130.074
130.060
128.700
128.631
128.384
128.321
128.120
128.083
128.013
79.826
78.743
77.482
77.228
76.973
73.913
72.966
71.832
65.068
61.854
27.148
19.481
TBDPSO
OH
BnO
OH
OBn
18
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.12/2016.12.8.u5_Ball-XYL-066_loc6_06.08_C13_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Feb 1 2018
Pulse Sequence: PRESAT
Sweep Width(Hz): 6009.62
Digital Res.(Hz/pt): 0.09
Acquisiton Time(s): 5
Hz per mm(Hz/mm): 25.04
Relaxation Delay(s): 0.1
Completed Scans 8
Bo-Shun, Ball-XYL-068
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
7.707 7.705 7.691 7.688 7.686 7.683 7.669 7.667 7.408 7.405 7.393 7.390 7.370 7.369 7.354 7.339 7.327 7.325 7.323 7.320 7.318 7.314 7.307 7.300 7.285 7.281 7.268 7.260 4.681 4.639 4.553 4.461 4.196 4.149 4.141 4.122 4.016 3.917 3.737 3.730 1.538 1.074 1.068 1.062 1.056
BnO
OH
O
OBn
OTBDPS
19
10 9 8 7 6 5 4 3 2 1 0 ppm
5.03
20.15
1.09 1.00 1.18 1.94 1.00 2.40 0.84 0.96 0.38 0.17 1.26 2.01
11.38
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2018.02/2018.02.01.u5_Ball-XYL-068_loc3_04.52_H1_1D

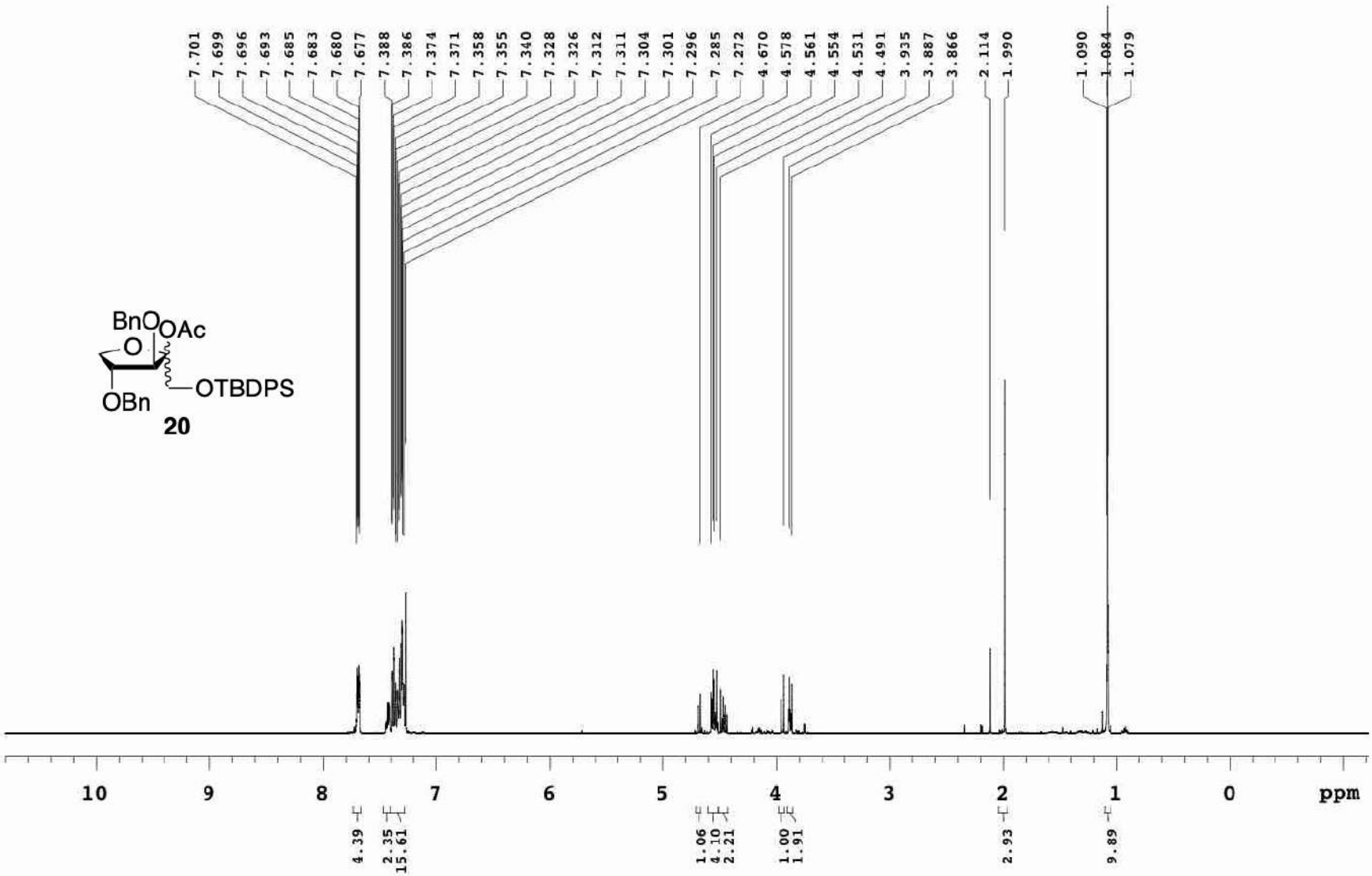

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Feb 1 2018
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.97
Relaxation Delay(s): 1
Completed Scans 812
Bo-Shun, Ball-XYL-068
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
137.949
137.838
137.684
137.391
135.986
135.951
135.867
135.803
133.488
133.334
133.033
129.919
129.901
128.771
128.680
128.625
128.348
128.237
128.196
128.045
128.012
127.913
127.877
127.464
127.212
105.823
103.575
86.201
83.113
82.895
81.964
77.483
77.228
76.974
73.332
72.573
72.199
71.845
71.139
69.449
66.695
65.294
27.079
19.541
19.500
BnO
OH
O
OBn
OTBDPS
19
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2018.02/2018.02.01.u5_Ball-XYL-068_loc3_04.53_C13_1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	u500, Feb 7 2018	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	25.04	Completed Scans	8

Bo-Shun, Ball-XYL-069
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



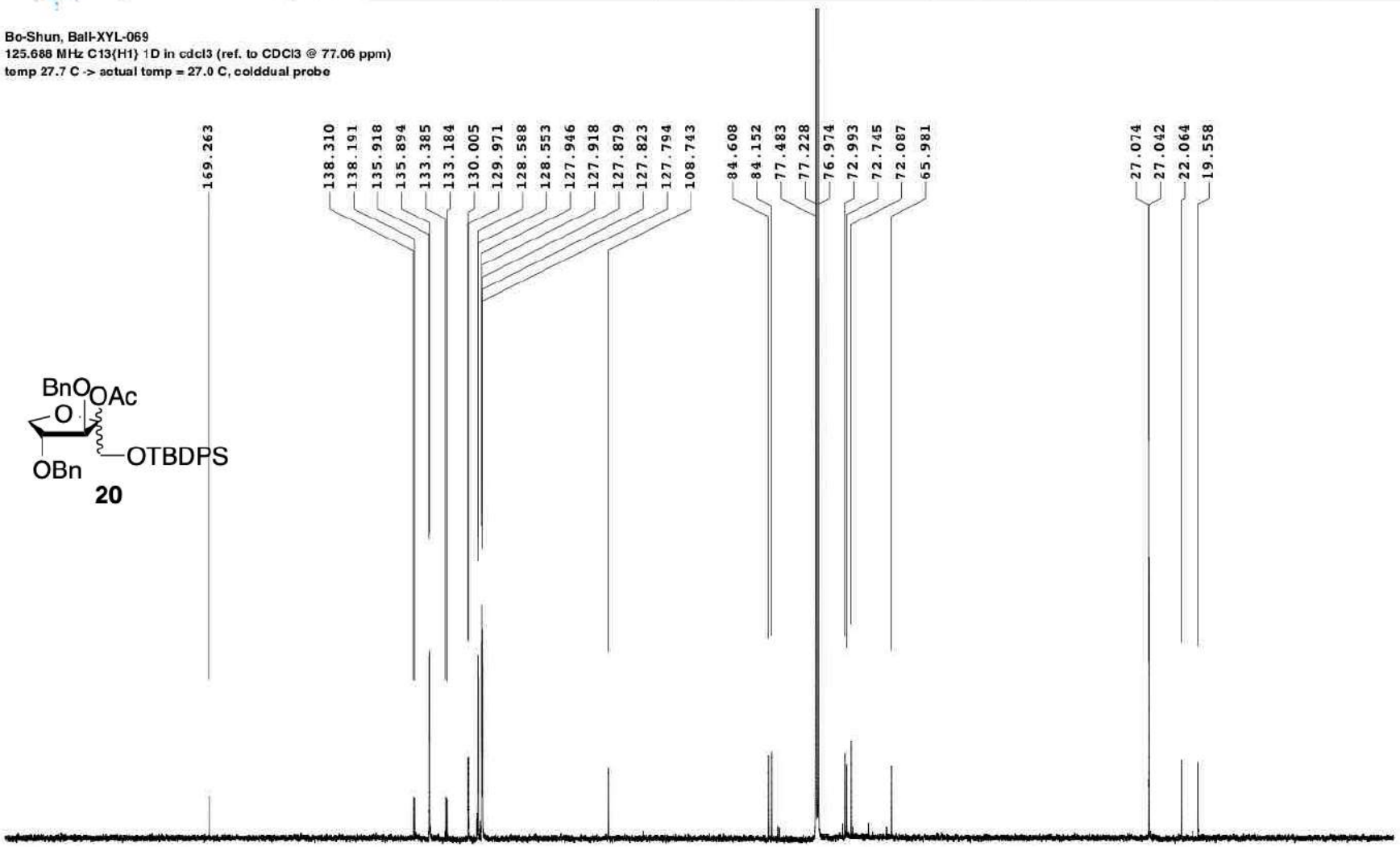
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2018.02/2018.02.07.u5_Ball-XYL-069_loc11_22.52_H1_1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on: u500, Feb 7 2018 | Sweep Width(Hz): 33783.8 | Acquisiton Time(s): 1 | Relaxation Delay(s): 1
Pulse Sequence: s2pul | Digital Res.(Hz/pt): 0.26 | Hz per mm(Hz/mm): 109.97 | Completed Scans 128

Bo-Shun, Ball-XYL-069
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



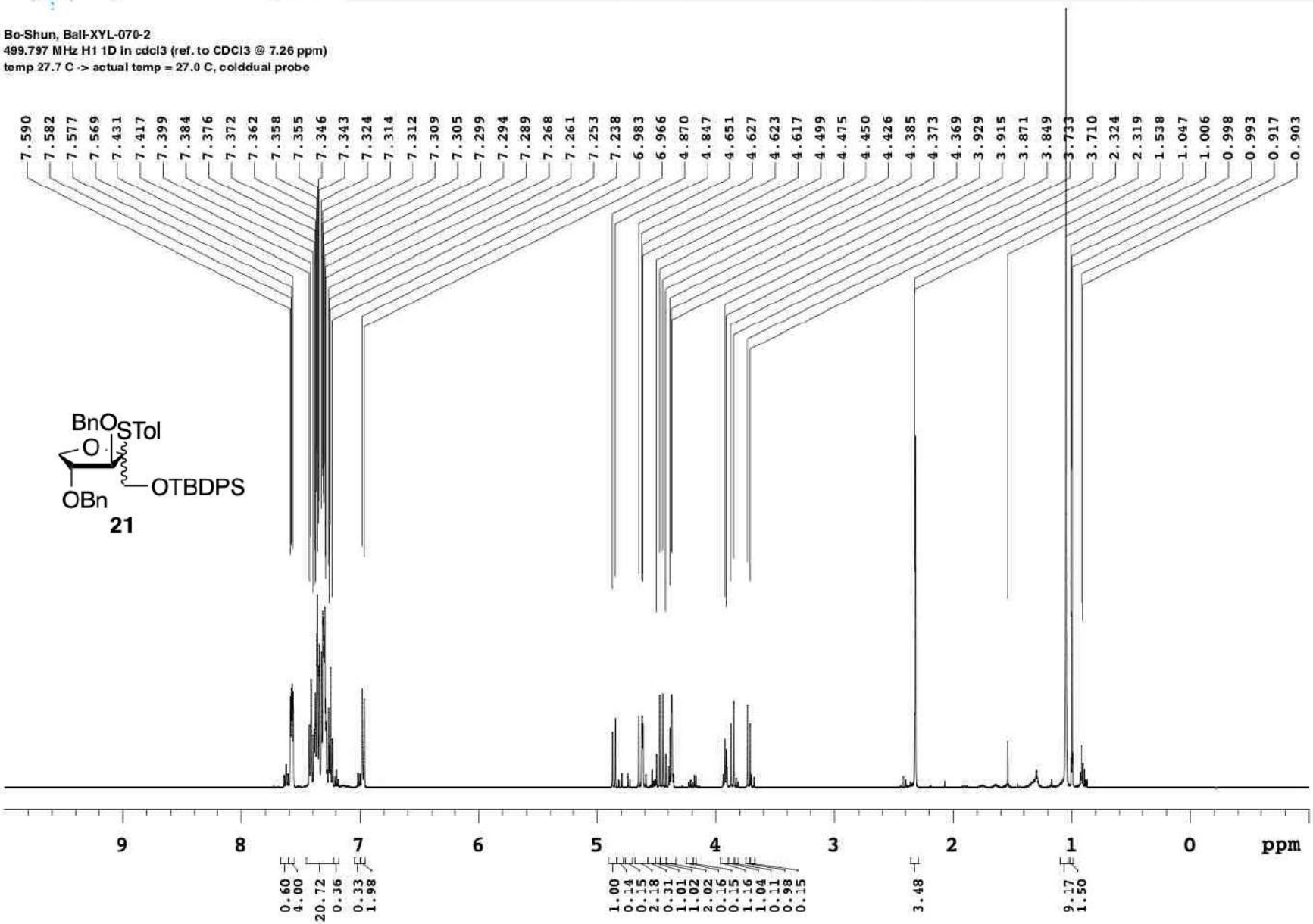
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2018.02/2018.02.07.u5_Ball-XYL-069_loc11_22.58_C13_1D

Department of Chemistry, University of Alberta

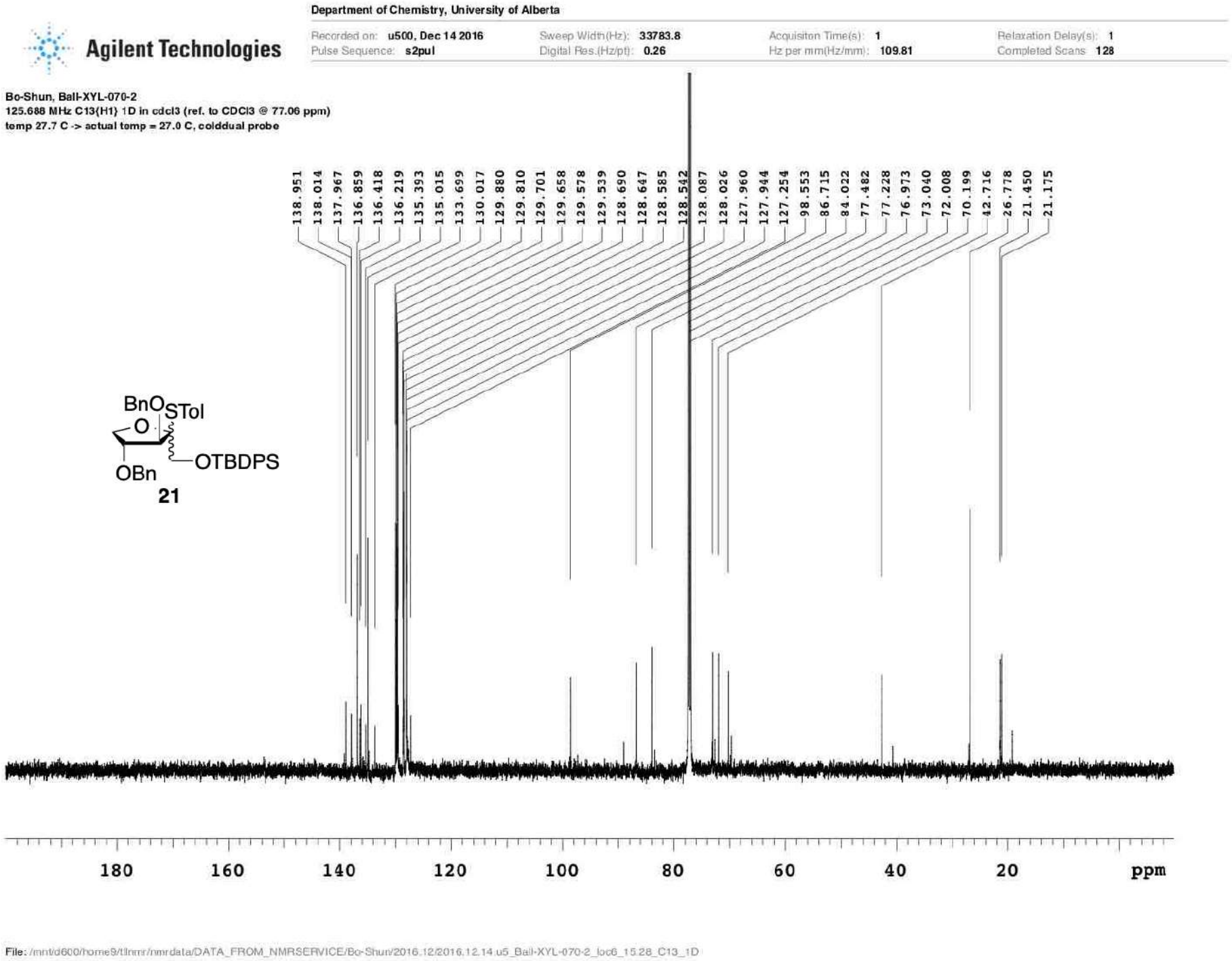
Agilent Technologies

Recorded on:	u500, Dec 16 2016	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.91	Completed Scans	16

Bo-Shun, Ball-XYL-070-2
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.12/2016.12.16.u5_Ball-XYL-070-2_loc6_20.03_H1_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Dec 14 2016
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.81
Relaxation Delay(s): 1
Completed Scans 128
Bo-Shun, Ball-XYL-070-2
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
138.951
138.014
137.967
136.859
136.418
136.219
135.393
135.015
133.699
130.017
129.880
129.810
129.701
129.658
129.578
129.539
128.690
128.647
128.585
128.542
128.087
128.026
127.960
127.944
127.254
98.553
86.715
84.022
77.482
77.228
76.973
73.040
72.008
70.199
42.716
26.778
21.450
21.175
BnO
STol
O
OTBDPS
OBn
21
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.12/2016.12.14.u5_Ball-XYL-070-2_loc6_15.28_C13_1D

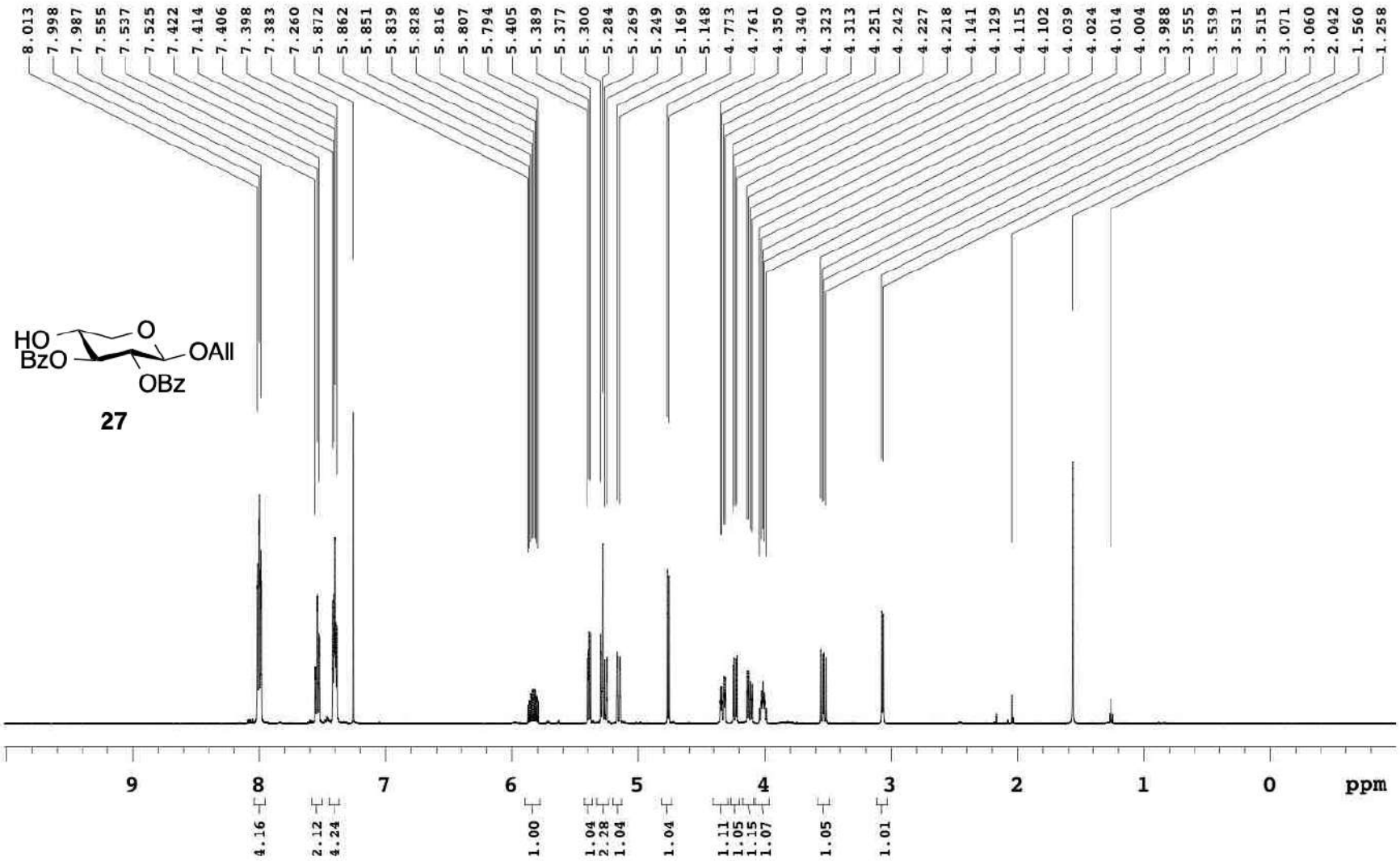
Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	u500, Nov 29 2016	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.92	Completed Scans	16

Bo-Shun, Ball-XYL-054

499.797 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.11/2016.11.29.u5_Ball-XYL-054_loc3_03.21_H1_1D

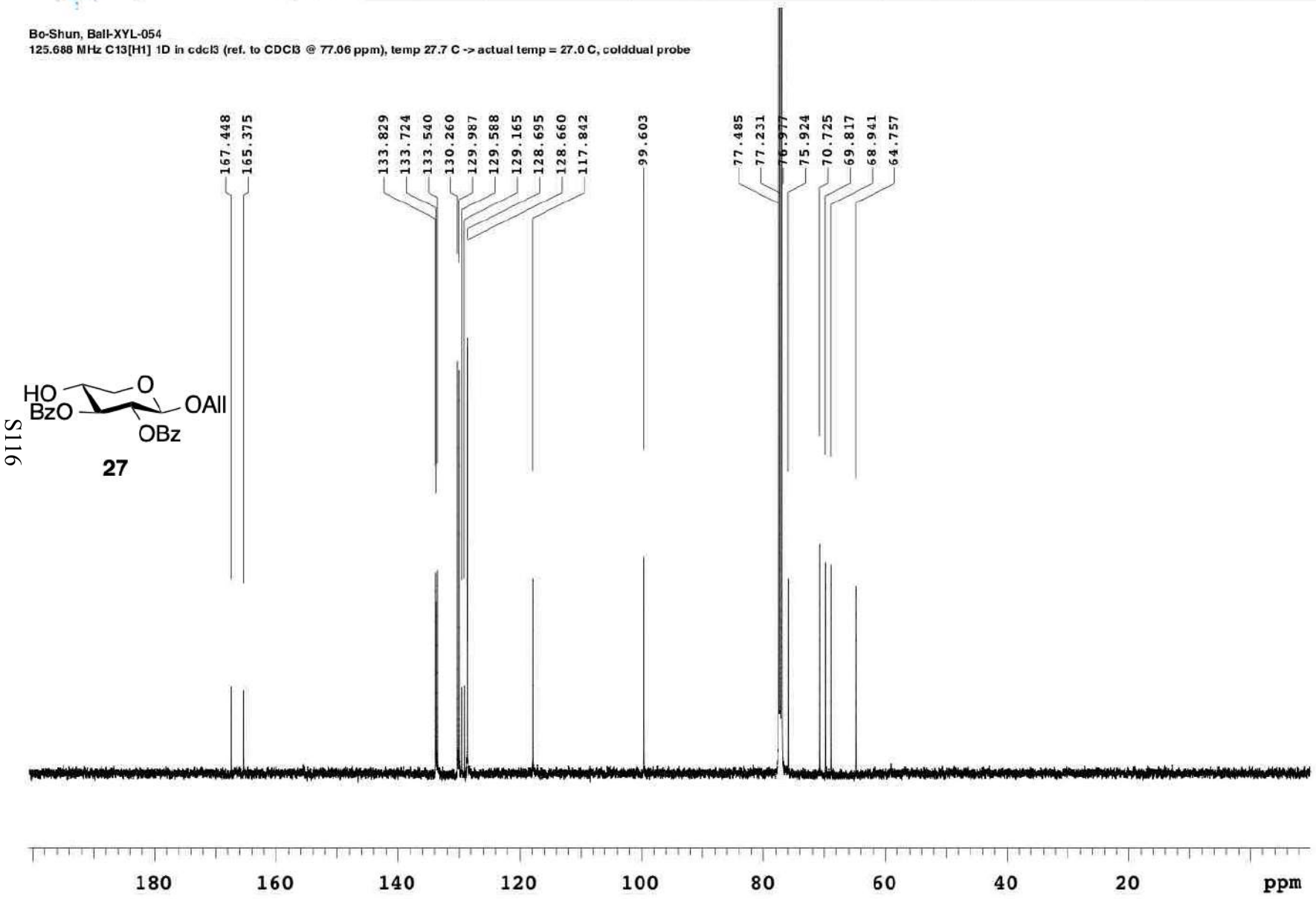
Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	u500, Nov 29 2016	Sweep Width(Hz):	33783.8	Acquisiton Time(s):	1	Relaxation Delay(s):	1
Pulse Sequence:	s2pul	Digital Res.(Hz/pt):	0.26	Hz per mm(Hz/mm):	110.08	Completed Scans	256

Bo-Shun, Ball-XYL-054

125.688 MHz C13[H1] 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe



27

File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.11/2016.11.29.u5_Ball-XYL-054_loc3_03.22_C13_1D

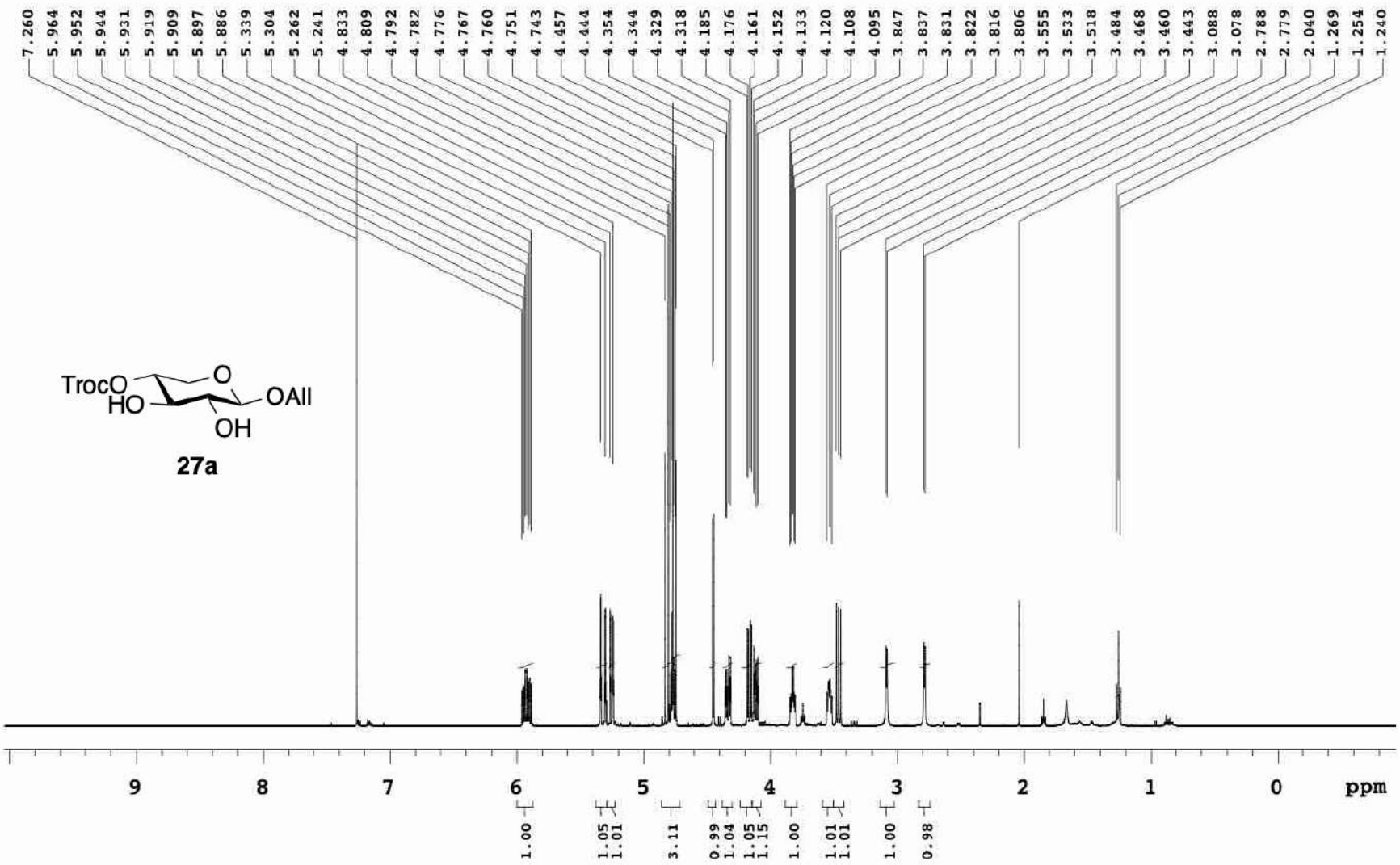
Department of Chemistry, University of Alberta

Agilent Technologies

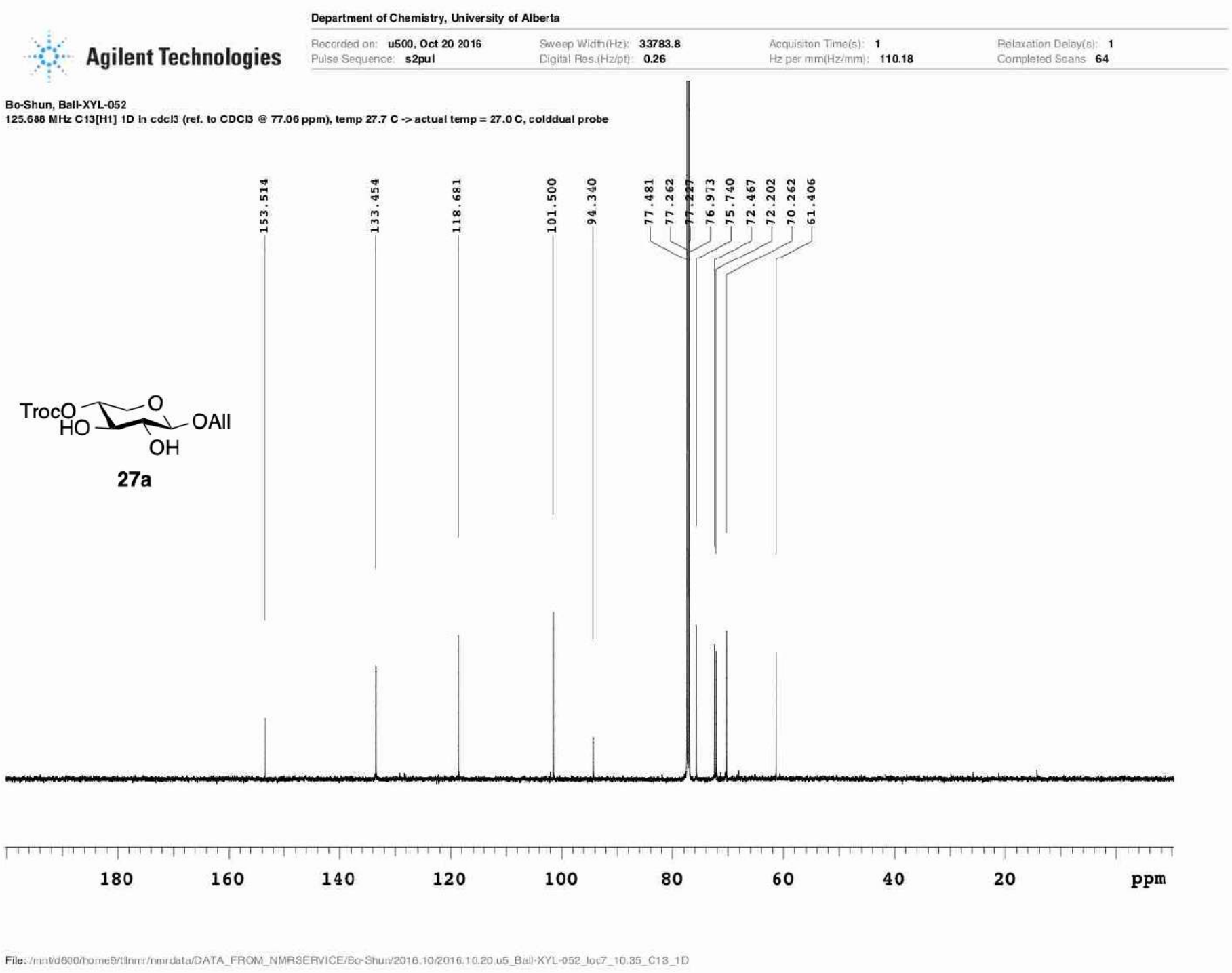
Recorded on:	u500, Oct 20 2016	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.84	Completed Scans	16

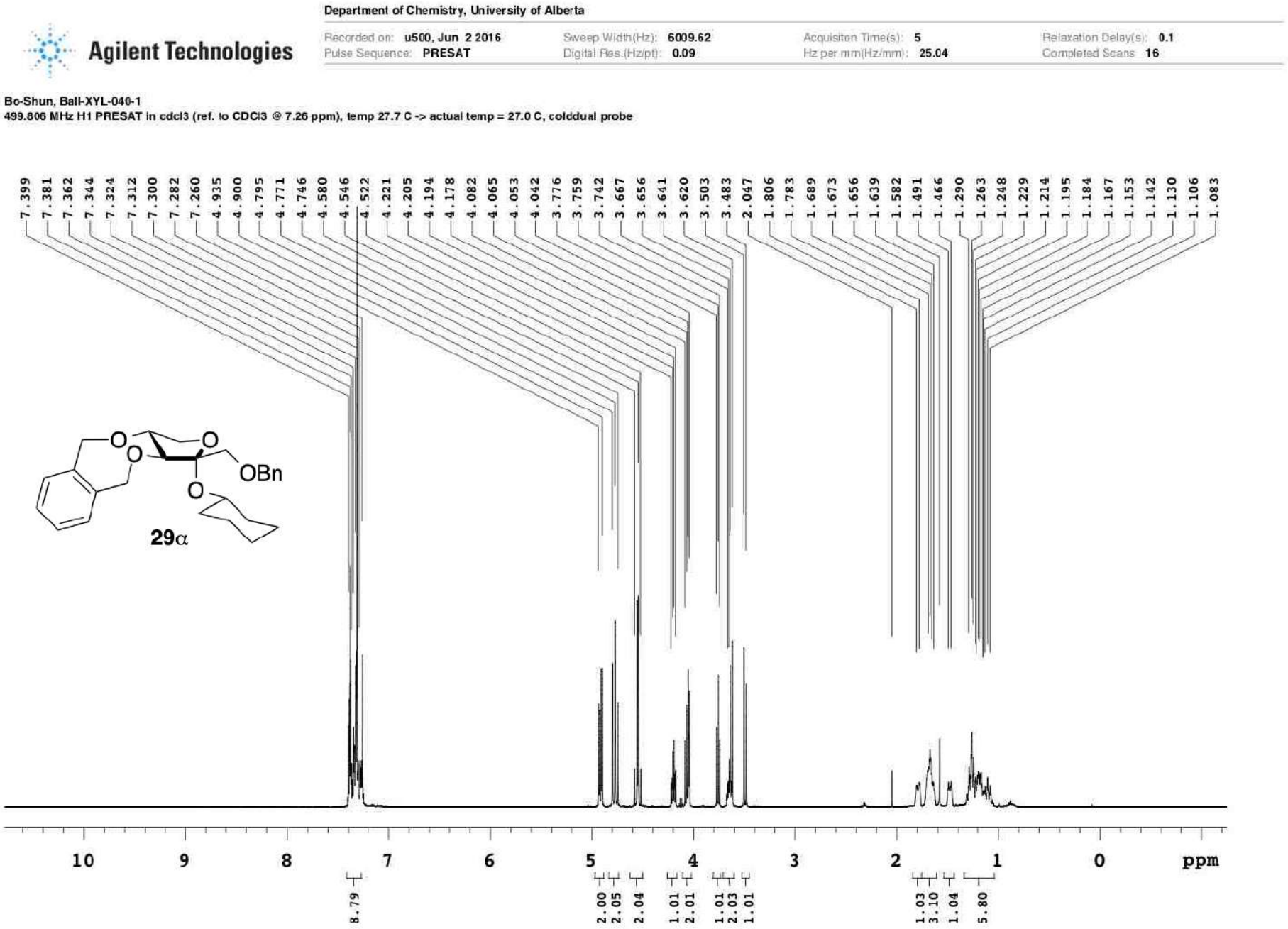
Bo-Shun, Ball-XYL-052

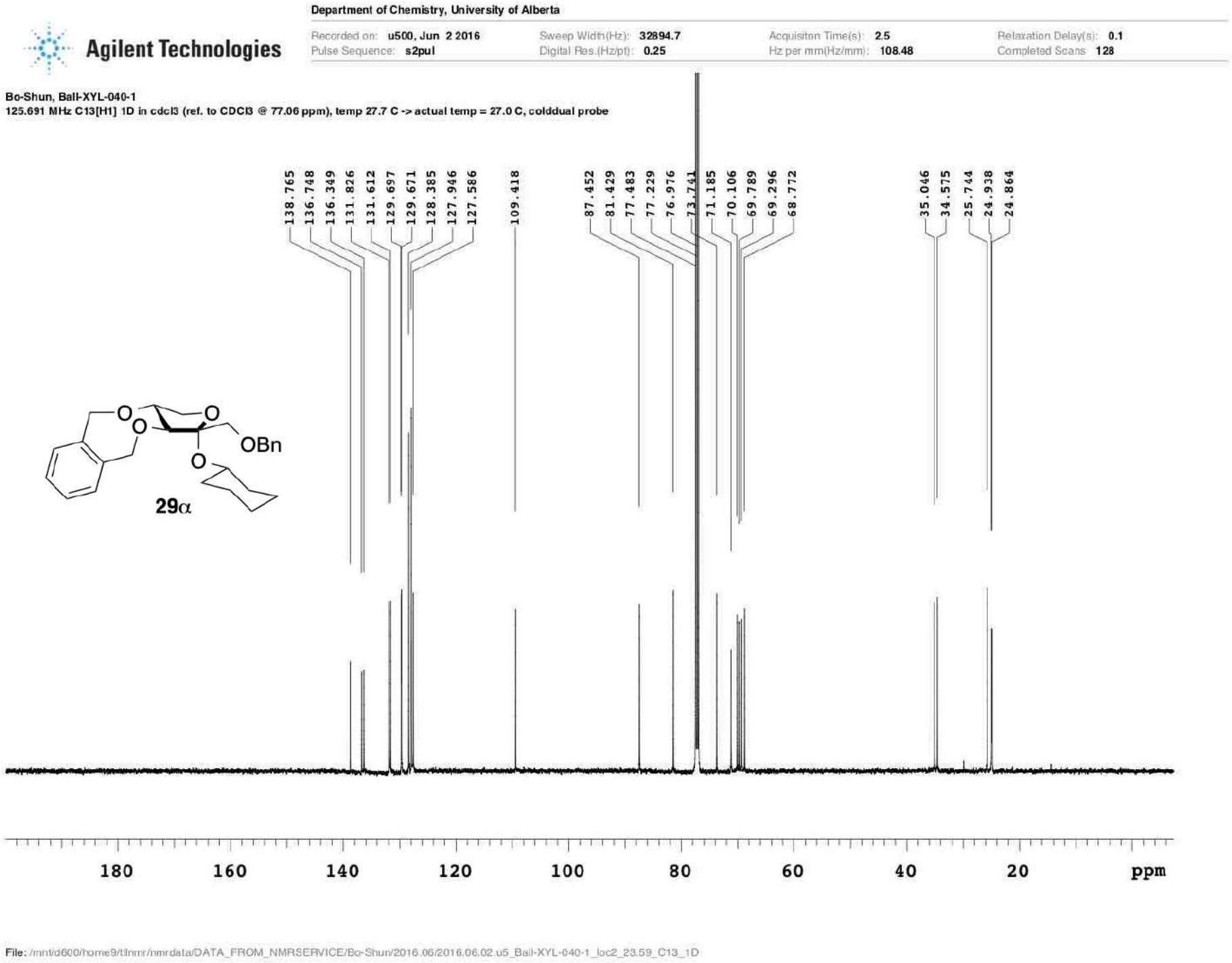
499.797 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe

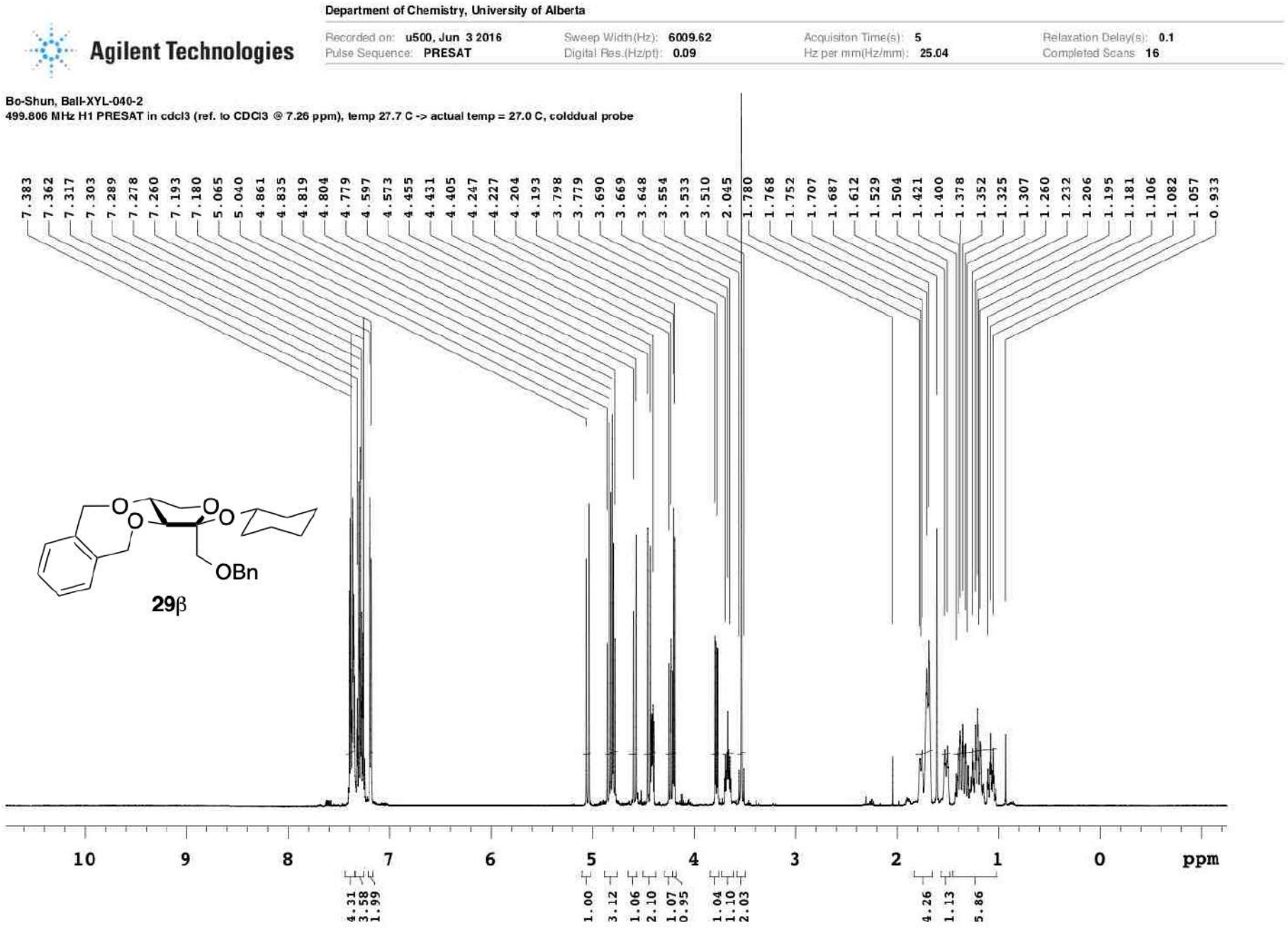


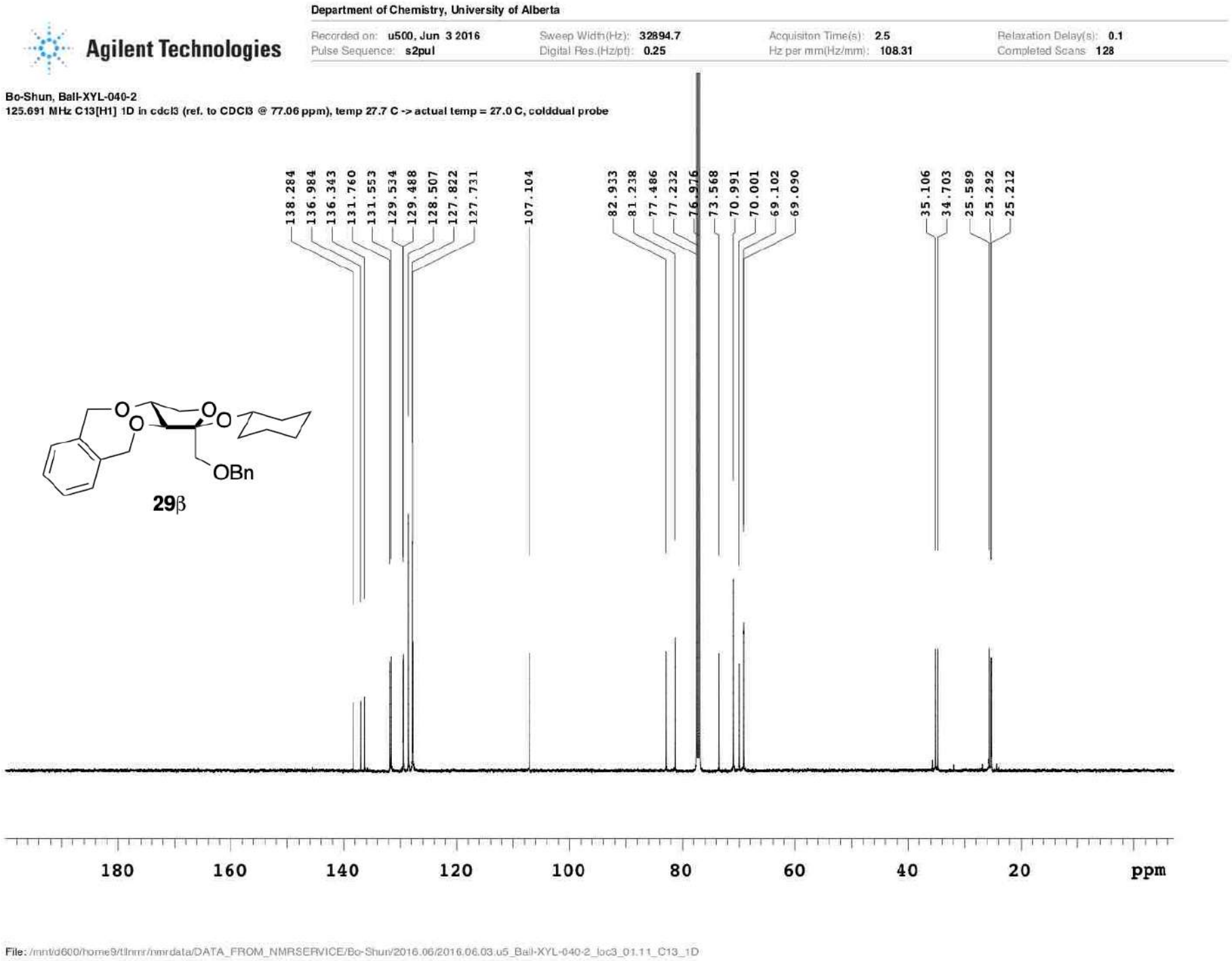
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.10/2016.10.20.u5_Ball-XYL-052_loc7_10.33_H1_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Oct 20 2016
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 110.18
Relaxation Delay(s): 1
Completed Scans 64
Bo-Shun, Ball-XYL-052
125.688 MHz C13[H1] 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
153.514
133.454
118.681
101.500
94.340
77.481
77.262
77.227
76.973
75.740
72.467
72.202
70.262
61.406
TrocO
HO
O
OAll
OH
27a
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.10/2016.10.20.u5_Ball-XYL-052_loc7_10.35_C13_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Jun 2 2016
Pulse Sequence: PRESAT
Sweep Width(Hz): 6009.62
Digital Res.(Hz/pt): 0.09
Acquisiton Time(s): 5
Hz per mm(Hz/mm): 25.04
Relaxation Delay(s): 0.1
Completed Scans 16
Bo-Shun, Ball-XYL-040-1
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
7.399 7.381 7.362 7.344 7.324 7.312 7.300 7.282 7.260 4.935 4.900 4.795 4.771 4.746 4.580 4.546 4.522 4.221 4.205 4.194 4.178 4.082 4.065 4.053 4.042 3.776 3.759 3.742 3.667 3.656 3.641 3.620 3.503 3.483 2.047 1.806 1.783 1.689 1.673 1.656 1.639 1.582 1.491 1.466 1.290 1.263 1.248 1.229 1.214 1.195 1.184 1.167 1.153 1.142 1.130 1.106 1.083
O
O
O
O
OBn
29α
10 9 8 7 6 5 4 3 2 1 0 ppm
8.79
2.00 2.05 2.04 1.01 2.01 1.01 2.03 1.01
1.03 3.10 1.04 5.80
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.06/2016.06.02.u5_Ball-XYL-040-1_loc2_23.57_H1_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Jun 2 2016
Pulse Sequence: s2pul
Sweep Width(Hz): 32894.7
Digital Res.(Hz/pt): 0.25
Acquisiton Time(s): 2.5
Hz per mm(Hz/mm): 108.48
Relaxation Delay(s): 0.1
Completed Scans 128
Bo-Shun, Ball-XYL-040-1
125.691 MHz C13[H1] 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
138.765
136.748
136.349
131.826
131.612
129.697
129.671
128.385
127.946
127.586
109.418
87.452
81.429
77.483
77.229
76.976
73.741
71.185
70.106
69.789
69.296
68.772
35.046
34.575
25.744
24.938
24.864
O
O
O
O
OBn
29α
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.06/2016.06.02.u5_Ball-XYL-040-1_loc2_23.59_C13_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Jun 3 2016
Pulse Sequence: PRESAT
Sweep Width(Hz): 6009.62
Digital Res.(Hz/pt): 0.09
Acquisiton Time(s): 5
Hz per mm(Hz/mm): 25.04
Relaxation Delay(s): 0.1
Completed Scans 16
Bo-Shun, Ball-XYL-040-2
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
7.383 7.362 7.317 7.303 7.289 7.278 7.260 7.193 7.180 5.065 5.040 4.861 4.835 4.819 4.804 4.779 4.597 4.573 4.455 4.431 4.405 4.247 4.227 4.204 4.193 3.798 3.779 3.690 3.669 3.648 3.554 3.533 3.510 2.045 1.780 1.768 1.752 1.707 1.687 1.612 1.529 1.504 1.421 1.400 1.378 1.352 1.325 1.307 1.260 1.232 1.206 1.195 1.181 1.106 1.082 1.057 0.933
OBn
29β
10 9 8 7 6 5 4 3 2 1 0 ppm
4.31 3.58 1.99
1.00 3.12 1.06 2.10 1.07 0.95 1.04 1.10 2.03
4.26 1.13 5.86
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.06/2016.06.03.u5_Ball-XYL-040-2_loc3_01.09_H1_1D

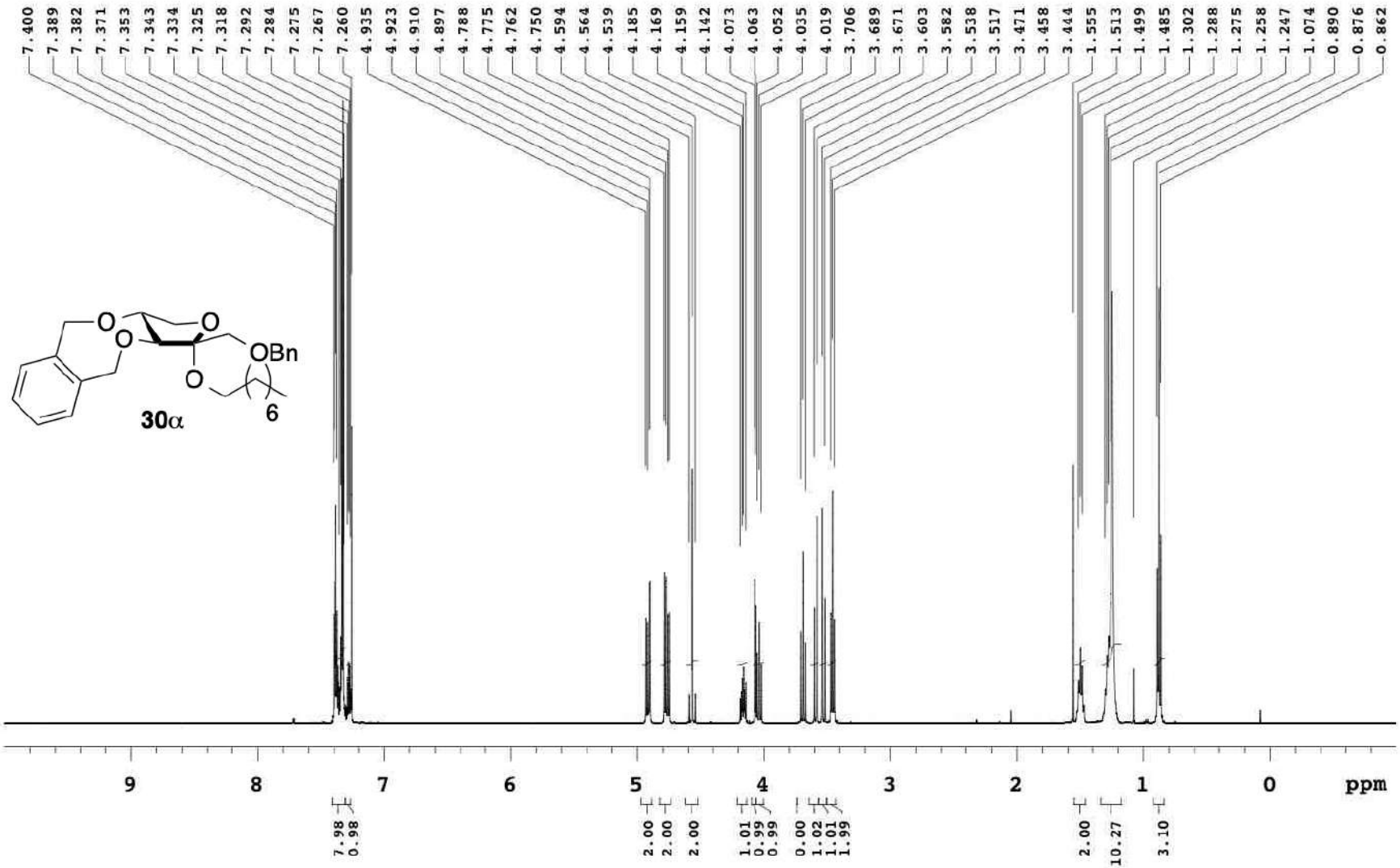

Agilent Technologies
Department of Chemistry, University of Alberta
Recorded on: u500, Jun 3 2016
Pulse Sequence: s2pul
Sweep Width(Hz): 32894.7
Digital Res.(Hz/pt): 0.25
Acquisiton Time(s): 2.5
Hz per mm(Hz/mm): 108.31
Relaxation Delay(s): 0.1
Completed Scans 128
Bo-Shun, Ball-XYL-040-2
125.691 MHz C13[H1] 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
138.284
136.984
136.343
131.760
131.553
129.534
129.488
128.507
127.822
127.731
107.104
82.933
81.238
77.486
77.232
76.976
73.568
70.991
70.001
69.102
69.090
35.106
34.703
25.589
25.292
25.212
OBn
29β
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.06/2016.06.03.u5_Ball-XYL-040-2_loc3_01.11_C13_1D

Department of Chemistry, University of Alberta

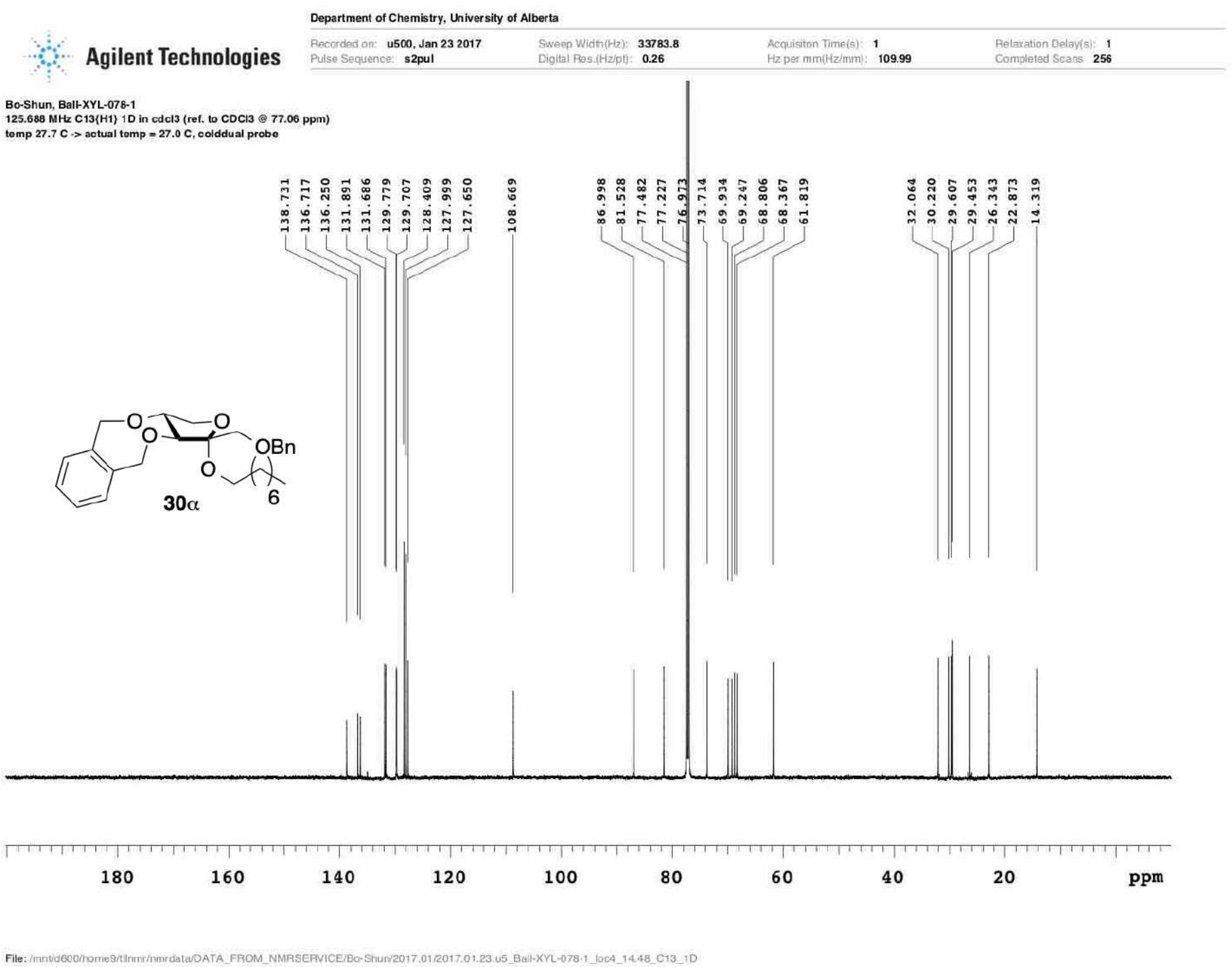
Agilent Technologies

Recorded on:	u500, Jan 23 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.89	Completed Scans	16

Bo-Shun, Ball-XYL-078-1
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.23.u5_Ball-XYL-078-1_loc4_14.46_H1_1D

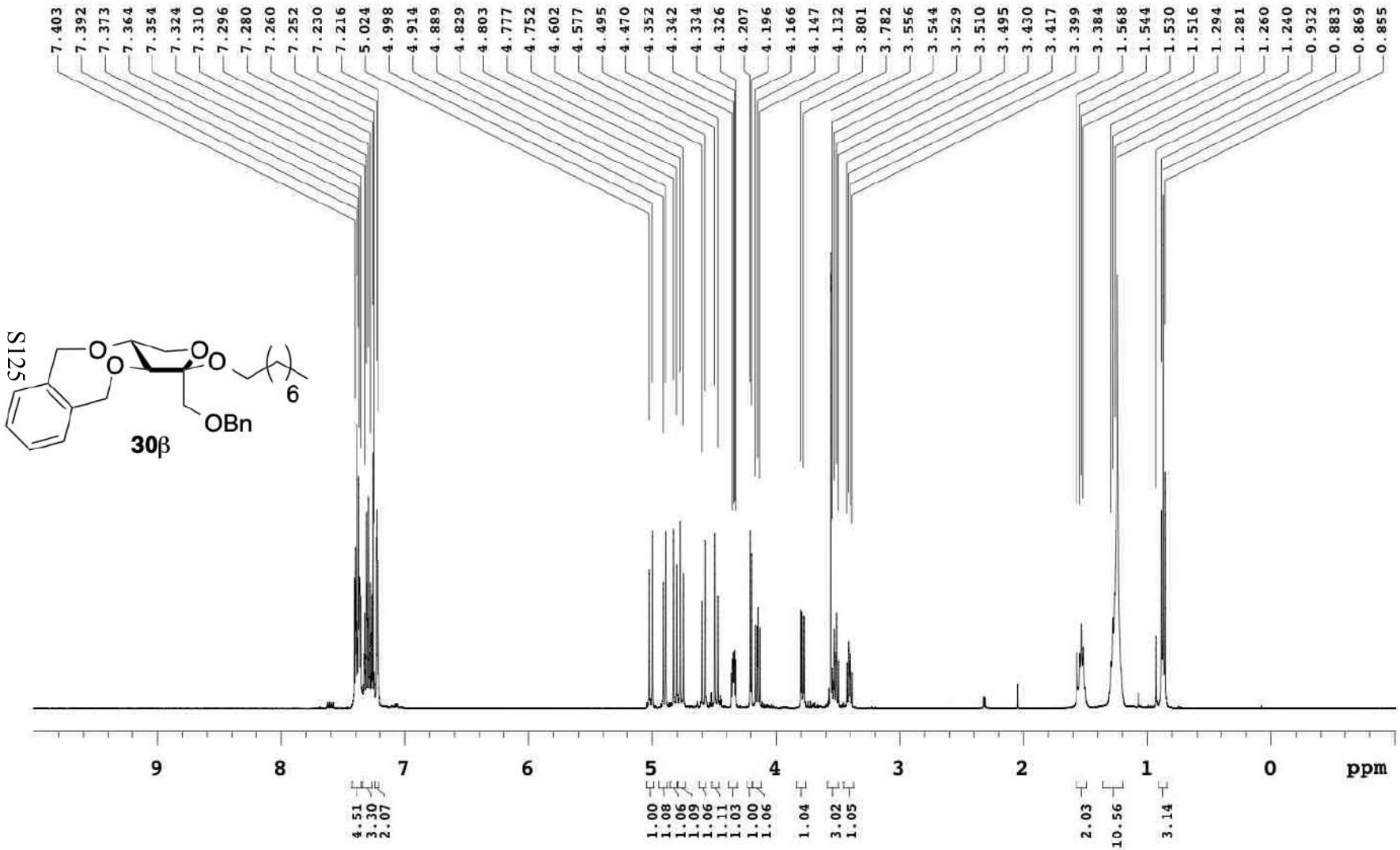

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Jan 23 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.99
Relaxation Delay(s): 1
Completed Scans 256
Bo-Shun, Ball-XYL-078-1
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
138.731
136.717
136.250
131.891
131.686
129.779
129.707
128.409
127.999
127.650
108.669
86.998
81.528
77.482
77.227
76.973
73.714
69.934
69.247
68.806
68.367
61.819
32.064
30.220
29.607
29.453
26.343
22.873
14.319
OBn
30α
6
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.23.u5_Ball-XYL-078-1_loc4_14.48_C13_1D

Department of Chemistry, University of Alberta

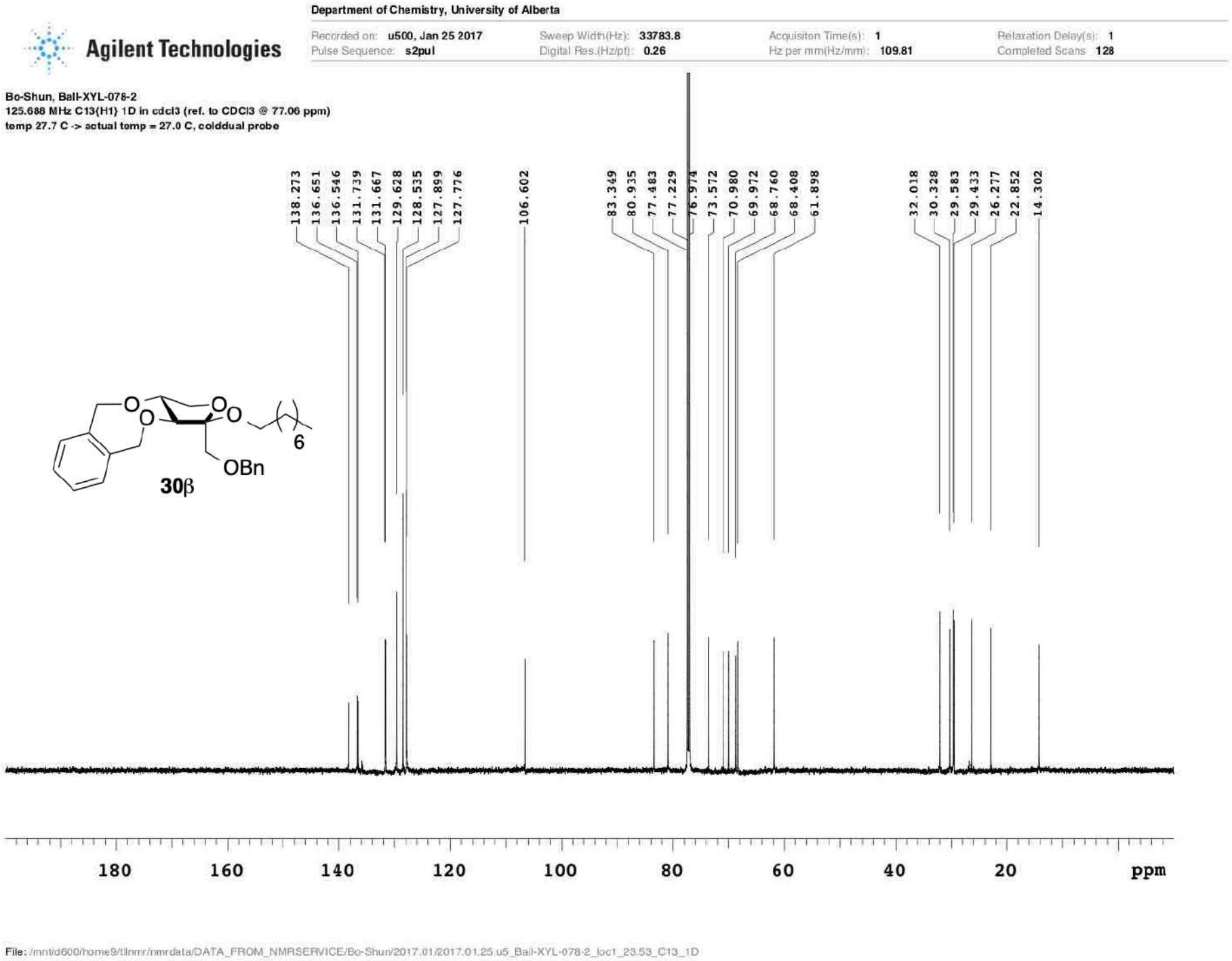
Agilent Technologies

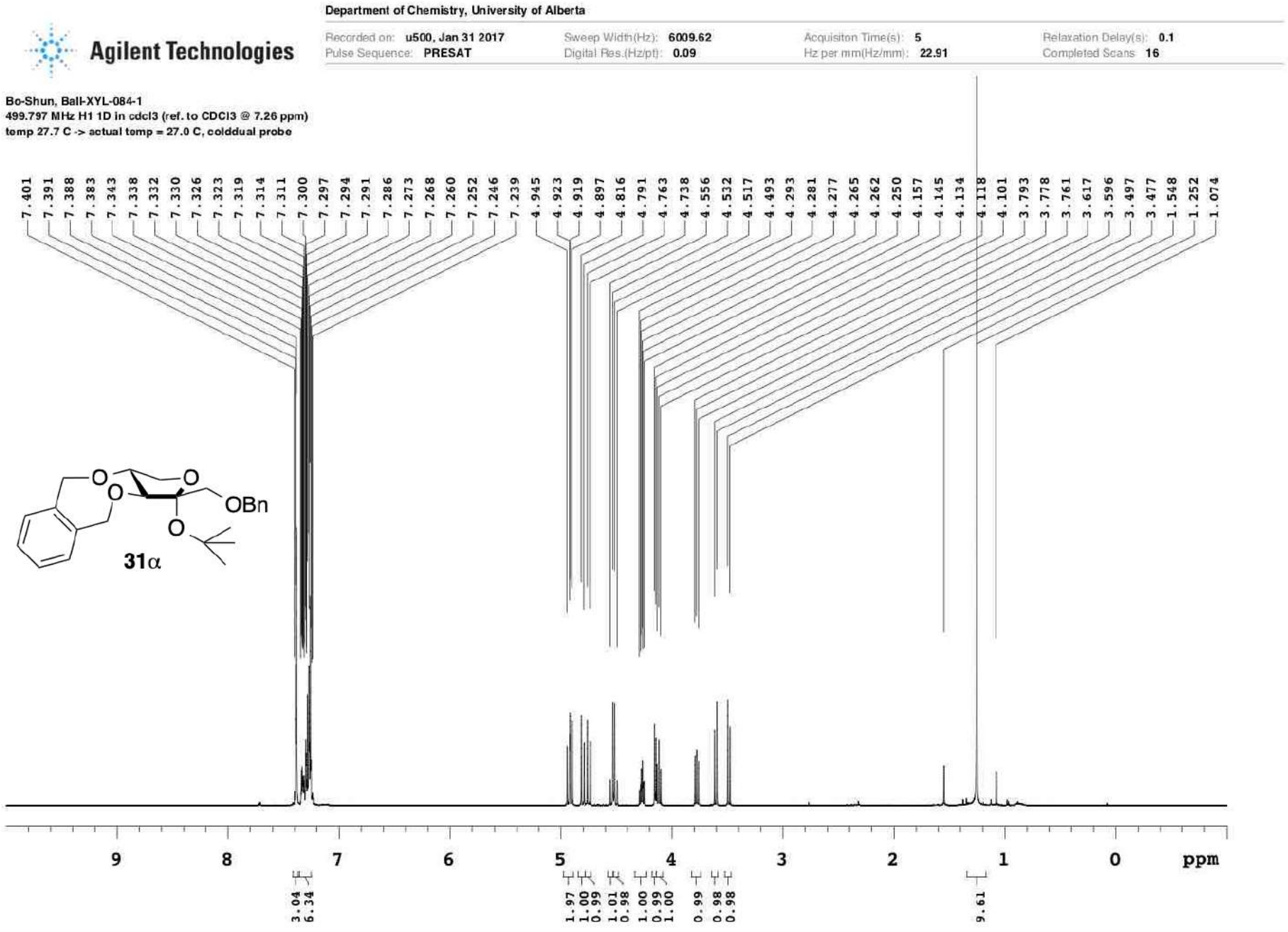
Recorded on: u500, Jan 25 2017	Sweep Width(Hz): 6009.62	Acquisiton Time(s): 5	Relaxation Delay(s): 0.1
Pulse Sequence: PRESAT	Digital Res.(Hz/pt): 0.09	Hz per mm(Hz/mm): 22.92	Completed Scans 16

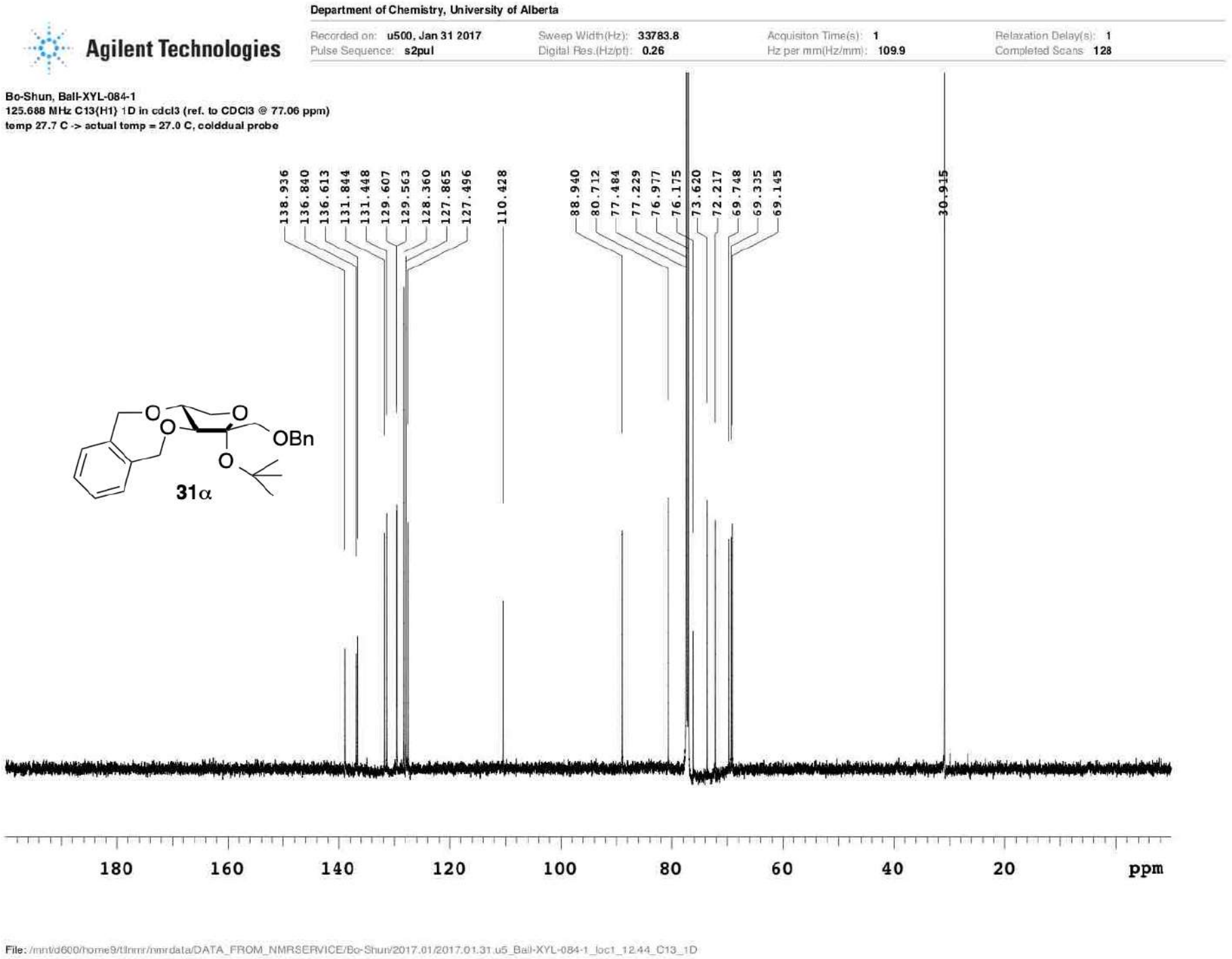
Bo-Shun, Ball-XYL-078-2
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe

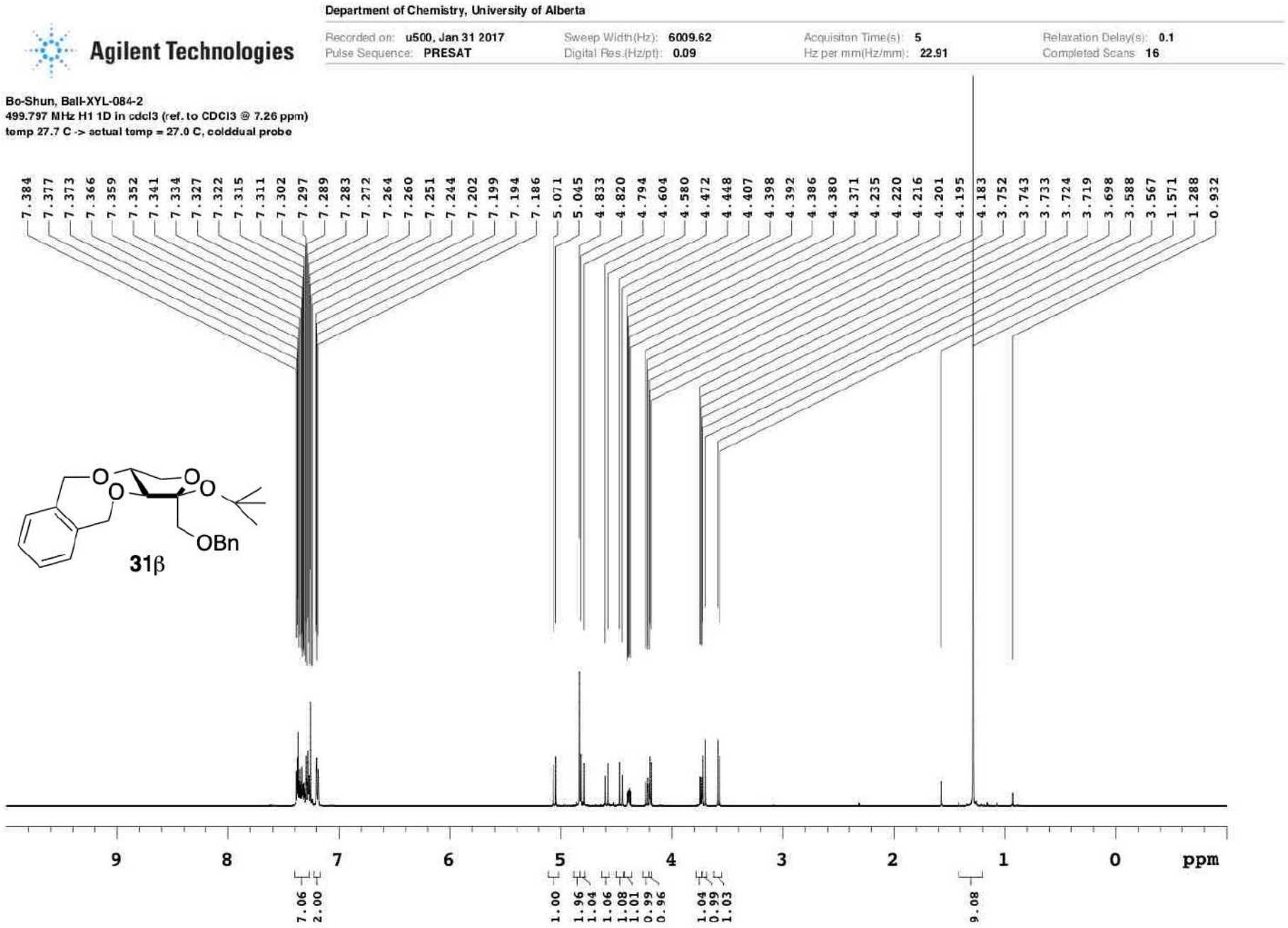


File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.25.u5_Ball-XYL-078-2_loc1_23.51_H1_1D

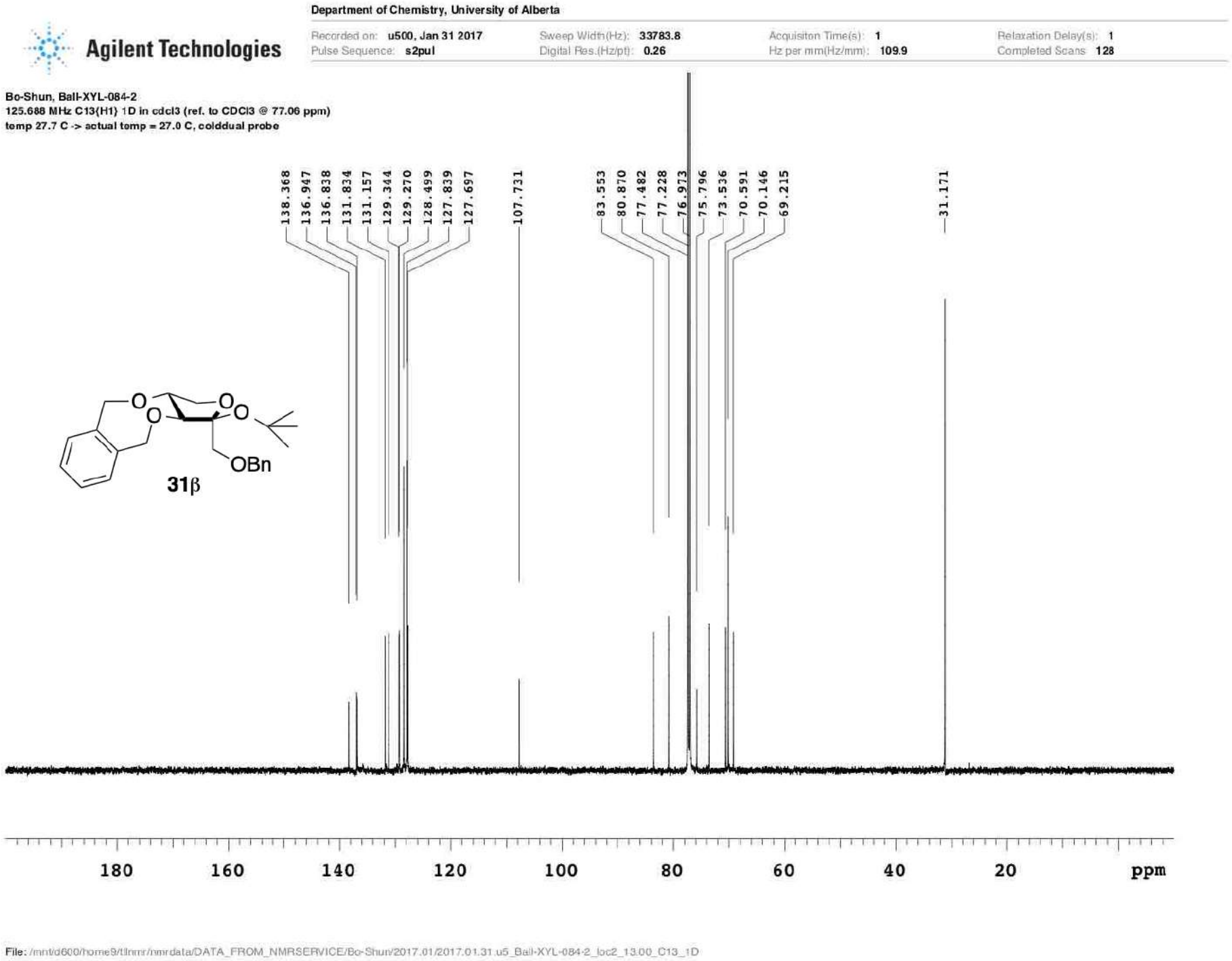

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Jan 25 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.81
Relaxation Delay(s): 1
Completed Scans 128
Bo-Shun, Ball-XYL-078-2
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
138.273
136.651
136.546
131.739
131.667
129.628
128.535
127.899
127.776
106.602
83.349
80.935
77.483
77.229
76.974
73.572
70.980
69.972
68.760
68.408
61.898
32.018
30.328
29.583
29.433
26.277
22.852
14.302
O
O
O
O
6
OBn
30β
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.25.u5_Ball-XYL-078-2_loc1_23.53_C13_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Jan 31 2017
Pulse Sequence: PRESAT
Sweep Width(Hz): 6009.62
Digital Res.(Hz/pt): 0.09
Acquisiton Time(s): 5
Hz per mm(Hz/mm): 22.91
Relaxation Delay(s): 0.1
Completed Scans 16
Bo-Shun, Ball-XYL-084-1
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
7.401 7.391 7.388 7.383 7.343 7.338 7.332 7.330 7.326 7.323 7.319 7.314 7.311 7.300 7.297 7.294 7.291 7.286 7.273 7.268 7.260 7.252 7.246 7.239
4.945 4.923 4.919 4.897 4.816 4.791 4.763 4.738 4.556 4.532 4.517 4.493 4.293 4.281 4.277 4.265 4.262 4.250 4.157 4.145 4.134 4.118 4.101
3.793 3.778 3.761 3.617 3.596 3.497 3.477
1.548 1.252 1.074
O
O
O
O
OBn
31α
9 8 7 6 5 4 3 2 1 0 ppm
3.04 6.34
1.97 1.00 0.99 1.01 0.98 1.00 0.99 1.00
0.99 0.98 0.98
9.61
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.31.u5_Ball-XYL-084-1_loc1_12.42_H1_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Jan 31 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.9
Relaxation Delay(s): 1
Completed Scans 128
Bo-Shun, Ball-XYL-084-1
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
138.936
136.840
136.613
131.844
131.448
129.607
129.563
128.360
127.865
127.496
110.428
88.940
80.712
77.484
77.229
76.977
76.175
73.620
72.217
69.748
69.335
69.145
30.915
OBn
31α
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.31.u5_Ball-XYL-084-1_loc1_12.44_C13_1D



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.31.u5_Ball-XYL-084-2_loc2_12.58_H1_1D

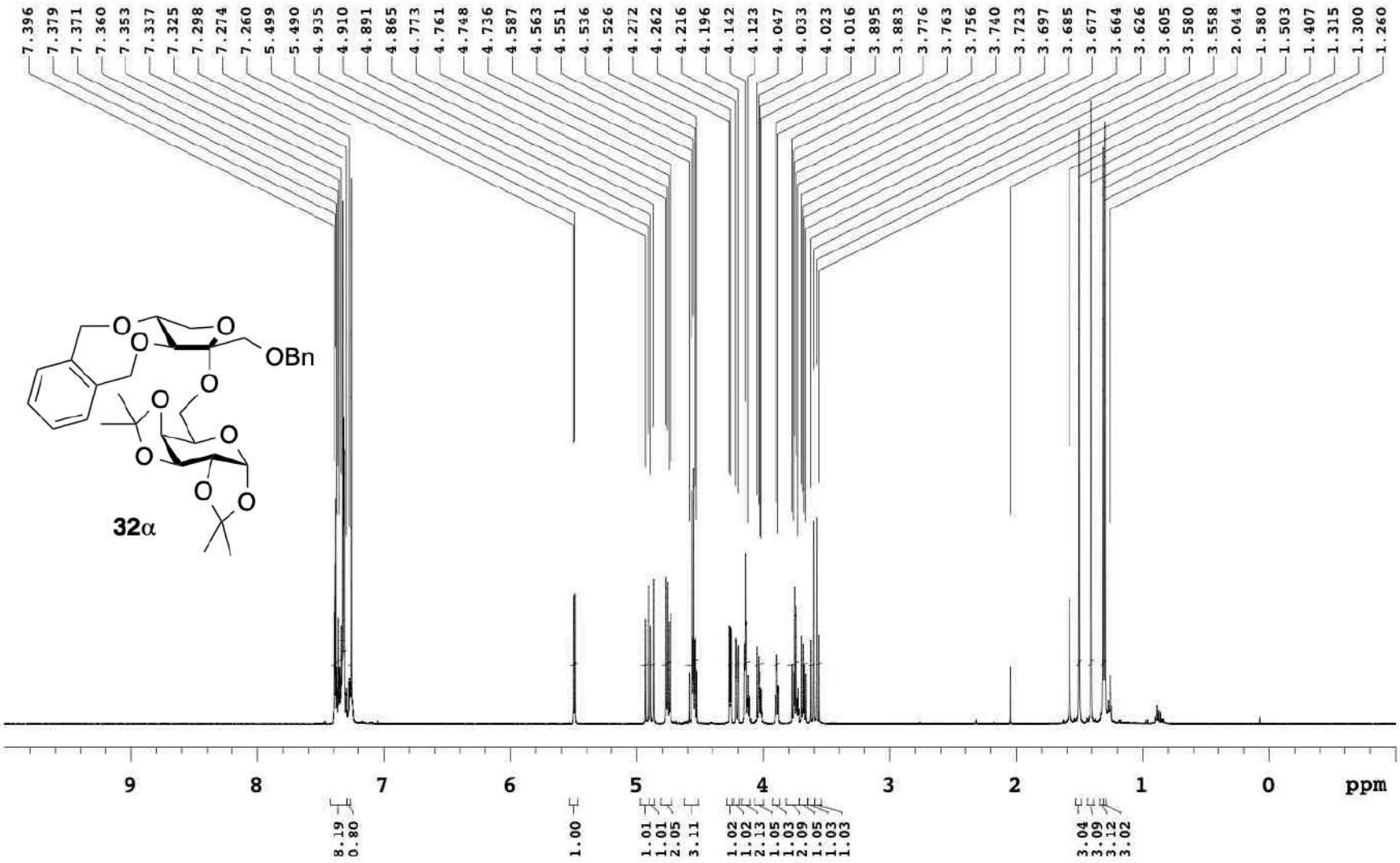

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Jan 31 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.9
Relaxation Delay(s): 1
Completed Scans 128
Bo-Shun, Ball-XYL-084-2
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
138.368
136.947
136.838
131.834
131.157
129.344
129.270
128.499
127.839
127.697
107.731
83.553
80.870
77.482
77.228
76.973
75.796
73.536
70.591
70.146
69.215
31.171
OBn
31β
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.31.u5_Ball-XYL-084-2_loc2_13.00_C13_1D

Department of Chemistry, University of Alberta

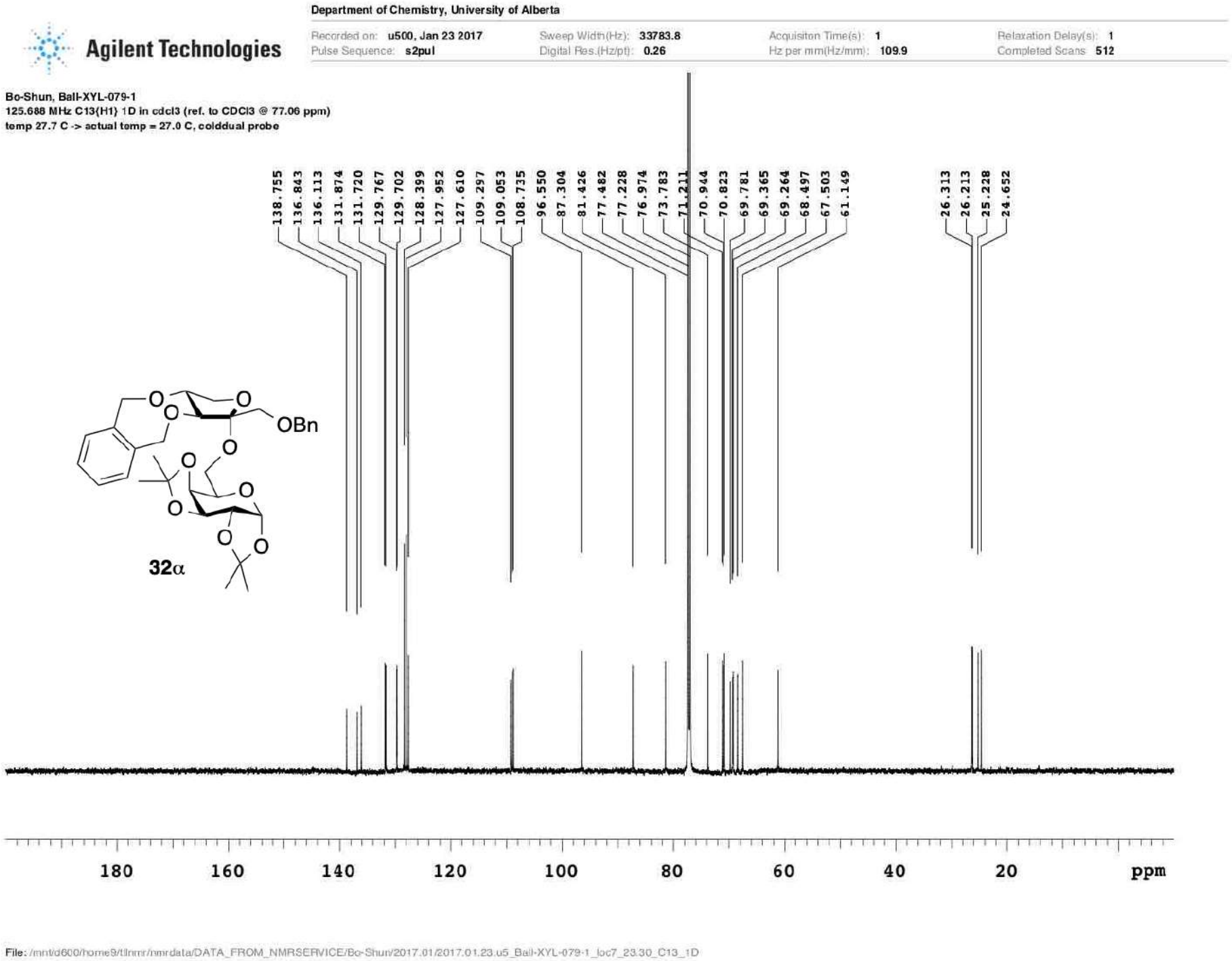
Agilent Technologies

Recorded on:	u500, Jan 23 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.91	Completed Scans	16

Bo-Shun, Ball-XYL-079-1
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.23.u5_Ball-XYL-079-1_loc7_23.28_H1_1D

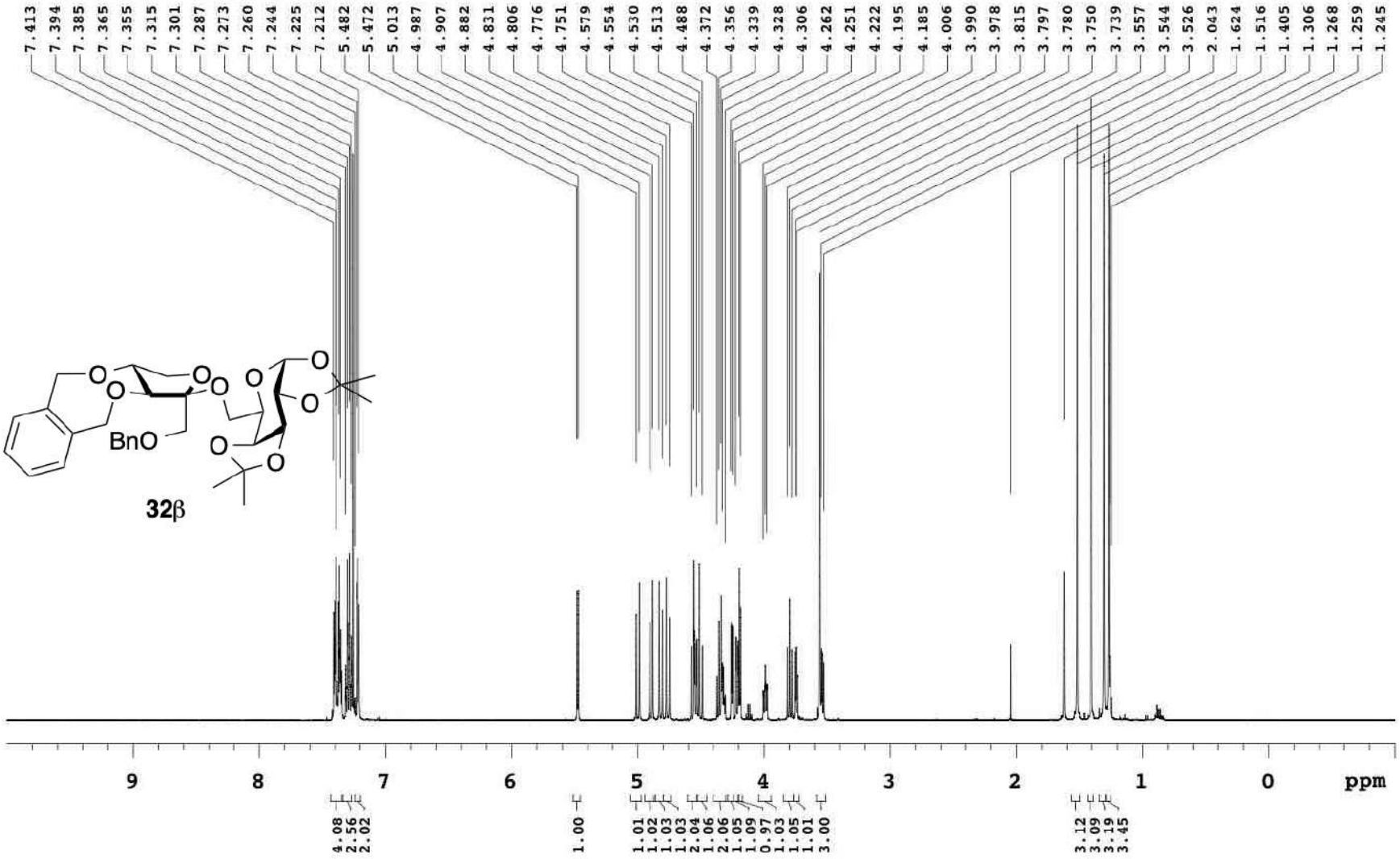

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Jan 23 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.9
Relaxation Delay(s): 1
Completed Scans 512
Bo-Shun, Ball-XYL-079-1
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
138.755
136.843
136.113
131.874
131.720
129.767
129.702
128.399
127.952
127.610
109.297
109.053
108.735
96.550
87.304
81.426
77.482
77.228
76.974
73.783
71.211
70.944
70.823
69.781
69.365
69.264
68.497
67.503
61.149
26.313
26.213
25.228
24.652
OBn
32α
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.23.u5_Ball-XYL-079-1_loc7_23.30_C13_1D

Department of Chemistry, University of Alberta

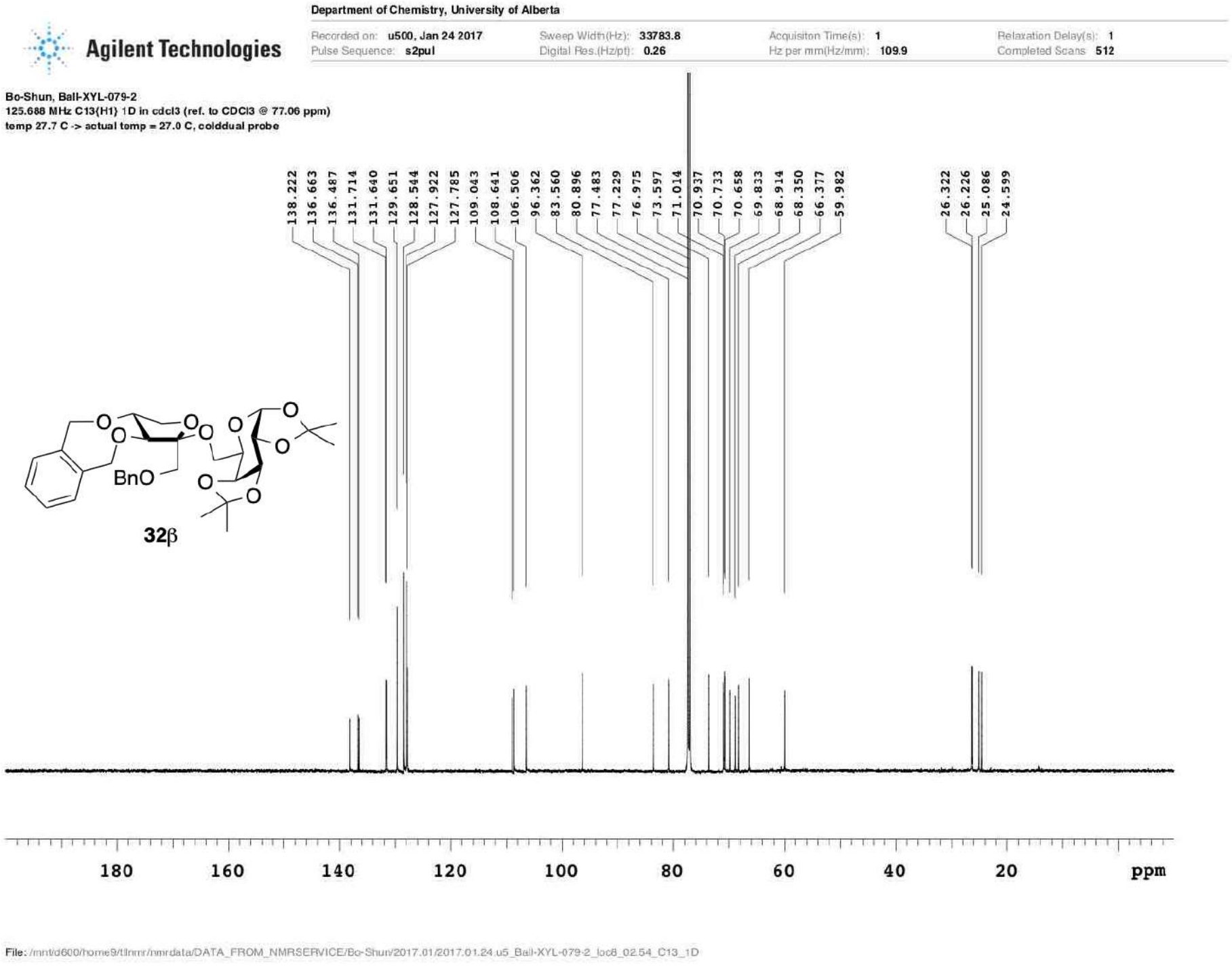
Agilent Technologies

Recorded on:	u500, Jan 24 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.91	Completed Scans	16

Bo-Shun, Ball-XYL-079-2
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.24.u5_Ball-XYL-079-2_loc8_02.53_H1_1D

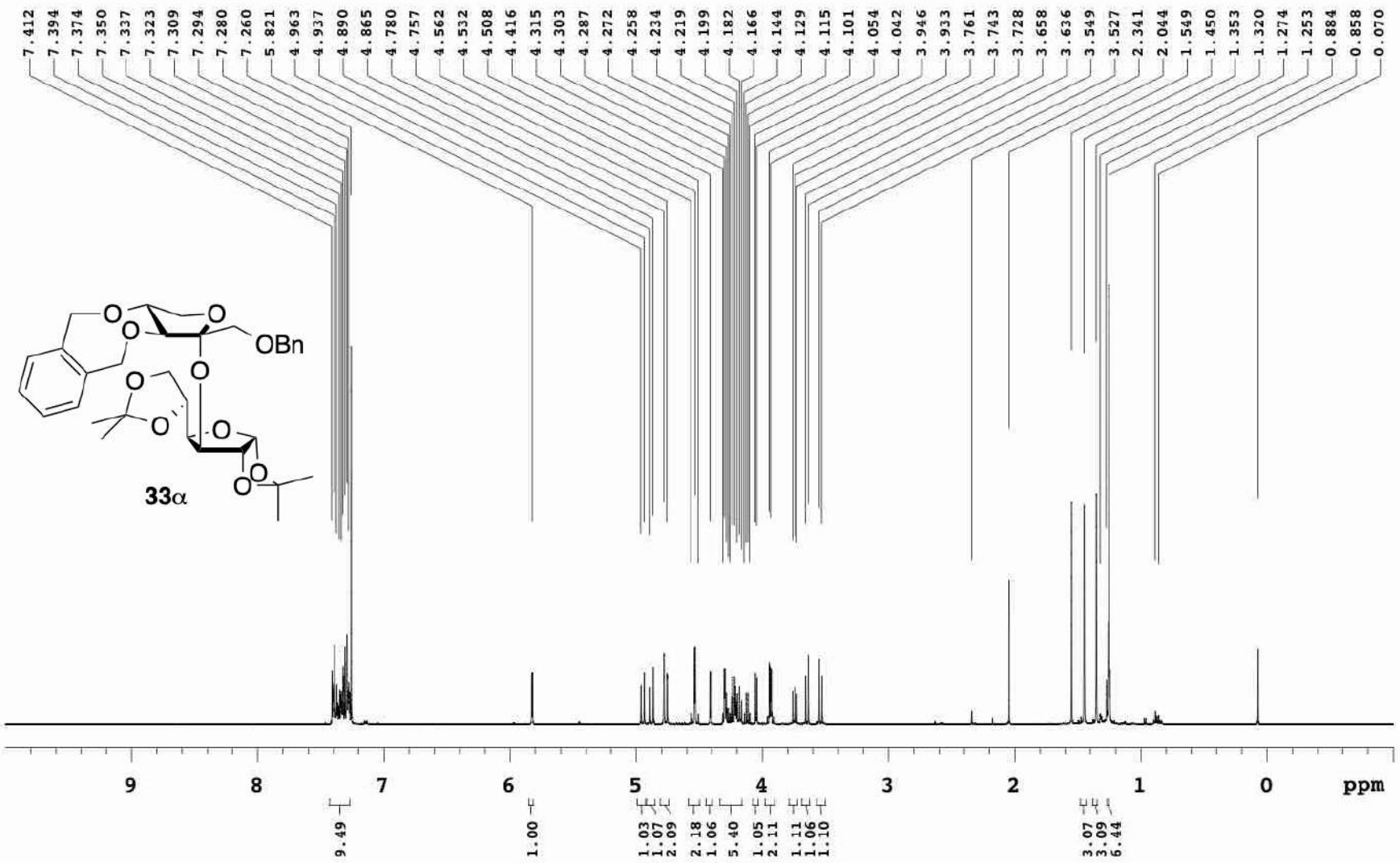

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Jan 24 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.9
Relaxation Delay(s): 1
Completed Scans 512
Bo-Shun, Ball-XYL-079-2
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
138.222
136.663
136.487
131.714
131.640
129.651
128.544
127.922
127.785
109.043
108.641
106.506
96.362
83.560
80.896
77.483
77.229
76.975
73.597
71.014
70.937
70.733
70.658
69.833
68.914
68.350
66.377
59.982
26.322
26.226
25.086
24.599
BnO
32β
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.24.u5_Ball-XYL-079-2_loc8_02.54_C13_1D

Department of Chemistry, University of Alberta

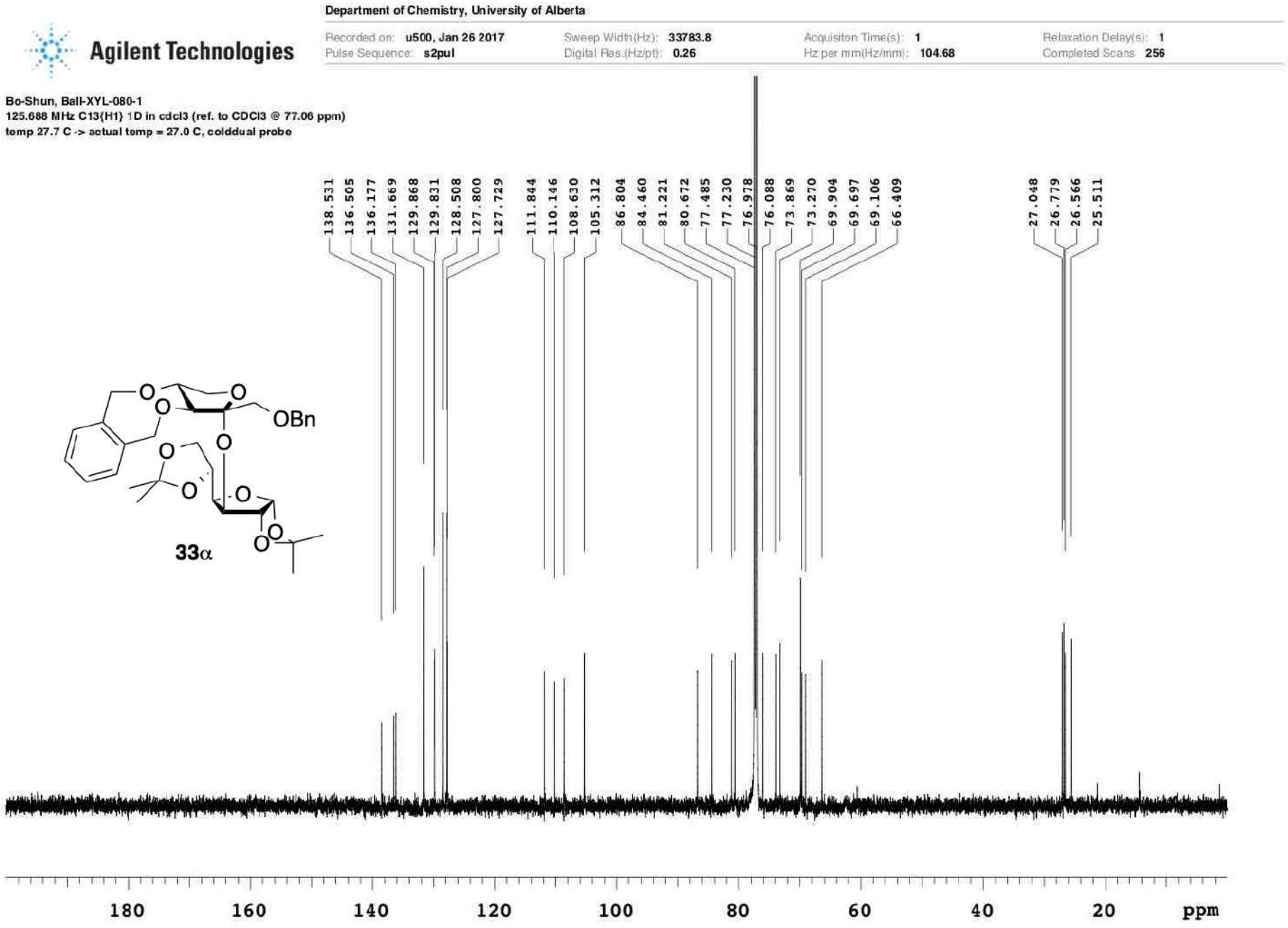
Agilent Technologies

Recorded on:	u500, Jan 26 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.91	Completed Scans	16

Bo-Shun, Ball-XYL-080-1
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.26.u5_Ball-XYL-080-1_loc2_02.49_H1_1D

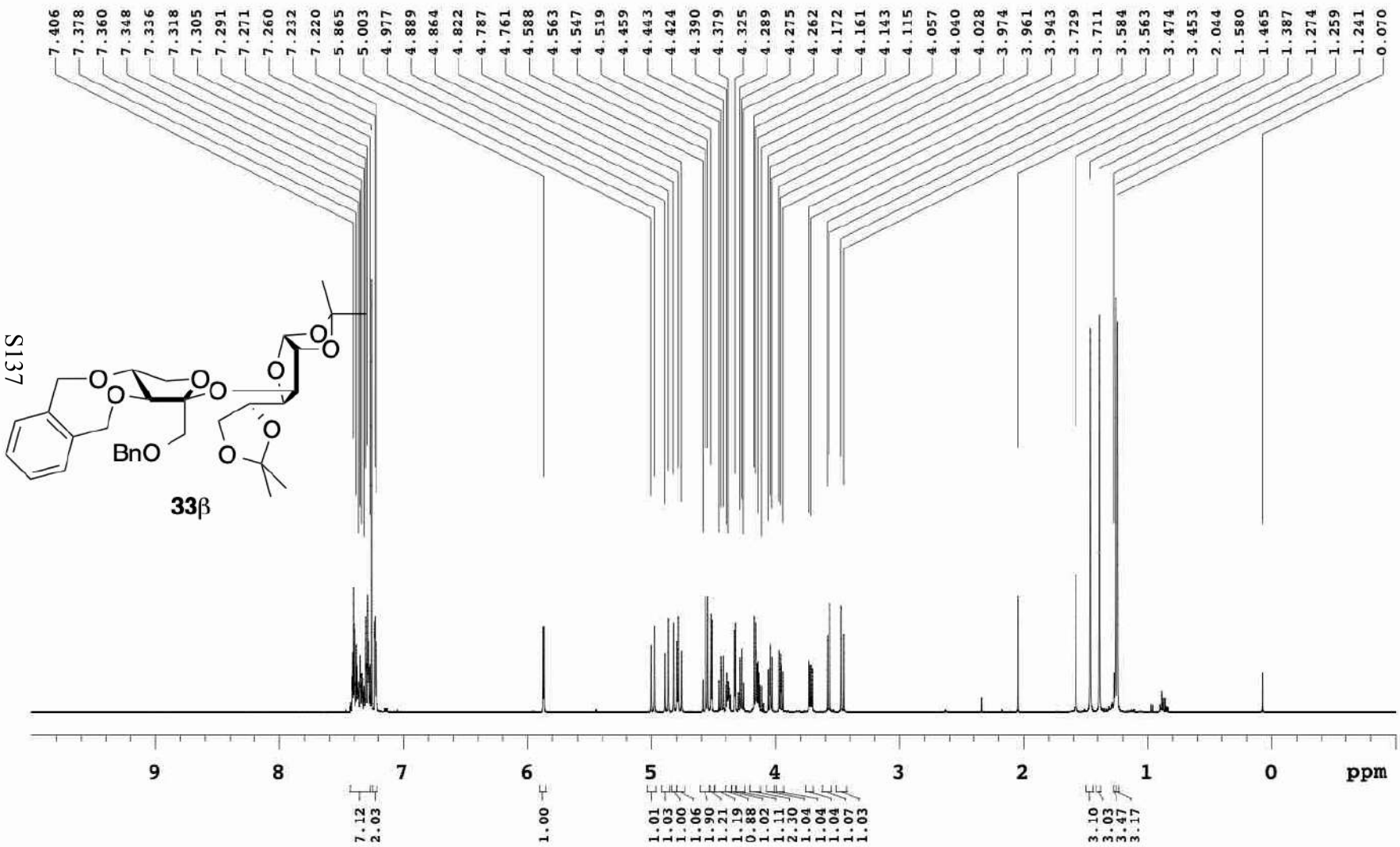

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Jan 26 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 104.68
Relaxation Delay(s): 1
Completed Scans 256
Bo-Shun, Ball-XYL-080-1
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
138.531
136.505
136.177
131.669
129.868
129.831
128.508
127.800
127.729
111.844
110.146
108.630
105.312
86.804
84.460
81.221
80.672
77.485
77.230
76.978
76.088
73.869
73.270
69.904
69.697
69.106
66.409
27.048
26.779
26.566
25.511
OBn
33α
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.26.u5_Ball-XYL-080-1_loc2_02.51_C13_1D

Department of Chemistry, University of Alberta

Agilent Technologies

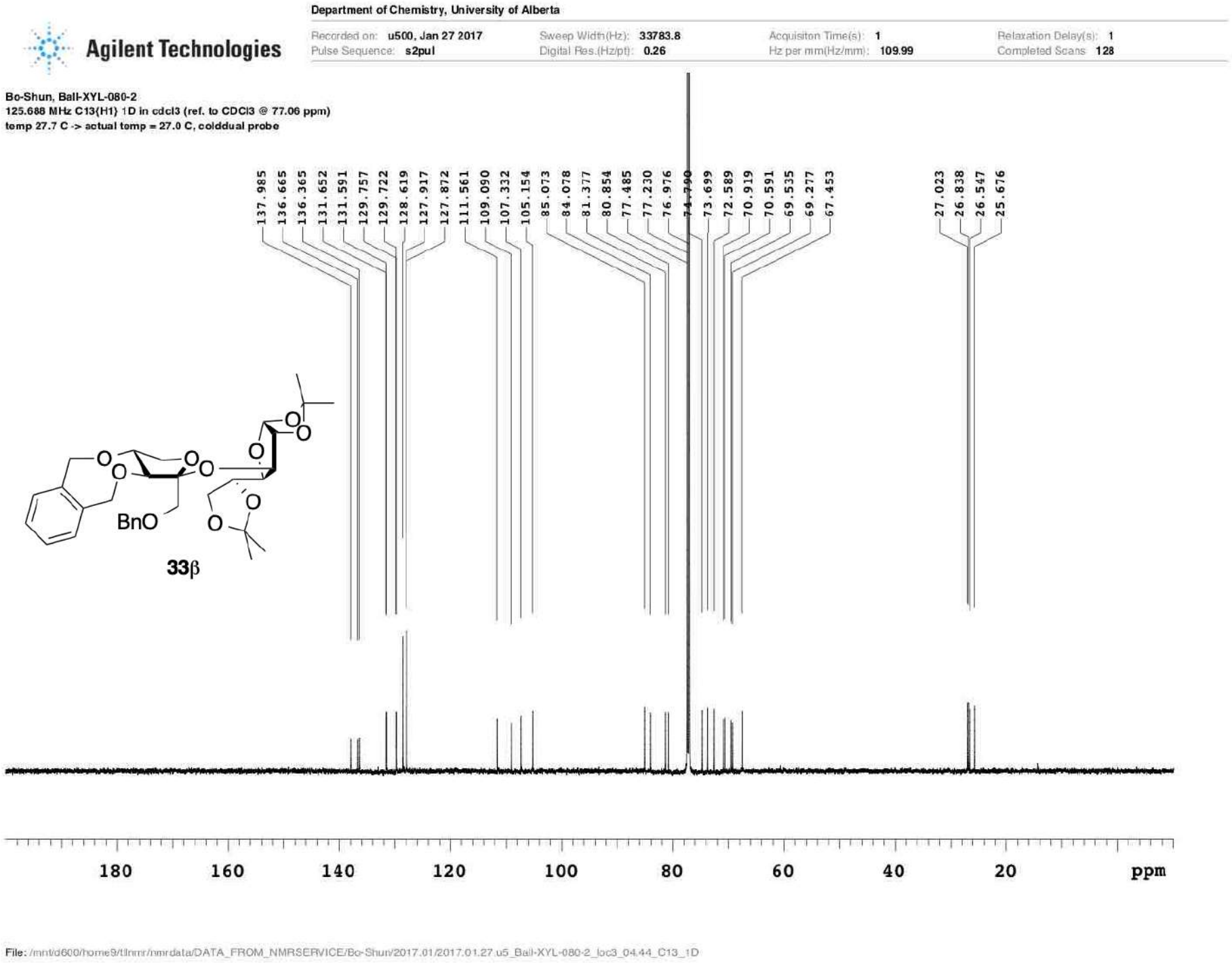
Recorded on:	u500, Jan 27 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.91	Completed Scans	16

Bo-Shun, Ball-XYL-080-2
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



33β

File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.27.u5_Ball-XYL-080-2_loc3_04.43_H1_1D

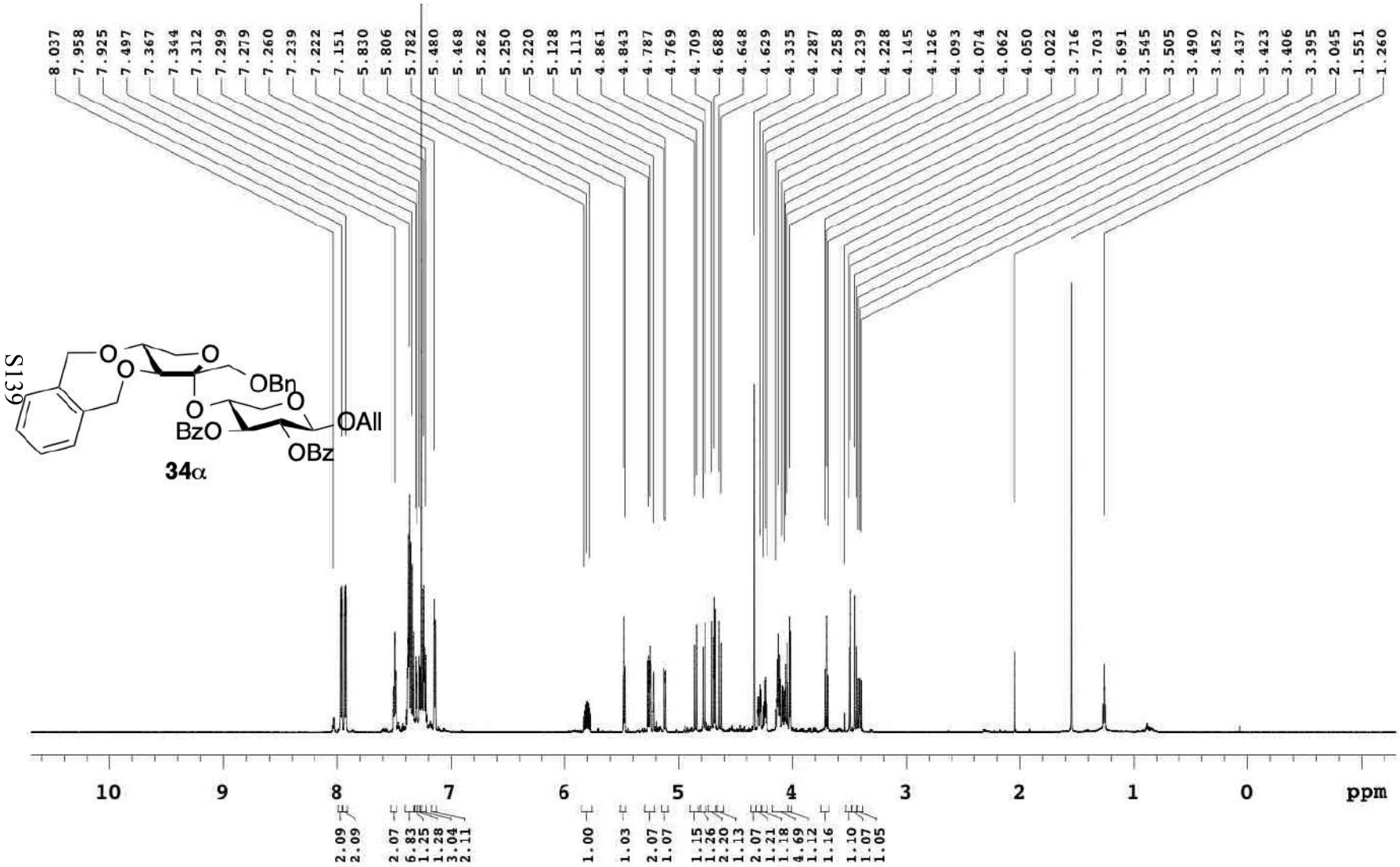

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Jan 27 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.99
Relaxation Delay(s): 1
Completed Scans 128
Bo-Shun, Ball-XYL-080-2
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
137.985
136.665
136.365
131.652
131.591
129.757
129.722
128.619
127.917
127.872
111.561
109.090
107.332
105.154
85.073
84.078
81.377
80.854
77.485
77.230
76.976
74.780
73.699
72.589
70.919
70.591
69.535
69.277
67.453
27.023
26.838
26.547
25.676
BnO
33β
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.27.u5_Ball-XYL-080-2_loc3_04.44_C13_1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	v700, Dec 7 2016	Sweep Width(Hz):	8389.26	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.13	Hz per mm(Hz/mm):	34.95	Completed Scans	16

Bo-Shun, Ball-XYL-067-1
699.762 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.12/2016.12.7.v7_Ball-XYL-067-1_loc19_20.03_H1_1D

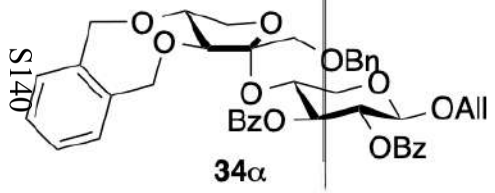
Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	v700, Dec 7 2016	Sweep Width(Hz):	48076.9	Acquisiton Time(s):	1	Relaxation Delay(s):	1
Pulse Sequence:	s2pul	Digital Res.(Hz/pt):	0.37	Hz per mm(Hz/mm):	153.79	Completed Scans	256

Bo-Shun, Ball-XYL-067-1
175.975 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe

165.687 165.486 138.491 136.704 136.062 133.859 133.171 133.150 131.722 131.643 130.079 130.044 129.996 129.904 129.741 129.502 128.457 128.361 127.776 127.555 117.622 109.752 99.713 88.324 80.972 77.409 77.228 77.046 73.617 72.533 71.422 69.830 69.748 69.619 69.525 69.100 69.035 64.837



34α

180 160 140 120 100 80 60 40 20 ppm

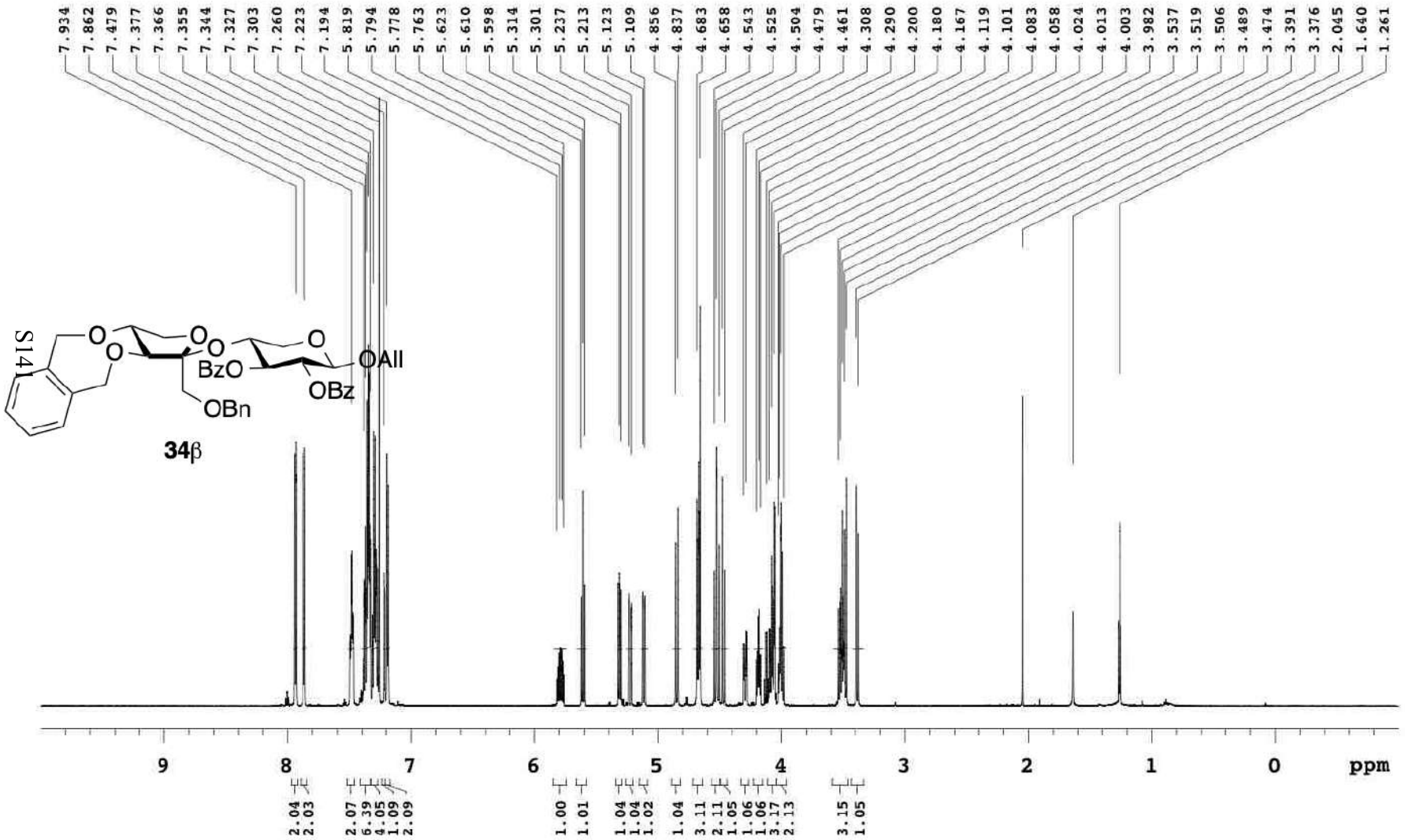
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.12/2016.12.7.v7_Ball-XYL-067-1_loc19_20.05_C13_1D

Department of Chemistry, University of Alberta

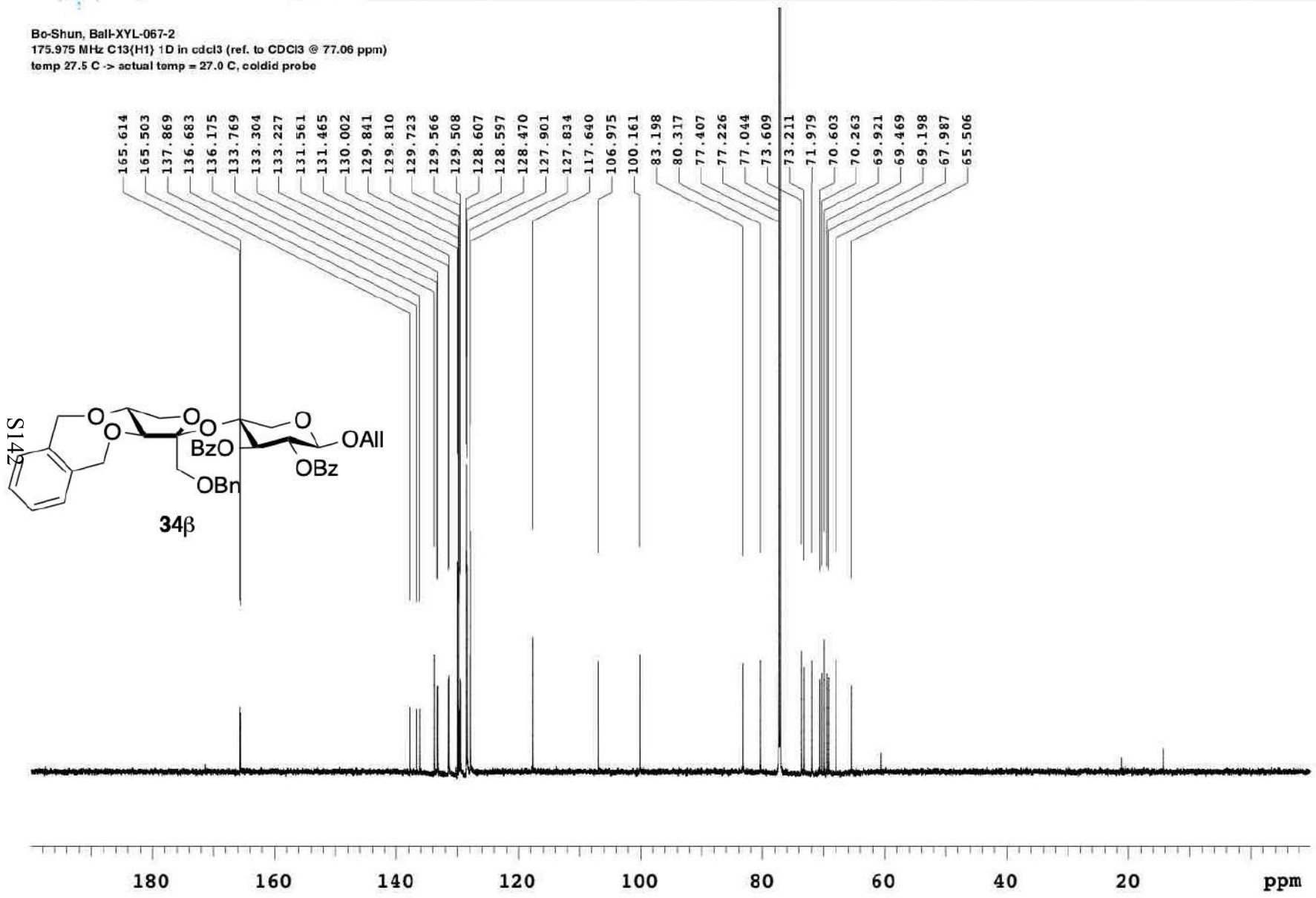
Agilent Technologies

Recorded on:	v700, Dec 8 2016	Sweep Width(Hz):	8389.26	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.13	Hz per mm(Hz/mm):	32.04	Completed Scans	16

Bo-Shun, Ball-XYL-067-2
699.762 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.12/2016.12.8.v7_Ball-XYL-067-2_loc20_00.14_H1_1D

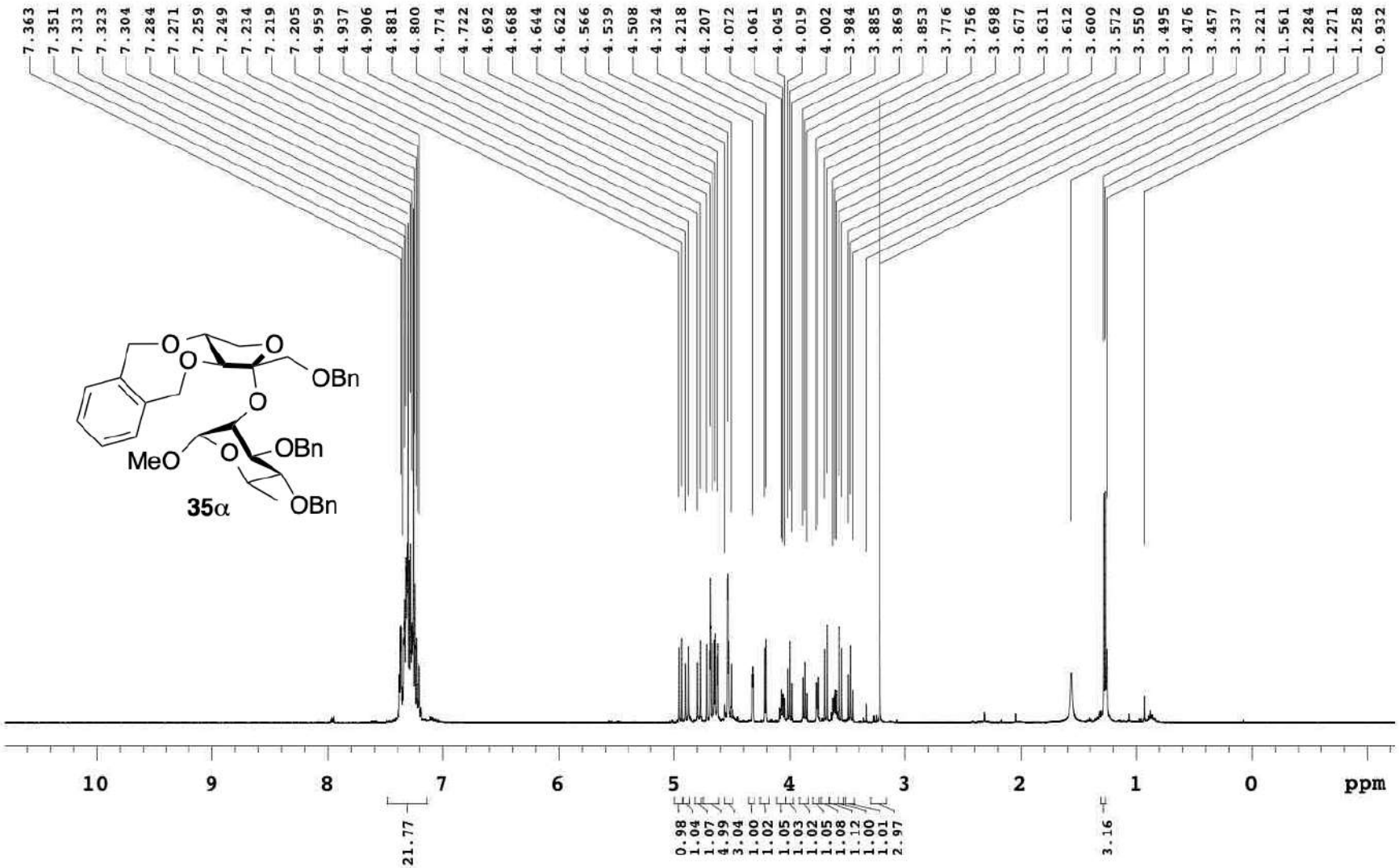

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: v700, Dec 8 2016
Pulse Sequence: s2pul
Sweep Width(Hz): 48076.9
Digital Res.(Hz/pt): 0.37
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 153.53
Relaxation Delay(s): 1
Completed Scans 256
Bo-Shun, Ball-XYL-067-2
175.975 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe
165.614
165.503
137.869
136.683
136.175
133.769
133.304
133.227
131.561
131.465
130.002
129.841
129.810
129.723
129.566
129.508
128.607
128.597
128.470
127.901
127.834
117.640
106.975
100.161
83.198
80.317
77.407
77.226
77.044
73.609
73.211
71.979
70.603
70.263
69.921
69.469
69.198
67.987
65.506
BzO
OBn
OBz
OAll
34β
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.12/2016.12.8.v7_Ball-XYL-067-2_loc20_00.16_C13_1D

Department of Chemistry, University of Alberta

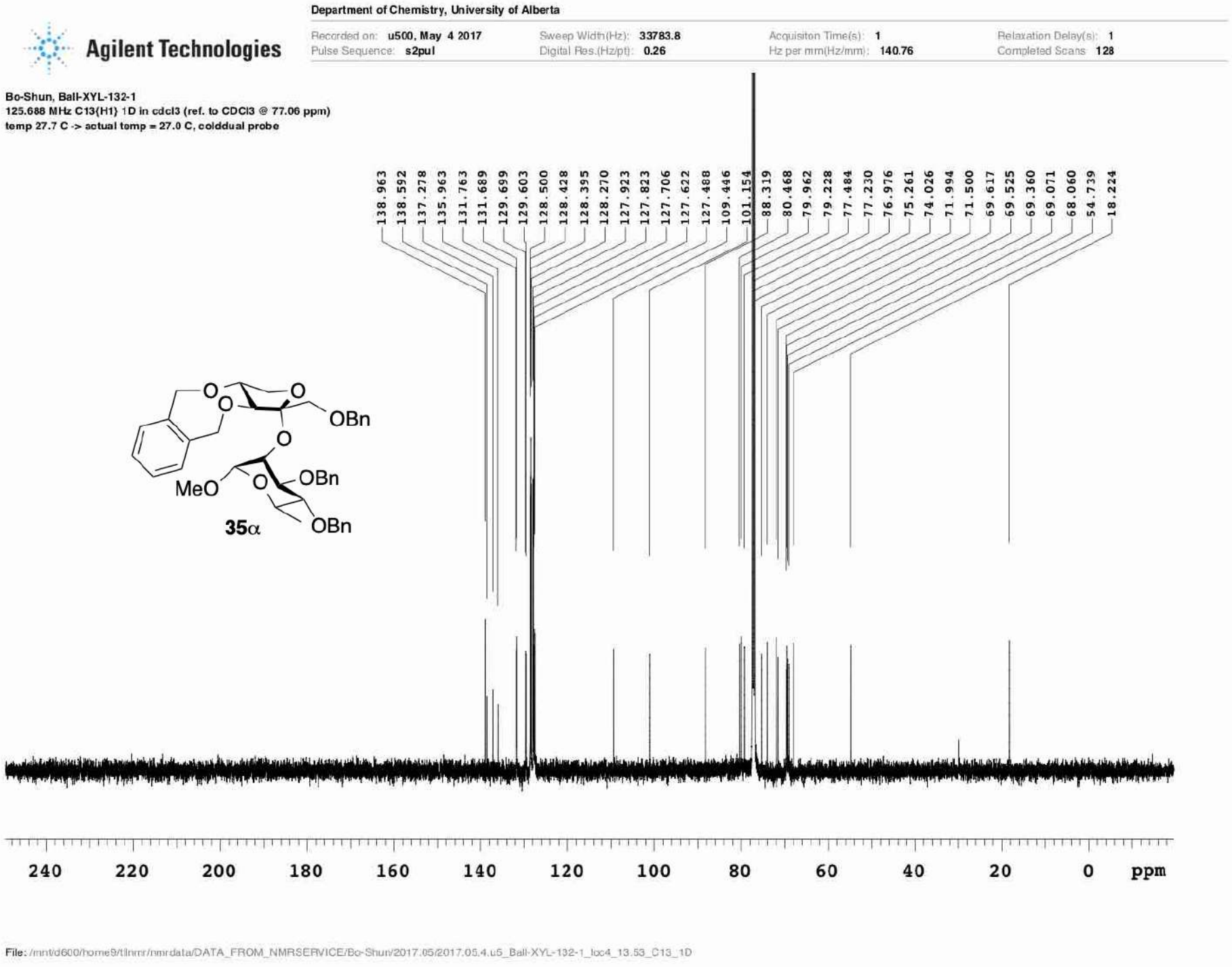
Agilent Technologies

Recorded on:	u500, May 4 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	25.04	Completed Scans	16

Bo-Shun, Ball-XYL-132-1
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.05/2017.05.4.u5_Ball-XYL-132-1_loc4_13.51_H1_1D

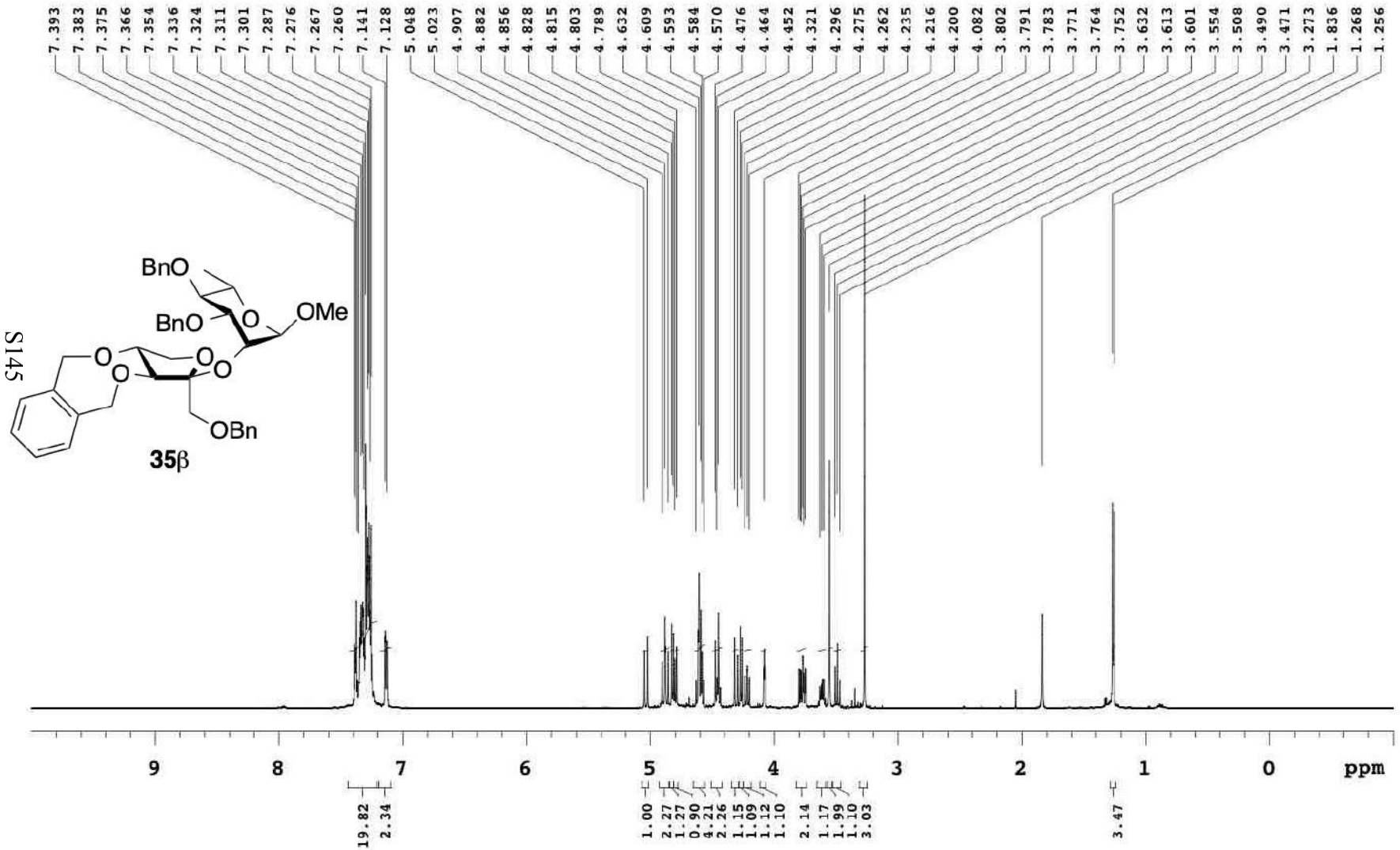

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, May 4 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 140.76
Relaxation Delay(s): 1
Completed Scans 128
Bo-Shun, Ball-XYL-132-1
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
138.963
138.592
137.278
135.963
131.763
131.689
129.699
129.603
128.500
128.428
128.395
128.270
127.923
127.823
127.706
127.622
127.488
109.446
101.154
88.319
80.468
79.962
79.228
77.484
77.230
76.976
75.261
74.026
71.994
71.500
69.617
69.525
69.360
69.071
68.060
54.739
18.224
OBn
OBn
OBn
MeO
35α
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.05/2017.05.4.u5_Ball-XYL-132-1_loc4_13.53_C13_1D

Department of Chemistry, University of Alberta

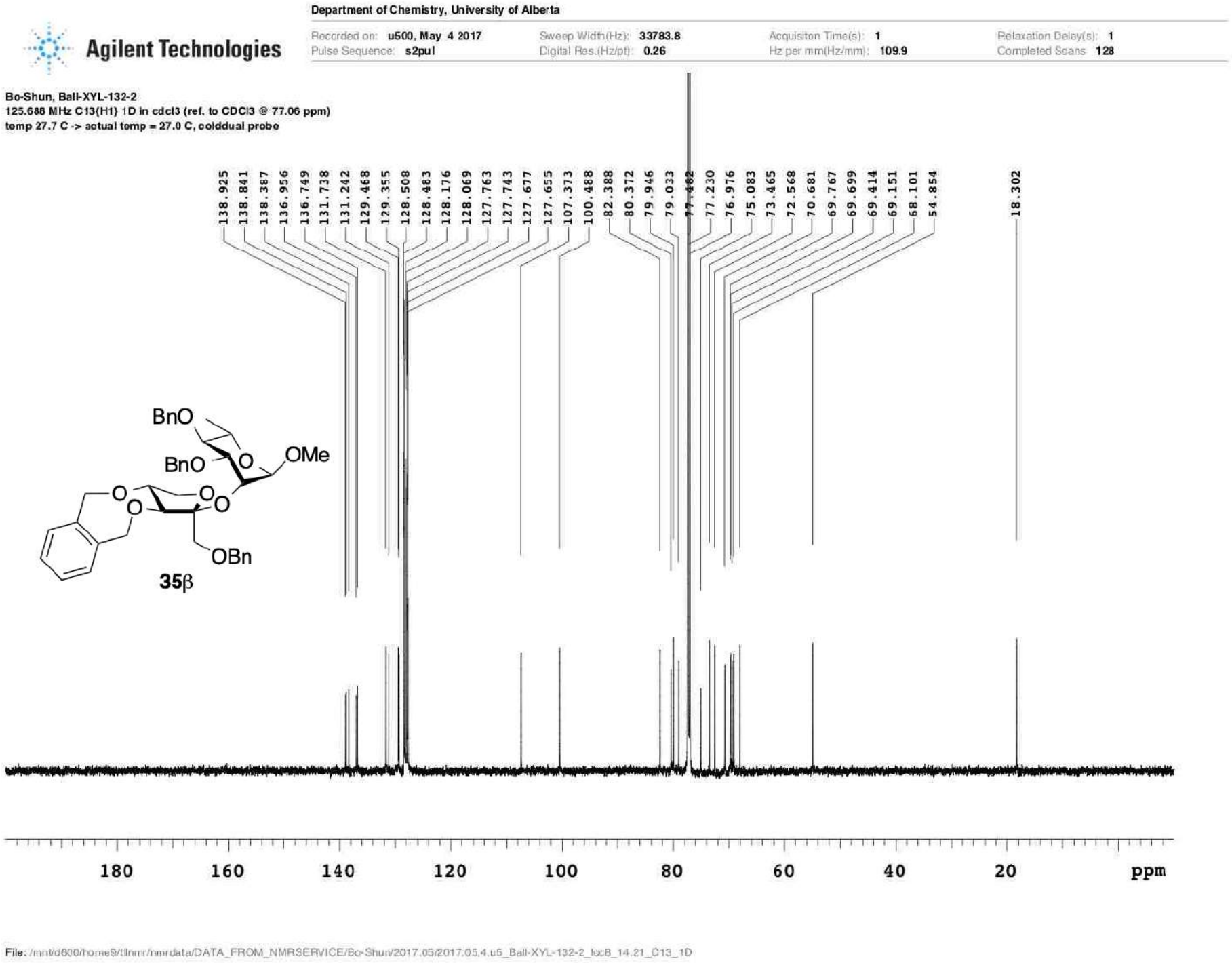
Agilent Technologies

Recorded on:	u500, May 4 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.91	Completed Scans	16

Bo-Shun, Ball-XYL-132-2
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.05/2017.05.4.u5_Ball-XYL-132-2_loc8_14.19_H1_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, May 4 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.9
Relaxation Delay(s): 1
Completed Scans 128
Bo-Shun, Ball-XYL-132-2
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
138.925
138.841
138.387
136.956
136.749
131.738
131.242
129.468
129.355
128.508
128.483
128.176
128.069
127.763
127.743
127.677
127.655
107.373
100.488
82.388
80.372
79.946
79.033
77.482
77.230
76.976
75.083
73.465
72.568
70.681
69.767
69.699
69.414
69.151
68.101
54.854
18.302
BnO
BnO
OMe
OBn
35β
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.05/2017.05.4.u5_Ball-XYL-132-2_loc8_14.21_C13_1D

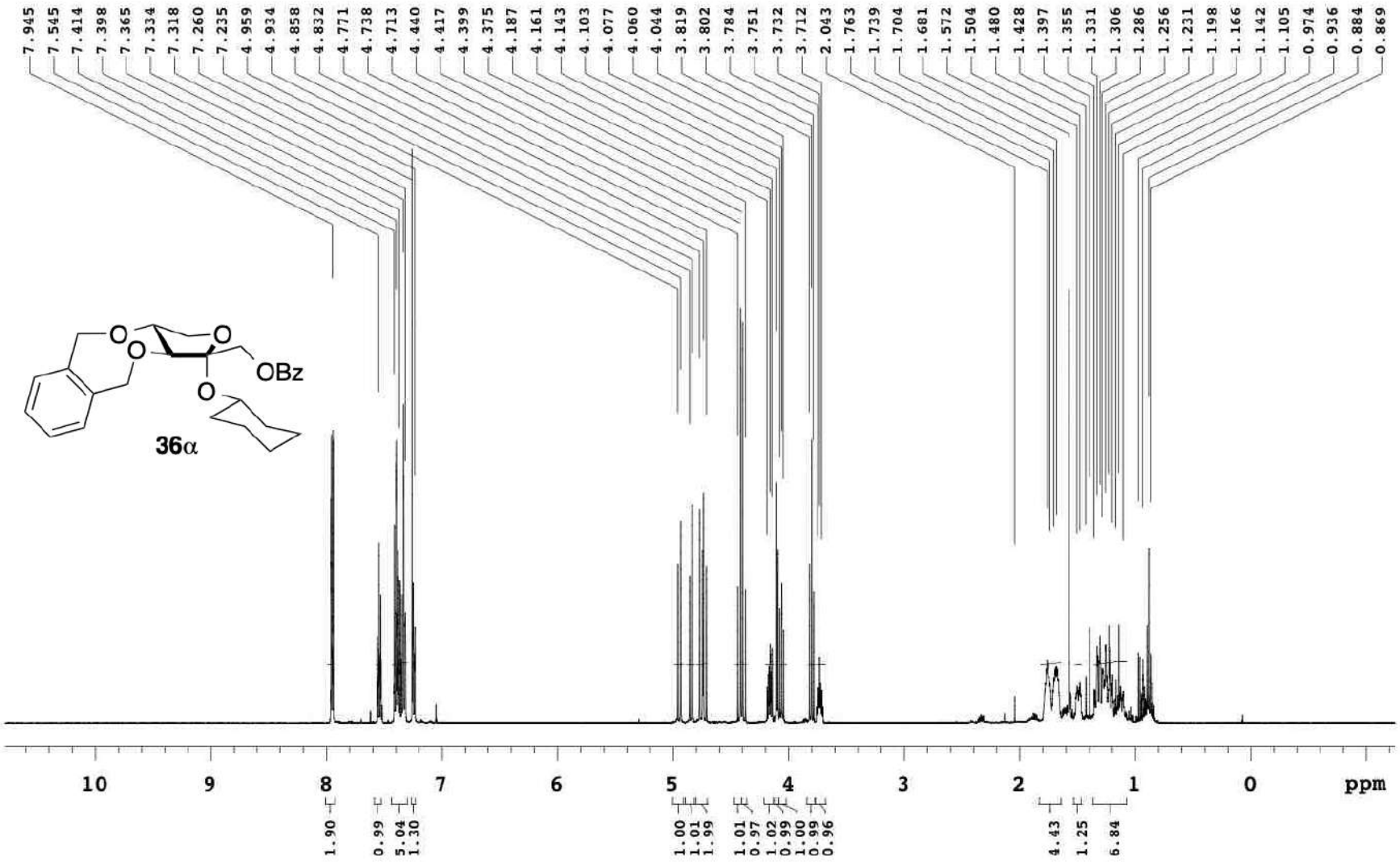
Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	u500, Jun 24 2016	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	25.04	Completed Scans	16

Bo-Shun, Ball-XYL-043-1

499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.06/2016.06.24.u5_Ball-XYL-043-1_loc5_20.03_H1_1D

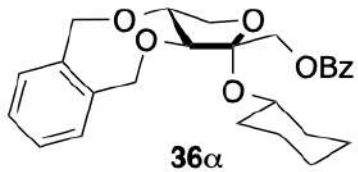
Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	u500, Jun 24 2016	Sweep Width(Hz):	32894.7	Acquisiton Time(s):	1	Relaxation Delay(s):	1
Pulse Sequence:	s2pul	Digital Res.(Hz/pt):	0.25	Hz per mm(Hz/mm):	137.06	Completed Scans	128

Bo-Shun, Ball-XYL-043-1

125.691 MHz C13[H1] 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe



36α

166.308, 136.719, 136.018, 132.995, 131.806, 131.621, 130.616, 129.857, 129.798, 129.694, 128.527, 108.734, 88.521, 81.242, 77.484, 77.230, 76.976, 71.375, 69.841, 69.061, 68.635, 63.014, 35.161, 34.553, 25.681, 24.820, 24.800

240 220 200 180 160 140 120 100 80 60 40 20 ppm

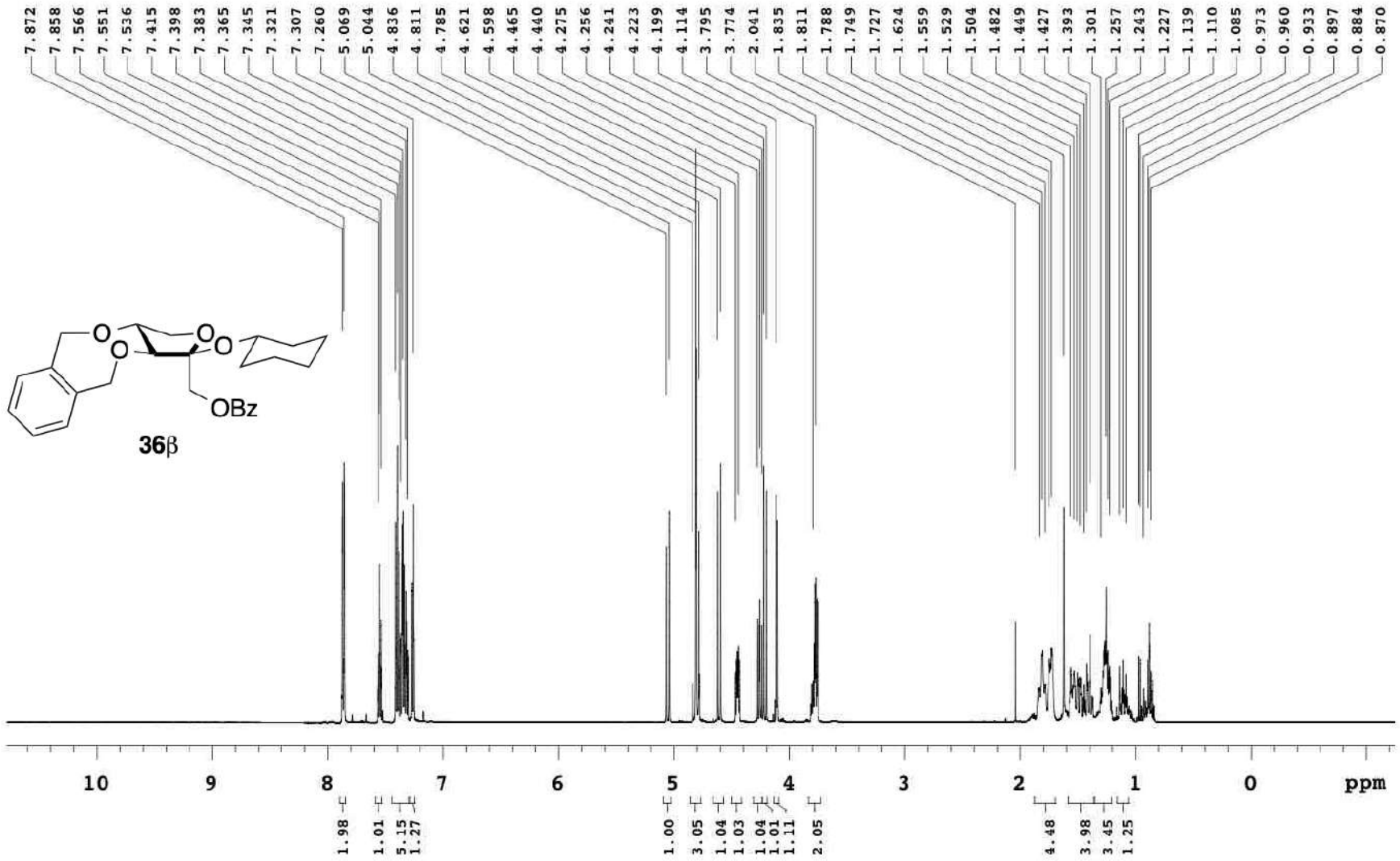
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.06/2016.06.24.u5_Ball-XYL-043-1_loc5_20.05_C13_1D

Agilent Technologies

Department of Chemistry, University of Alberta

Recorded on:	u500, Jun 24 2016	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	25.04	Completed Scans	16

Bo-Shun, Ball-XYL-043-2
499.806 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe



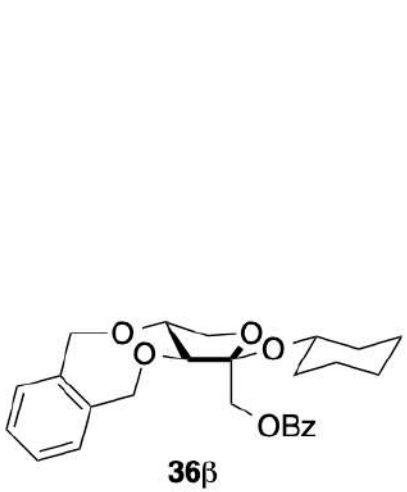
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.06/2016.06.24.u5_Ball-XYL-043-2_loc6_22.55_H1_1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	u500, Jun 24 2016	Sweep Width(Hz):	32894.7	Acquisiton Time(s):	1	Relaxation Delay(s):	1
Pulse Sequence:	s2pul	Digital Res.(Hz/pt):	0.25	Hz per mm(Hz/mm):	137.06	Completed Scans	128

Bo-Shun, Ball-XYL-043-2
125.691 MHz C13[H1] 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe



36β

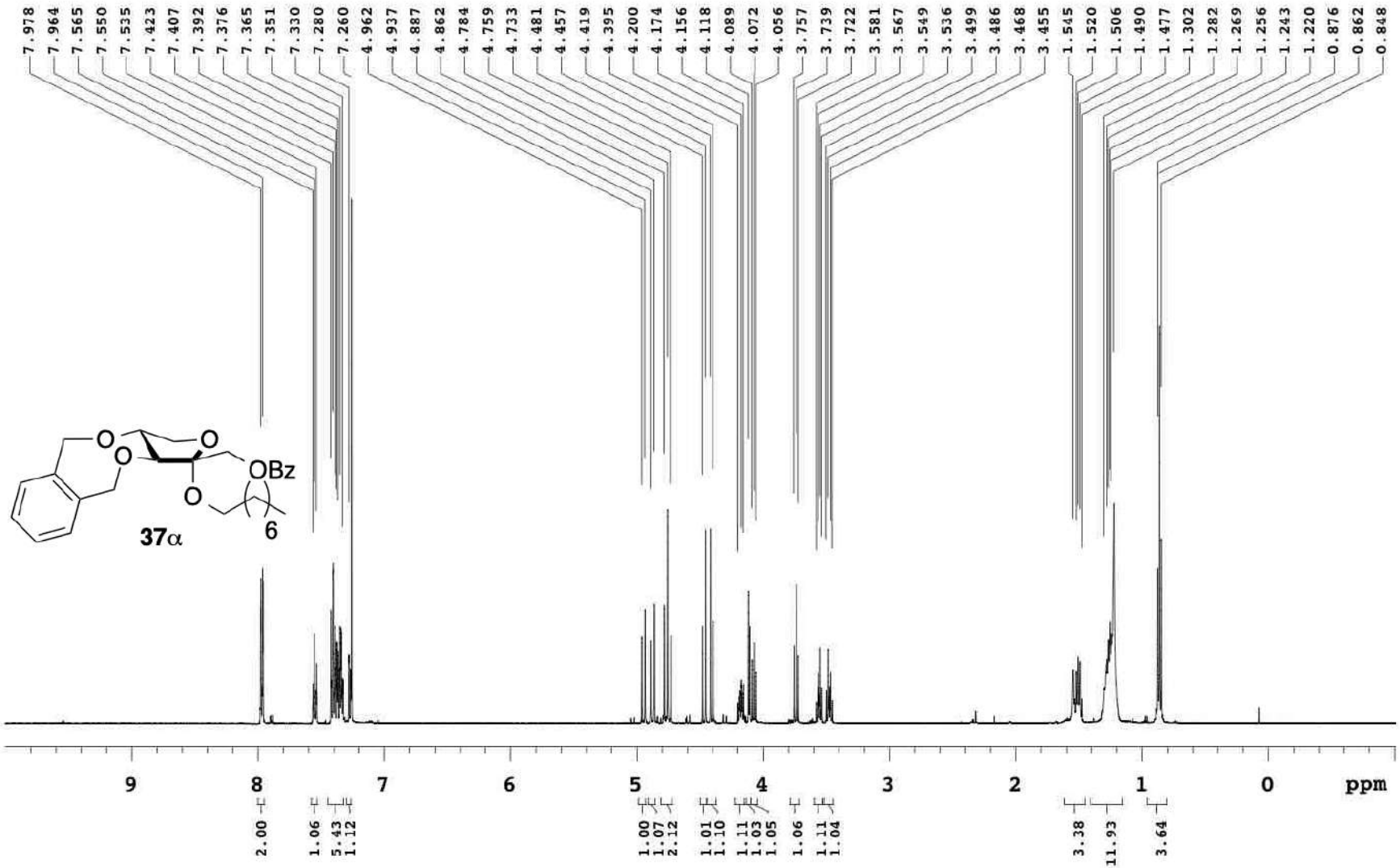
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.06/2016.06.24.u5_Ball-XYL-043-2_loc6_22.57_C13_1D

Department of Chemistry, University of Alberta

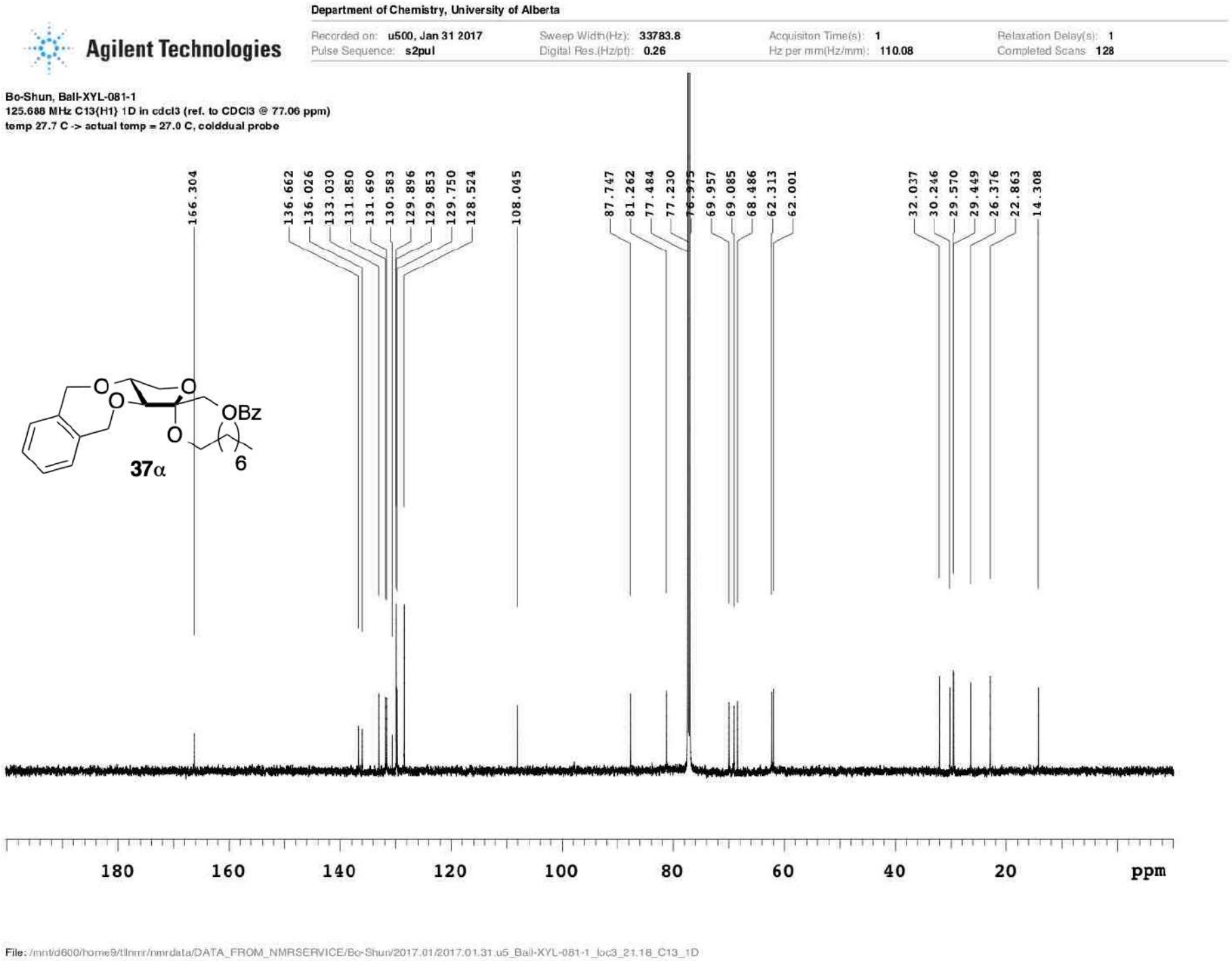
Agilent Technologies

Recorded on:	u500, Jan 31 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.92	Completed Scans	16

Bo-Shun, Ball-XYL-081-1
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.31.u5_Ball-XYL-081-1_loc3_21.16_H1_1D

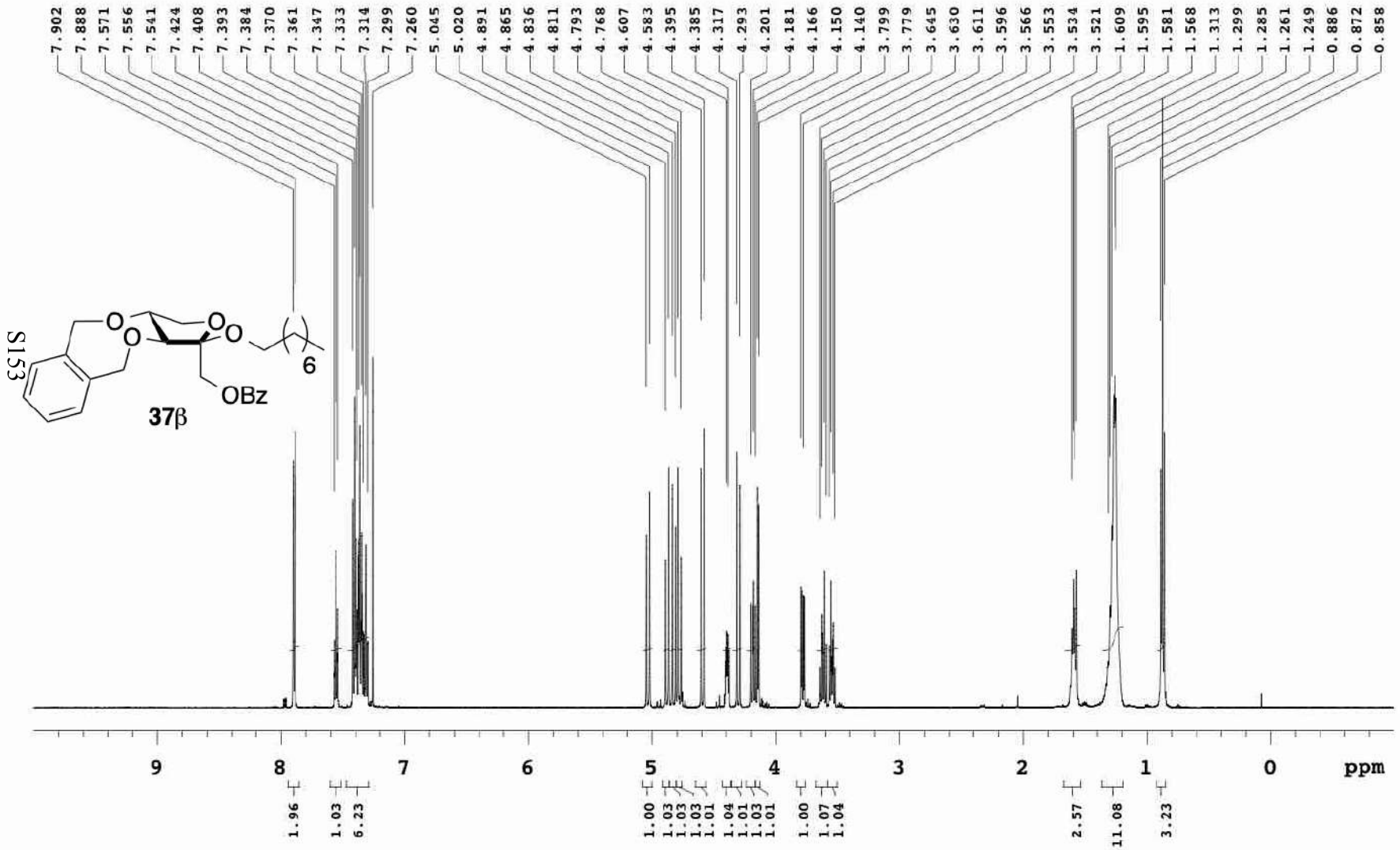

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Jan 31 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 110.08
Relaxation Delay(s): 1
Completed Scans 128
Bo-Shun, Ball-XYL-081-1
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
166.304
136.662
136.026
133.030
131.850
131.690
130.583
129.896
129.853
129.750
128.524
108.045
87.747
81.262
77.484
77.230
76.975
69.957
69.085
68.486
62.313
62.001
32.037
30.246
29.570
29.449
26.376
22.863
14.308
OBz
6
37α
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.31.u5_Ball-XYL-081-1_loc3_21.18_C13_1D

Department of Chemistry, University of Alberta

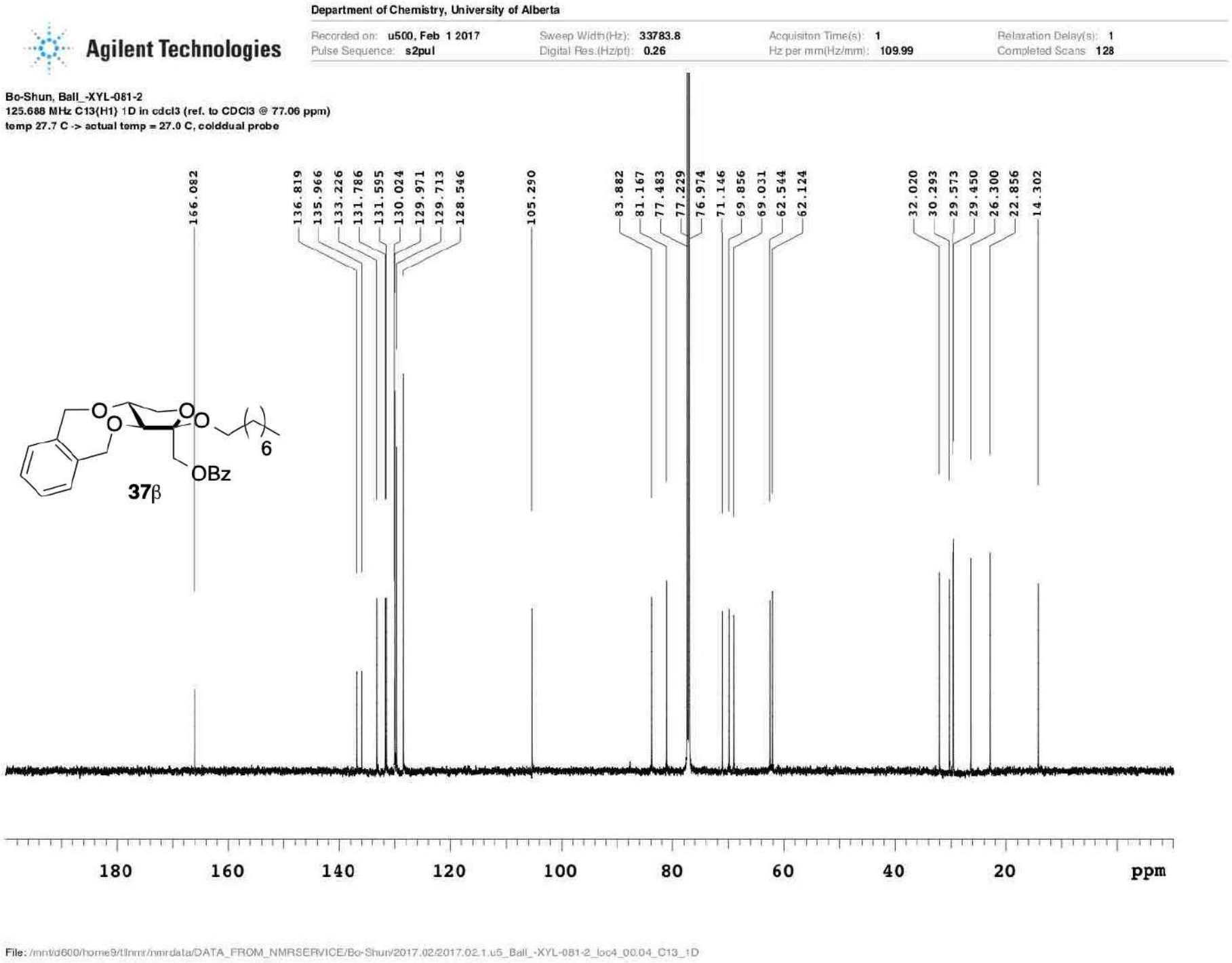
Agilent Technologies

Recorded on:	u500, Feb 1 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.89	Completed Scans	16

Bo-Shun, Ball_-XYL-081-2
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.1.u5_Ball_-XYL-081-2_loc4_00.03_H1_1D

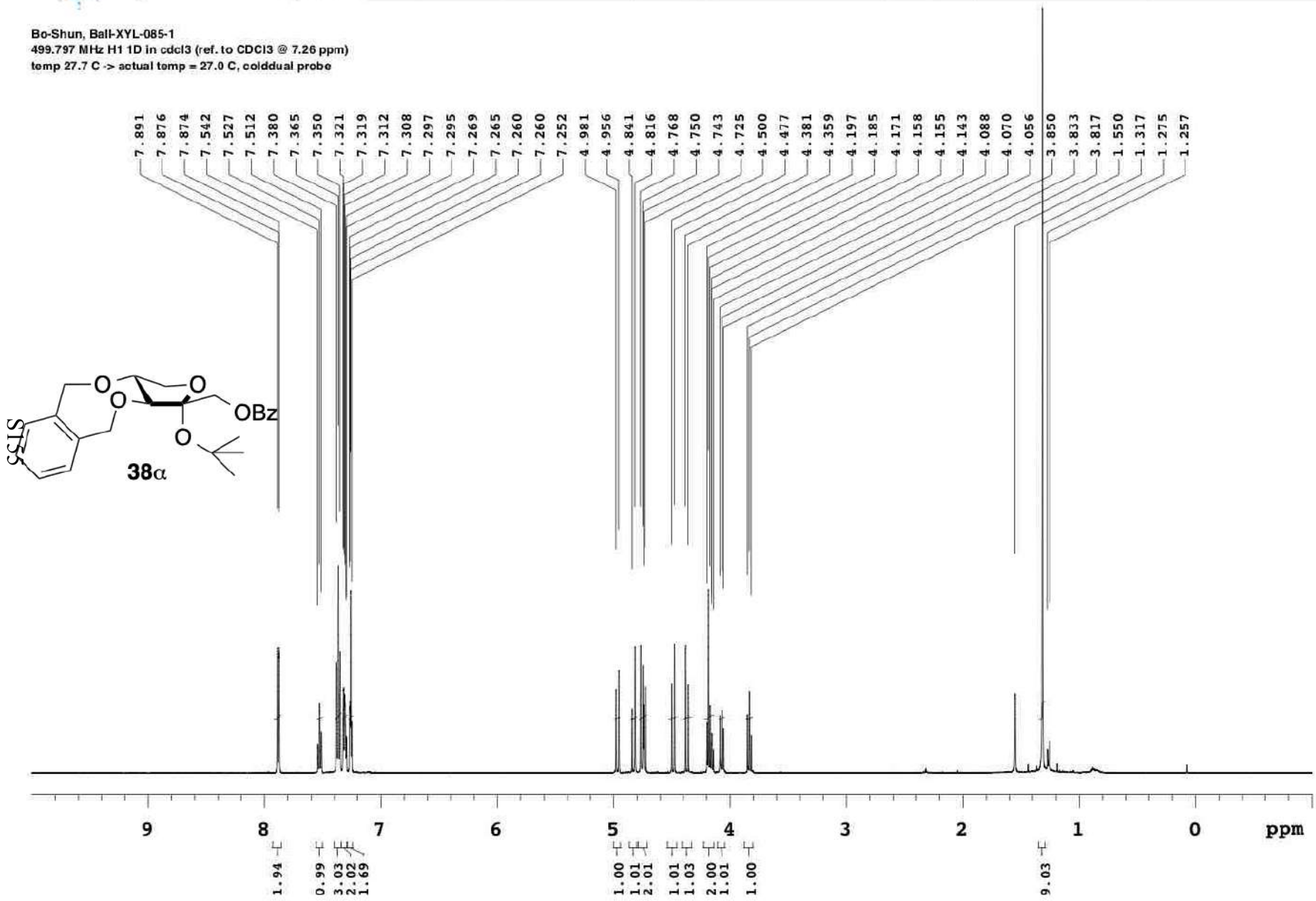

Agilent Technologies
Department of Chemistry, University of Alberta
Recorded on: u500, Feb 1 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.99
Relaxation Delay(s): 1
Completed Scans 128
Bo-Shun, Ball_-XYL-081-2
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
166.082
136.819
135.966
133.226
131.786
131.595
130.024
129.971
129.713
128.546
105.290
83.882
81.167
77.483
77.229
76.974
71.146
69.856
69.031
62.544
62.124
32.020
30.293
29.573
29.450
26.300
22.856
14.302
O
O
O
O
6
OBz
37β
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.1.u5_Ball_-XYL-081-2_loc4_00.04_C13_1D

Department of Chemistry, University of Alberta

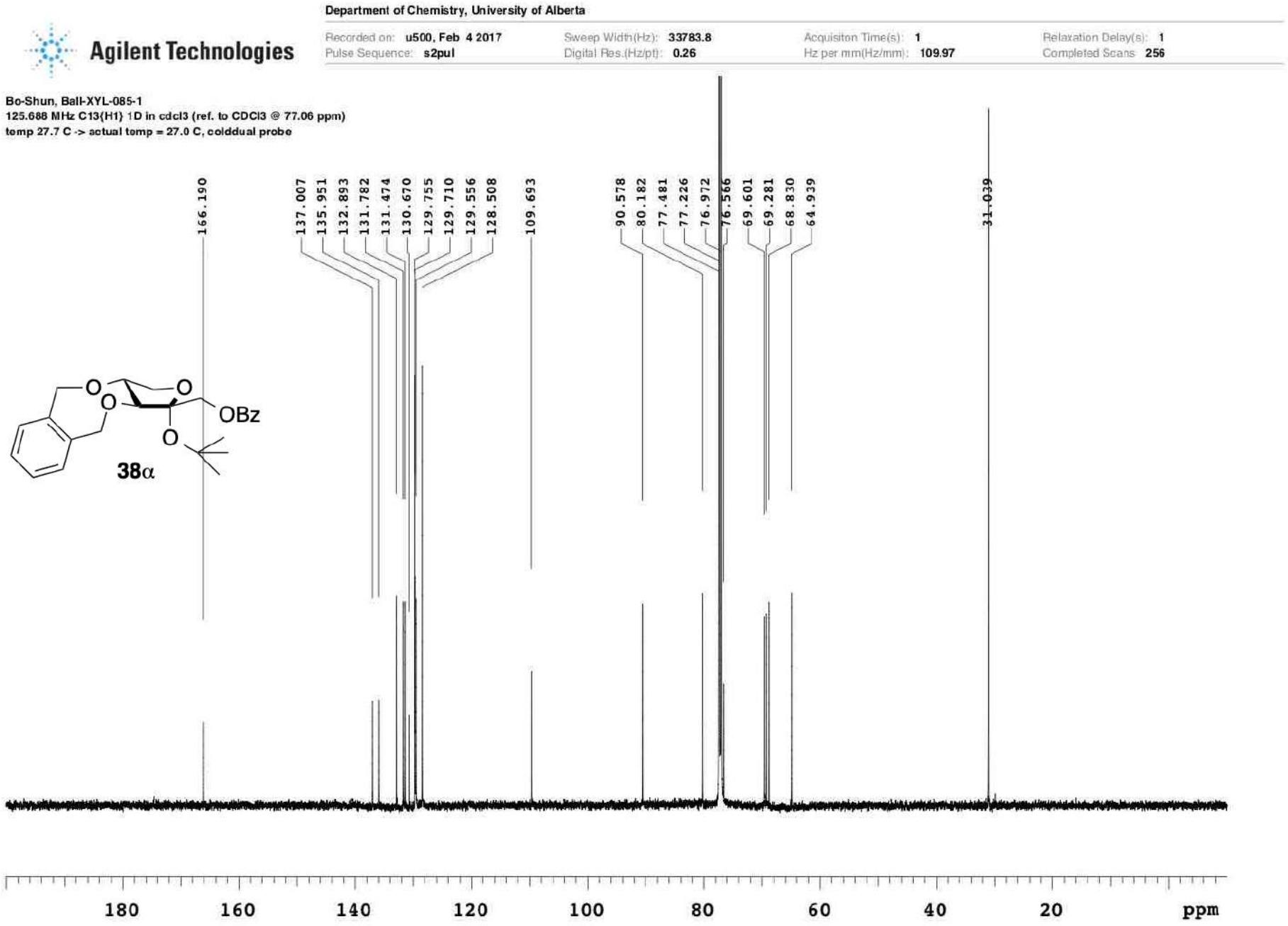
Agilent Technologies

Recorded on:	u500, Feb 4 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.91	Completed Scans	16

Bo-Shun, Ball-XYL-085-1
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.4.u5_Ball-XYL-085-1_loc10_20.03_H1_1D

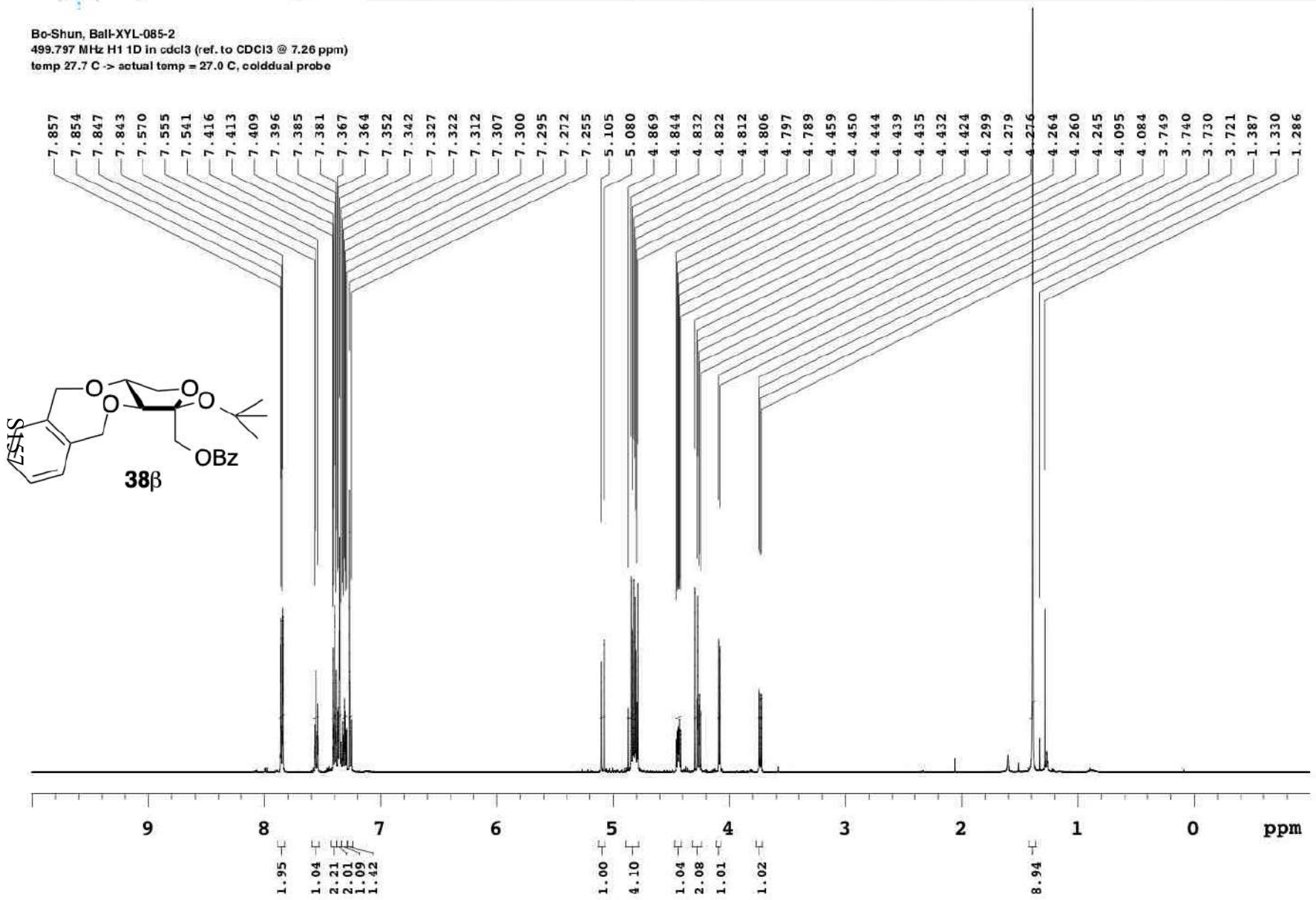

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Feb 4 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.97
Relaxation Delay(s): 1
Completed Scans 256
Bo-Shun, Ball-XYL-085-1
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
166.190
137.007
135.951
132.893
131.782
131.474
130.670
129.755
129.710
129.556
128.508
109.693
90.578
80.182
77.481
77.226
76.972
76.566
69.601
69.281
68.830
64.939
31.039
OBz
38α
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.4.u5_Ball-XYL-085-1_lcc10_20.05_C13_1D

Department of Chemistry, University of Alberta

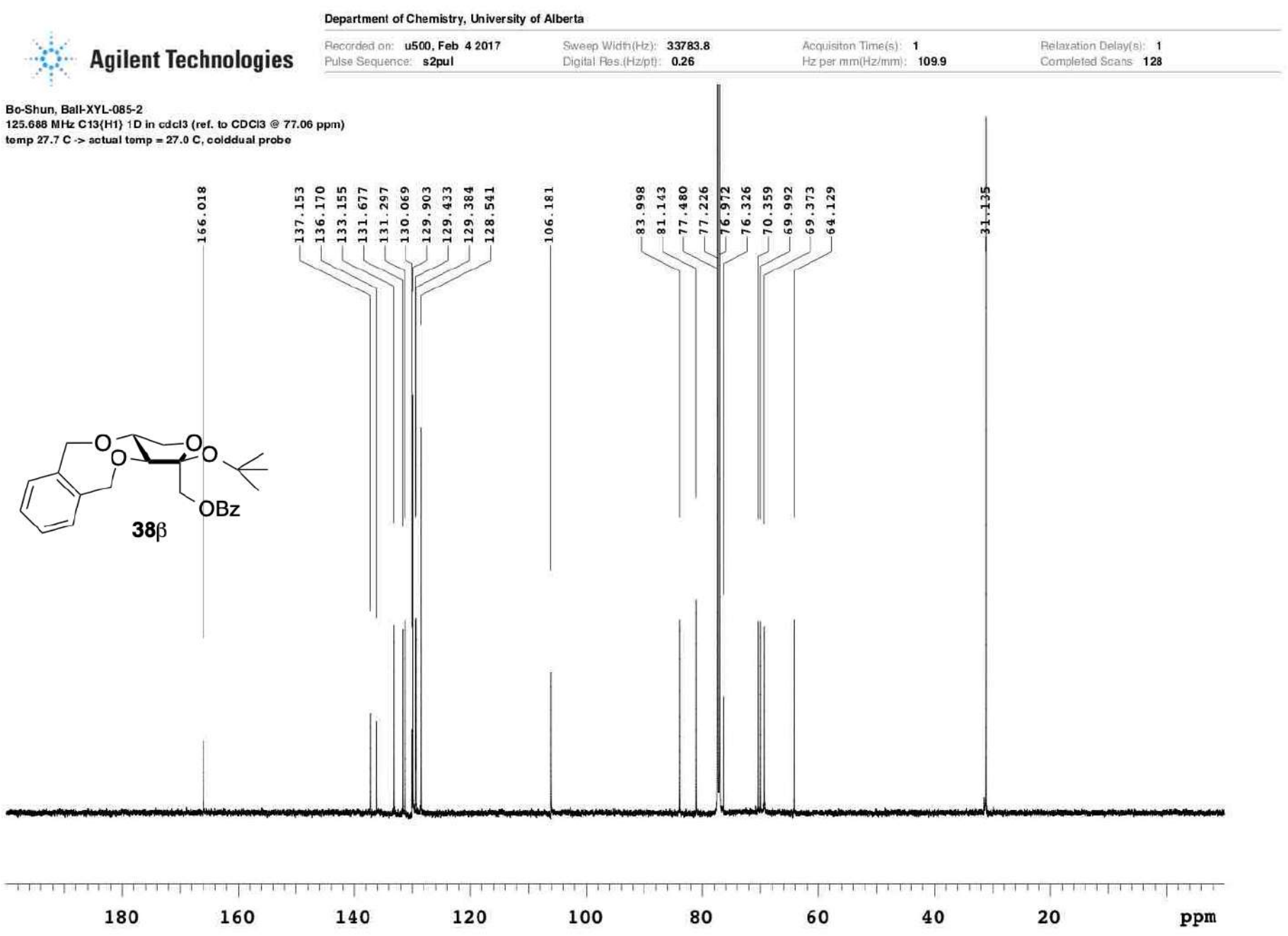
Agilent Technologies

Recorded on:	u500, Feb 4 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.91	Completed Scans	16

Bo-Shun, Ball-XYL-085-2
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.4.u5_Ball-XYL-085-2_1cc11_23.23_H1_1D

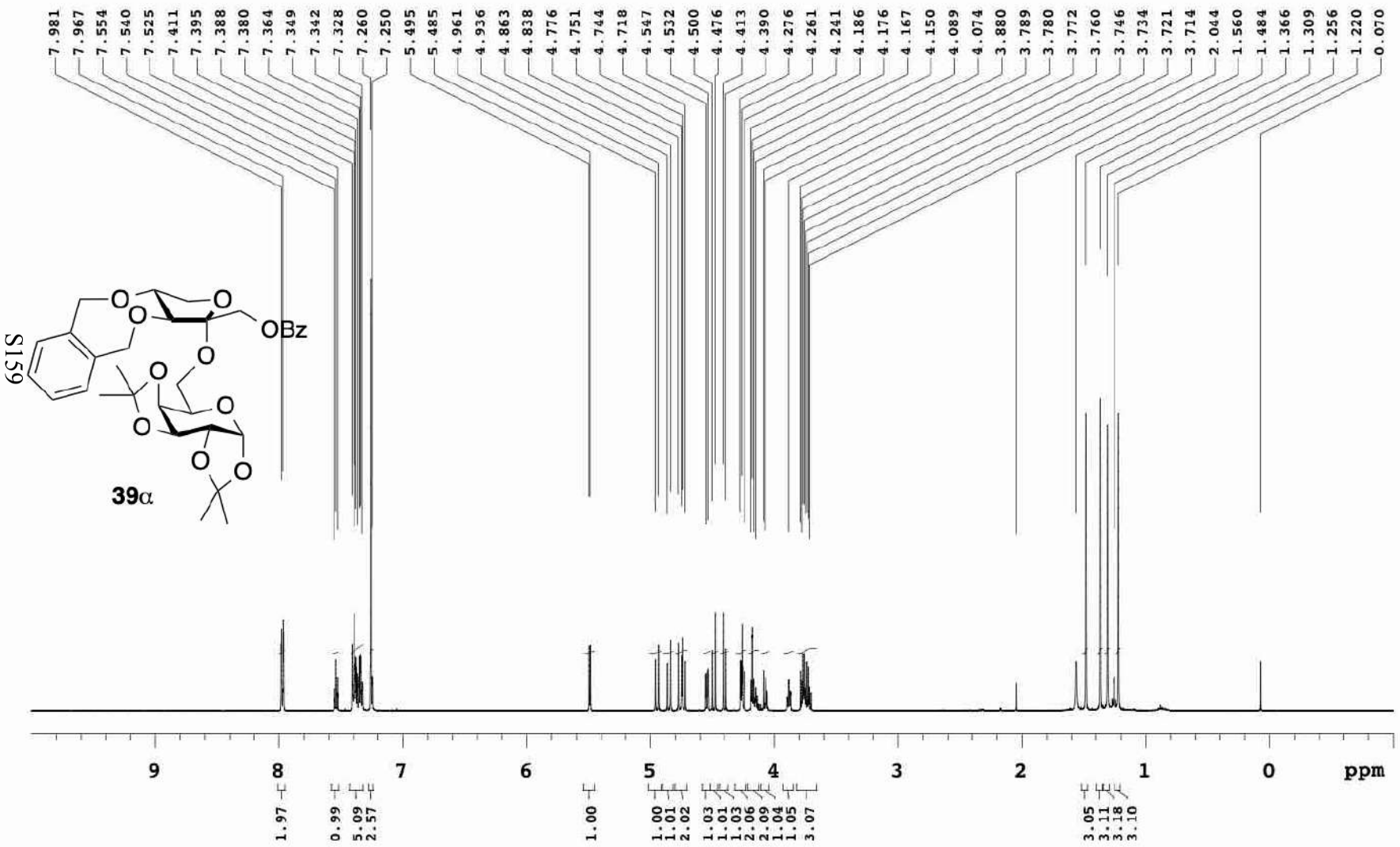

Agilent Technologies
Department of Chemistry, University of Alberta
Recorded on: u500, Feb 4 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.9
Relaxation Delay(s): 1
Completed Scans 128
Bo-Shun, Ball-XYL-085-2
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
166.018
137.153
136.170
133.155
131.677
131.297
130.069
129.903
129.433
129.384
128.541
106.181
83.998
81.143
77.480
77.226
76.972
76.326
70.359
69.992
69.373
64.129
31.135
OBz
38β
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.4.u5_Ball-XYL-085-2_lcc11_23.25_C13_1D

Agilent Technologies

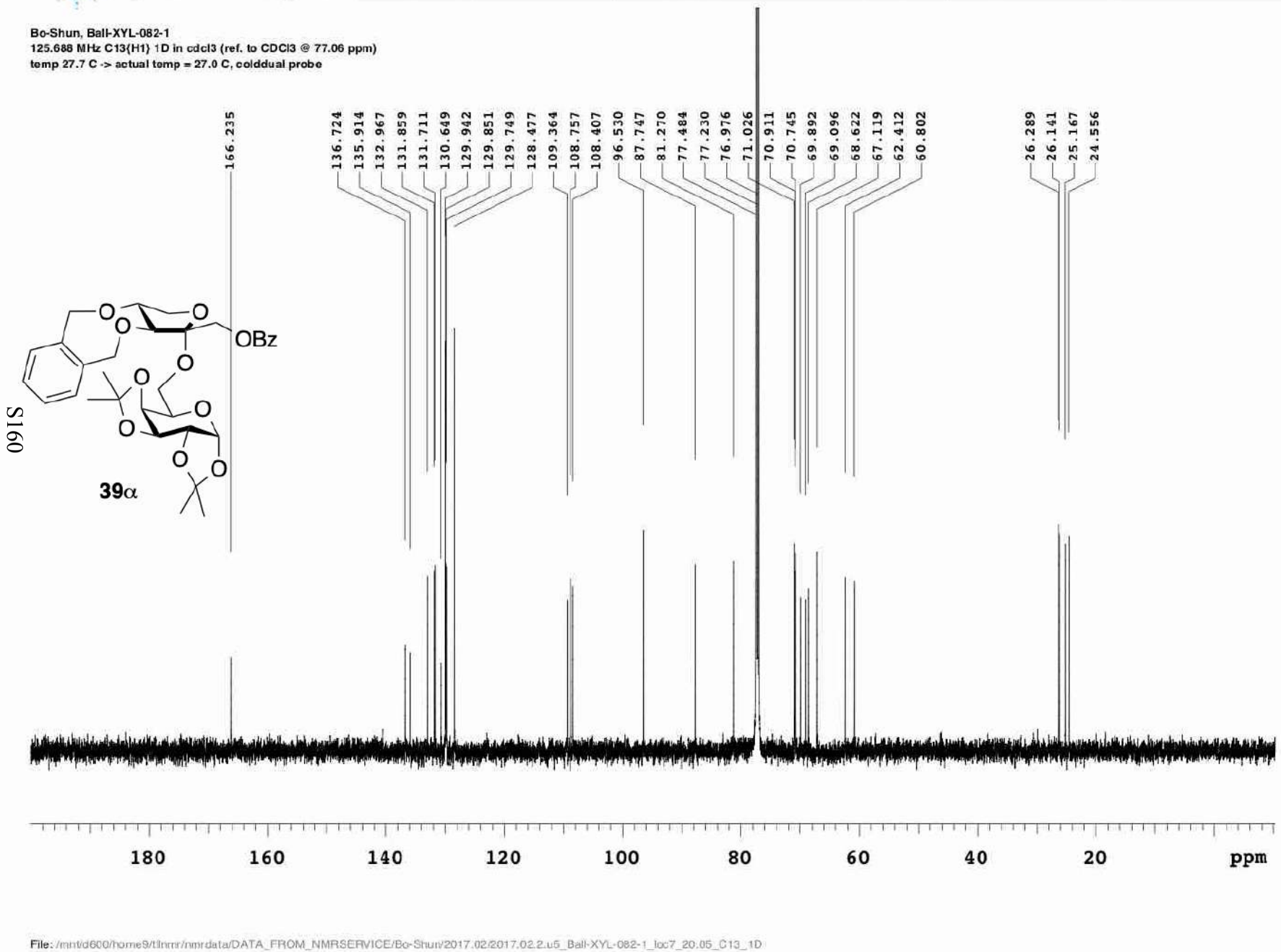
Department of Chemistry, University of Alberta

Recorded on:	u500, Feb 2 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.91	Completed Scans	16

Bo-Shun, Ball-XYL-082-1
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.2.u5_Ball-XYL-082-1_1cc7_20.03_H1_1D

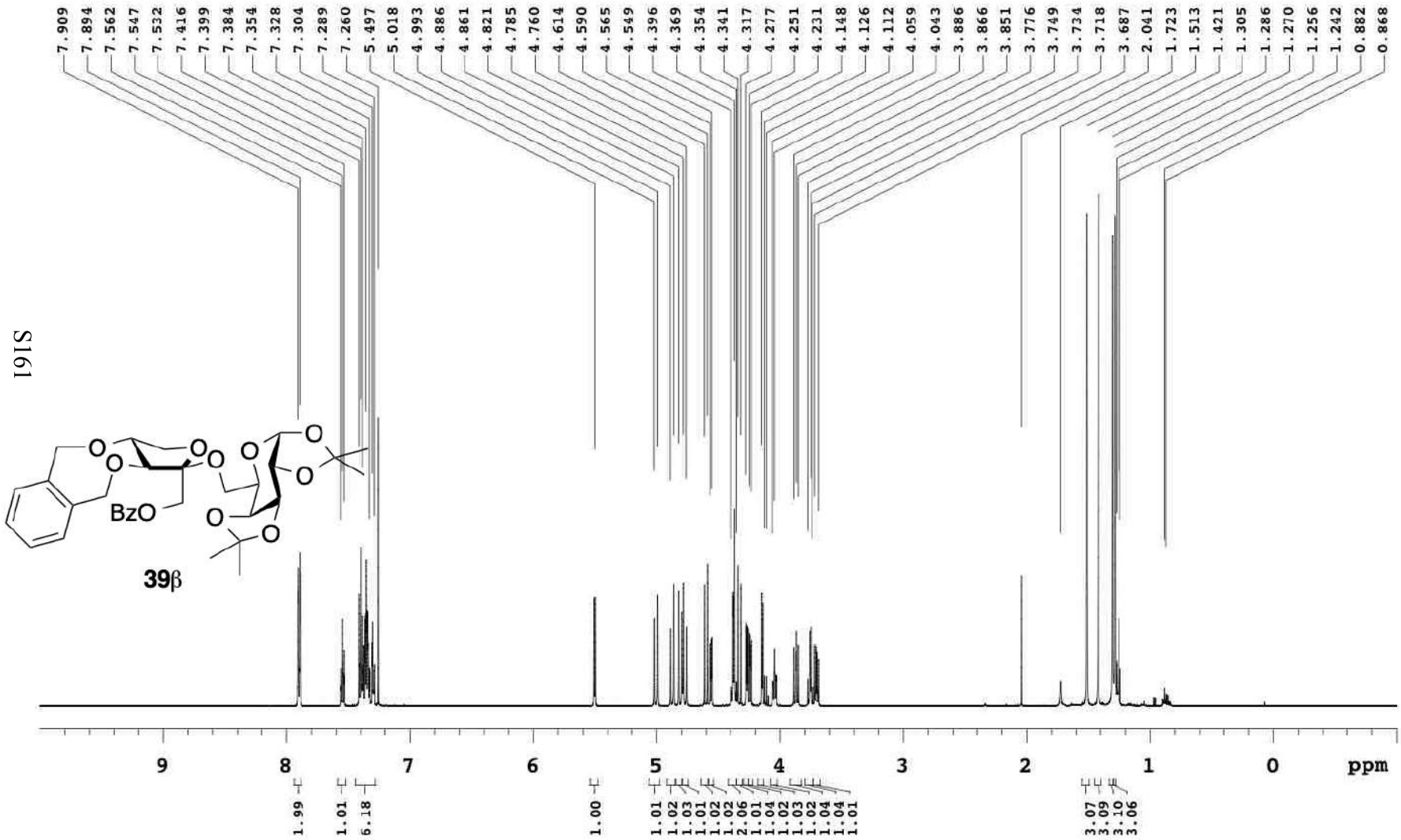

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Feb 2 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 110.08
Relaxation Delay(s): 1
Completed Scans 128
Bo-Shun, Ball-XYL-082-1
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
166.235
136.724
135.914
132.967
131.859
131.711
130.649
129.942
129.851
129.749
128.477
109.364
108.757
108.407
96.530
87.747
81.270
77.484
77.230
76.976
71.026
70.911
70.745
69.892
69.096
68.622
67.119
62.412
60.802
26.289
26.141
25.167
24.556
OBz
39α
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.2.u5_Ball-XYL-082-1_loc7_20.05_C13_1D

Department of Chemistry, University of Alberta

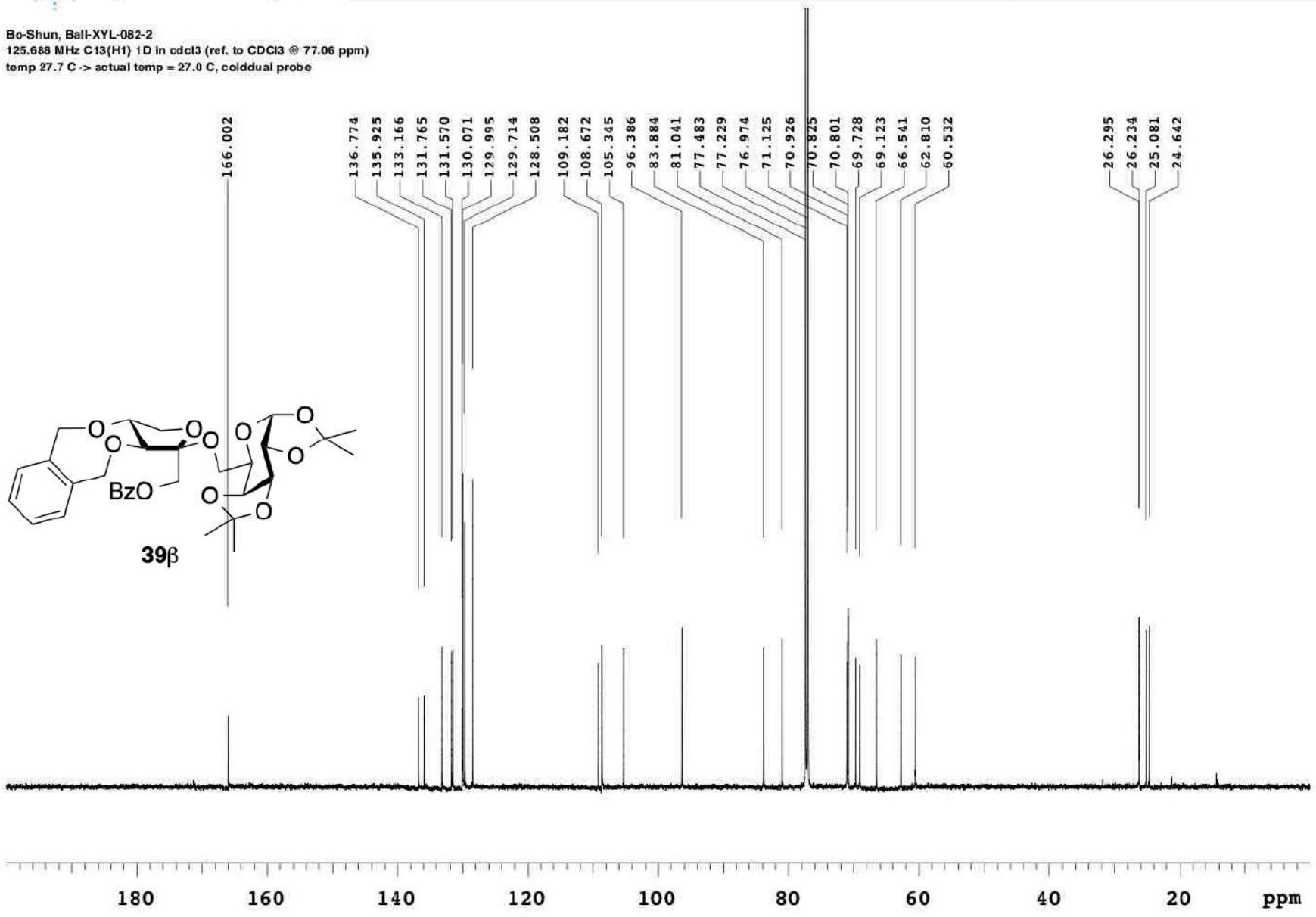
Agilent Technologies

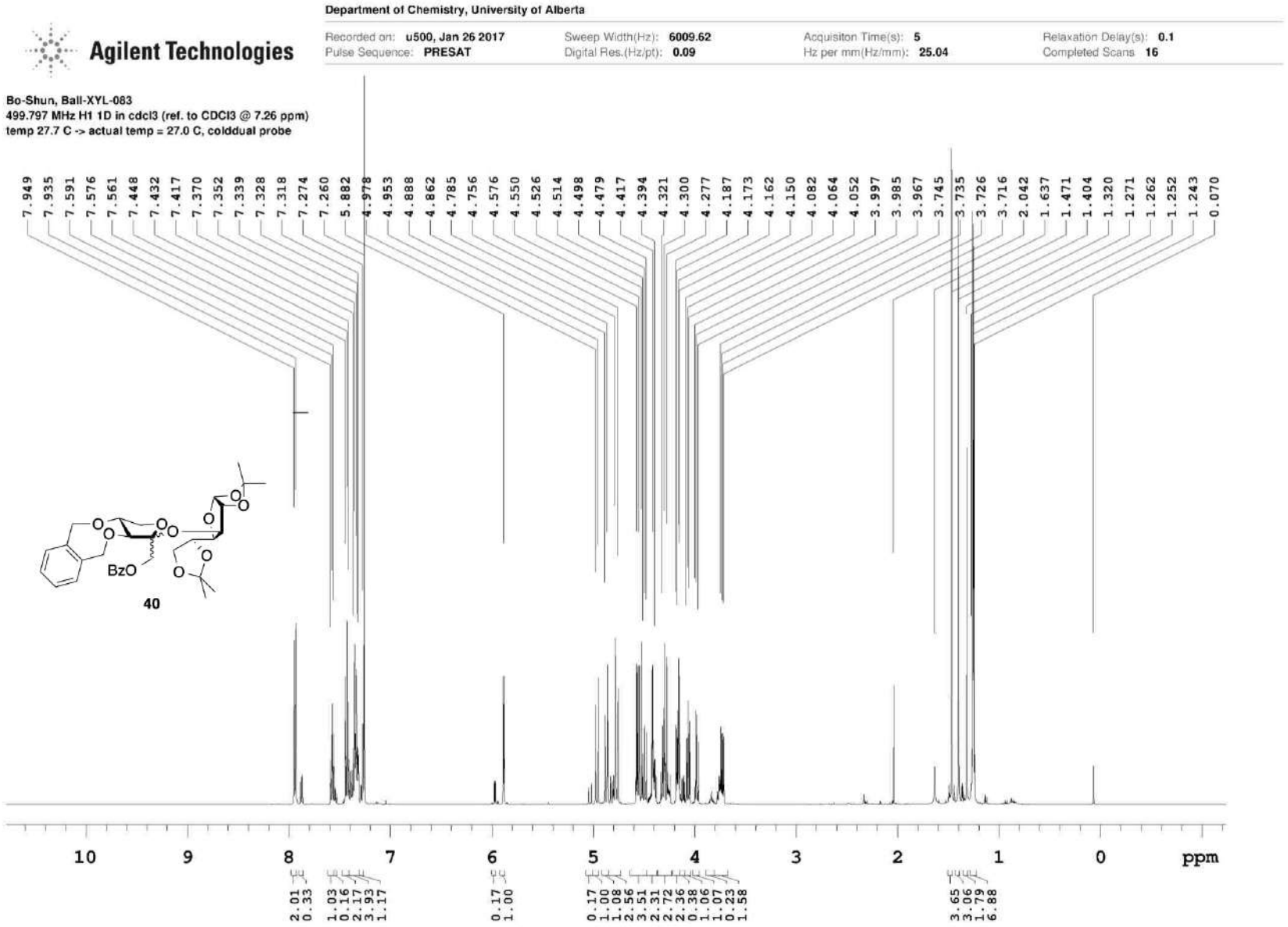
Recorded on: u500, Feb 2 2017	Sweep Width(Hz): 6009.62	Acquisiton Time(s): 5	Relaxation Delay(s): 0.1
Pulse Sequence: PRESAT	Digital Res.(Hz/pt): 0.09	Hz per mm(Hz/mm): 22.91	Completed Scans 16

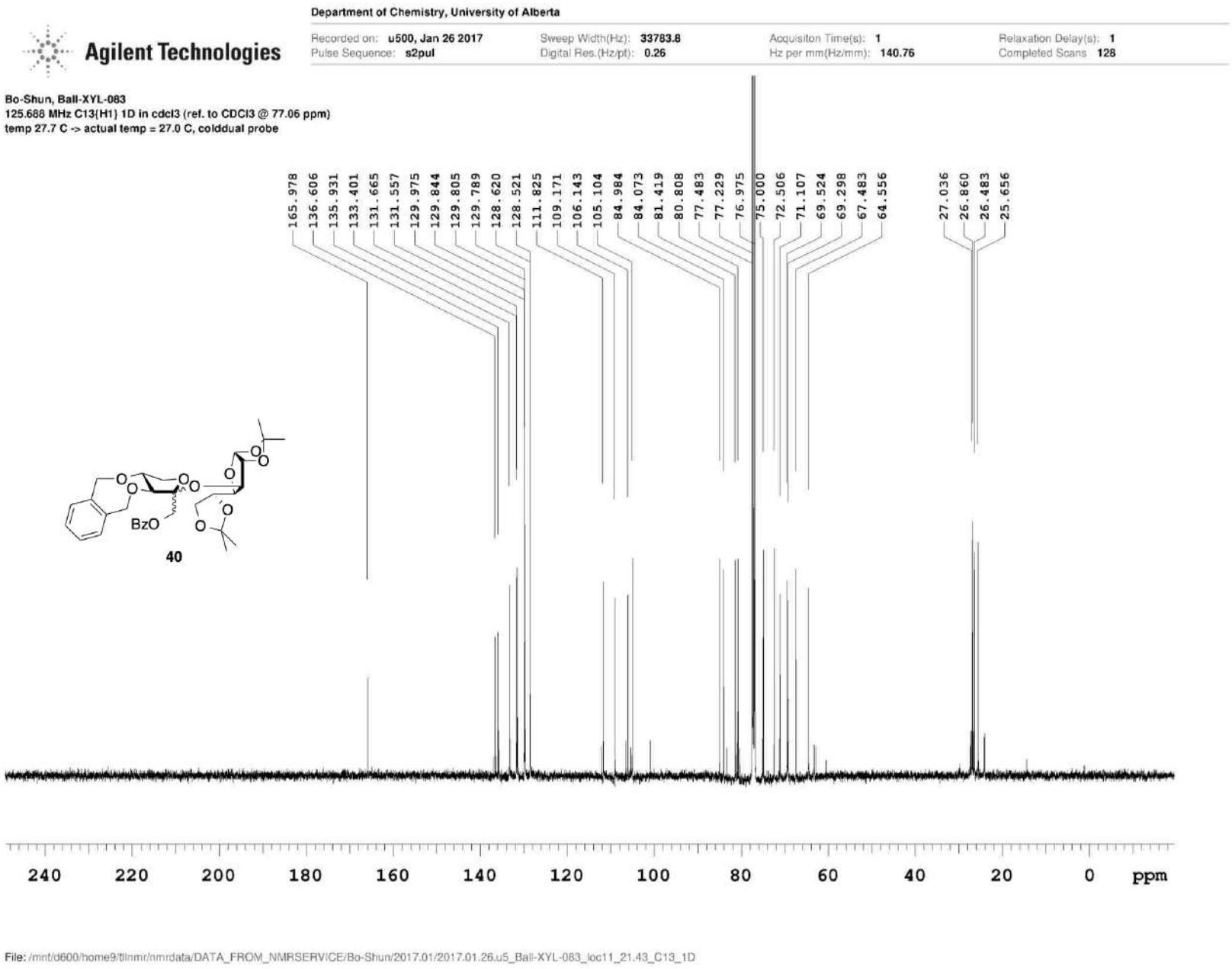
Bo-Shun, Ball-XYL-082-2
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe

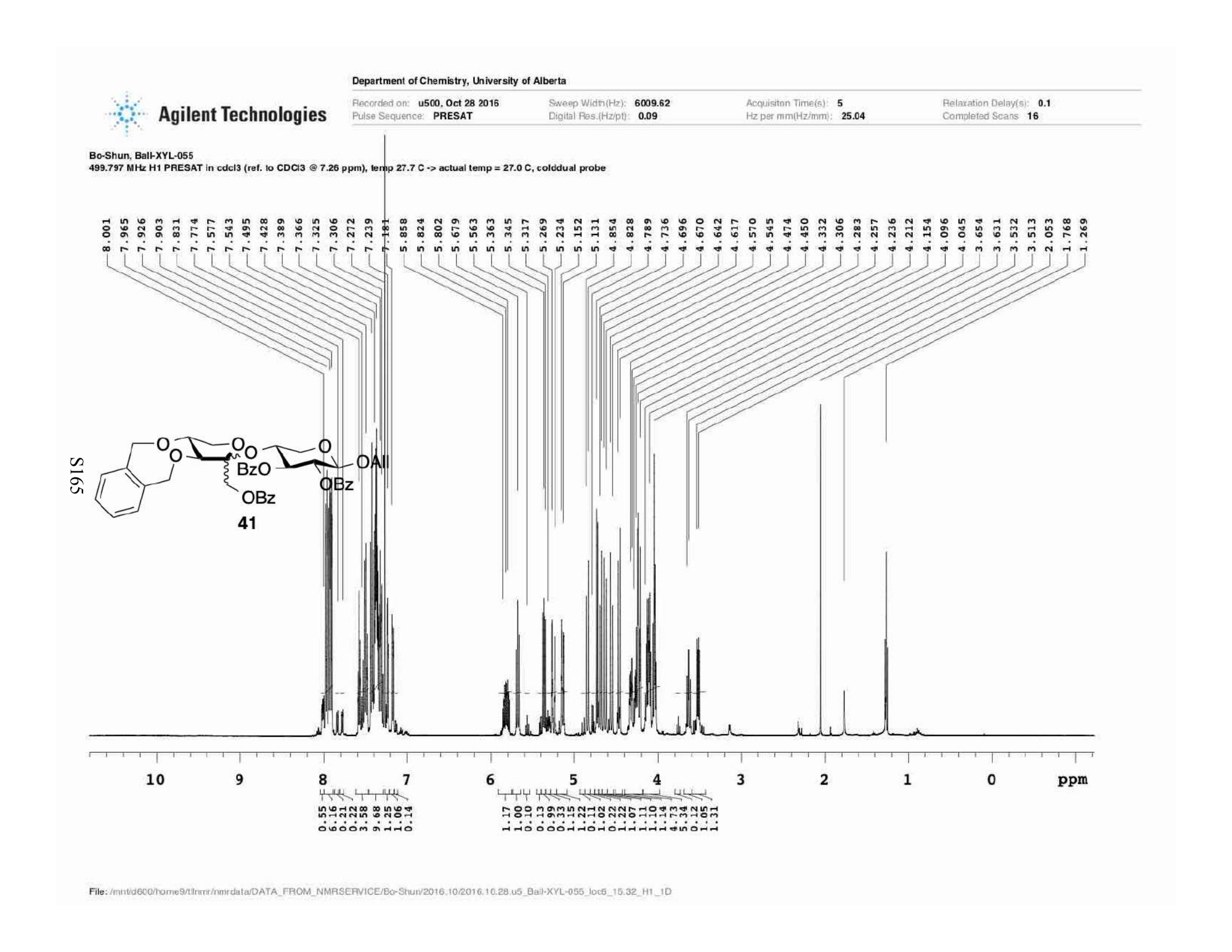


File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.2.u5_Ball-XYL-082-2_loc8_23.02_H1_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Feb 2 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 104.68
Relaxation Delay(s): 1
Completed Scans 128
Bo-Shun, Ball-XYL-082-2
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
166.002
136.774
135.925
133.166
131.765
131.570
130.071
129.995
129.714
128.508
109.182
108.672
105.345
96.386
83.884
81.041
77.483
77.229
76.974
71.125
70.926
70.825
70.801
69.728
69.123
66.541
62.810
60.532
26.295
26.234
25.081
24.642
BzO
39β
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.2.u5_Ball-XYL-082-2_loc8_23.03_C13_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Jan 26 2017
Pulse Sequence: PRESAT
Sweep Width(Hz): 6009.62
Digital Res.(Hz/pt): 0.09
Acquisiton Time(s): 5
Hz per mm(Hz/mm): 25.04
Relaxation Delay(s): 0.1
Completed Scans 16
Bo-Shun, Ball-XYL-083
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
7.949 7.935 7.591 7.576 7.561 7.448 7.432 7.417 7.370 7.352 7.339 7.328 7.318 7.274 7.260 5.882 4.978 4.953 4.888 4.862 4.785 4.756 4.576 4.550 4.526 4.514 4.498 4.479 4.417 4.394 4.321 4.300 4.277 4.187 4.173 4.162 4.150 4.082 4.064 4.052 3.997 3.985 3.967 3.745 3.735 3.726 3.716 2.042 1.637 1.471 1.404 1.320 1.271 1.262 1.252 1.243 0.070
BzO
40
10 9 8 7 6 5 4 3 2 1 0 ppm
2.01 0.33 1.03 0.16 2.17 3.93 1.17 0.17 1.00 0.17 1.00 1.08 2.56 3.51 2.31 2.72 2.36 0.38 1.06 1.07 0.23 1.58 3.65 3.06 1.79 6.88
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.26.u5_Ball-XYL-083_loc11_21.42_H1_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Jan 26 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 140.76
Relaxation Delay(s): 1
Completed Scans 128
Bo-Shun, Ball-XYL-083
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
165.978
136.606
135.931
133.401
131.665
131.557
129.975
129.844
129.805
129.789
128.620
128.521
111.825
109.171
106.143
105.104
84.984
84.073
81.419
80.808
77.483
77.229
76.975
75.000
72.506
71.107
69.524
69.298
67.483
64.556
27.036
26.860
26.483
25.656
BzO
40
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.26.u5_Ball-XYL-083_loc11_21.43_C13_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Oct 28 2016
Pulse Sequence: PRESAT
Sweep Width(Hz): 6009.62
Digital Res.(Hz/pt): 0.09
Acquisiton Time(s): 5
Hz per mm(Hz/mm): 25.04
Relaxation Delay(s): 0.1
Completed Scans 16
Bo-Shun, Ball-XYL-055
499.797 MHz H1 PRESAT in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe
8.001 7.965 7.926 7.903 7.831 7.774 7.577 7.543 7.495 7.428 7.389 7.366 7.325 7.306 7.272 7.239 7.181 5.858 5.824 5.802 5.679 5.563 5.363 5.345 5.317 5.269 5.234 5.152 5.131 4.854 4.828 4.789 4.736 4.696 4.670 4.642 4.617 4.570 4.545 4.474 4.450 4.332 4.306 4.283 4.257 4.236 4.212 4.154 4.096 4.045 3.654 3.631 3.532 3.513 2.053 1.768 1.269
BzO
OBz
OBz
OAll
41
10 9 8 7 6 5 4 3 2 1 0 ppm
0.55 6.16 0.21 0.22 3.58 9.68 1.25 1.06 0.14
1.17 1.00 0.10 0.13 0.99 0.33 1.15 1.22 0.11 1.02 0.22 1.22 1.07 1.11 1.10 1.14 4.73 5.34 0.12 1.05 1.31
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.10/2016.10.28.u5_Ball-XYL-055_loc5_15.32_H1_1D

Department of Chemistry, University of Alberta

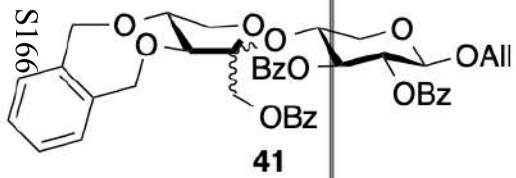
Agilent Technologies

Recorded on:	u500, Oct 28 2016	Sweep Width(Hz):	33783.8	Acquisiton Time(s):	1	Relaxation Delay(s):	1
Pulse Sequence:	s2pul	Digital Res.(Hz/pt):	0.26	Hz per mm(Hz/mm):	109.63	Completed Scans	128

Bo-Shun, Ball-XYL-055

125.688 MHz C13[H1] 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe

165.815 165.603 165.472 136.705 135.645 133.742 133.362 133.344 133.243 131.554 131.422 129.989 129.919 129.857 129.786 129.747 129.679 129.603 129.564 128.615 128.594 128.471 117.640 105.753 99.969 83.477 80.522 77.474 77.425 77.220 76.965 72.962 71.783 70.638 69.849 69.346 69.301 68.274 65.088 64.168



41

180 160 140 120 100 80 60 40 20 ppm

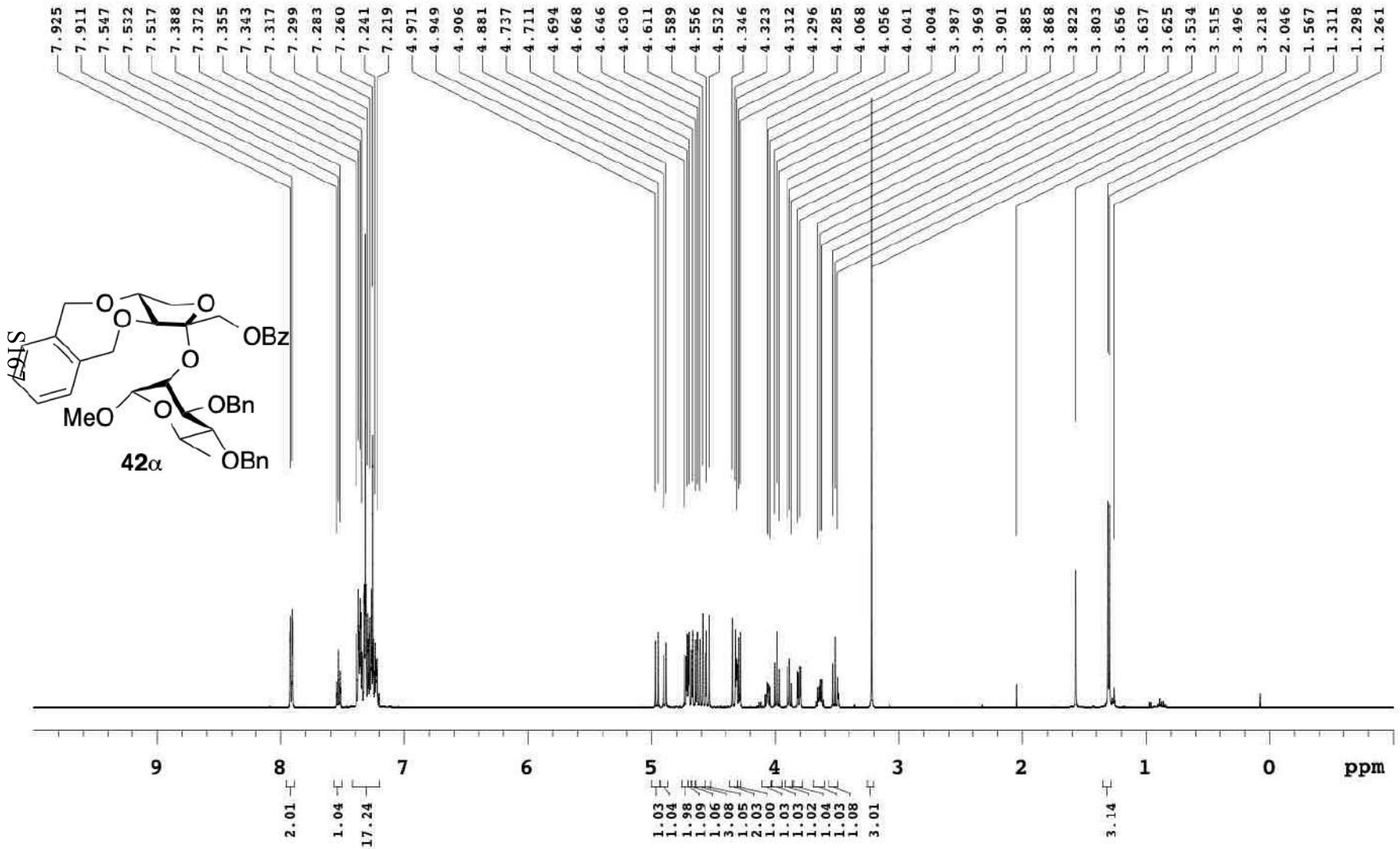
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.10/2016.10.28.u5_Ball-XYL-055_loc5_15.33_C13_1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	u500, Apr 27 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.91	Completed Scans	16

Bo-Shun, Ball-XYL-128-1
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.04/2017.04.27.u5_Ball-XYL-128-1_loc10_15.04_H1_1D

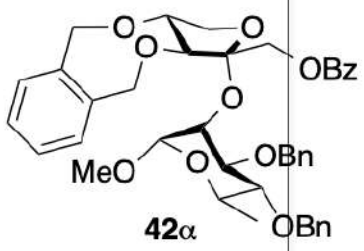
Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	u500, Apr 27 2017	Sweep Width(Hz):	33783.8	Acquisiton Time(s):	1	Relaxation Delay(s):	1
Pulse Sequence:	s2pul	Digital Res.(Hz/pt):	0.26	Hz per mm(Hz/mm):	109.9	Completed Scans	128

Bo-Shun, Ball-XYL-128-1
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe

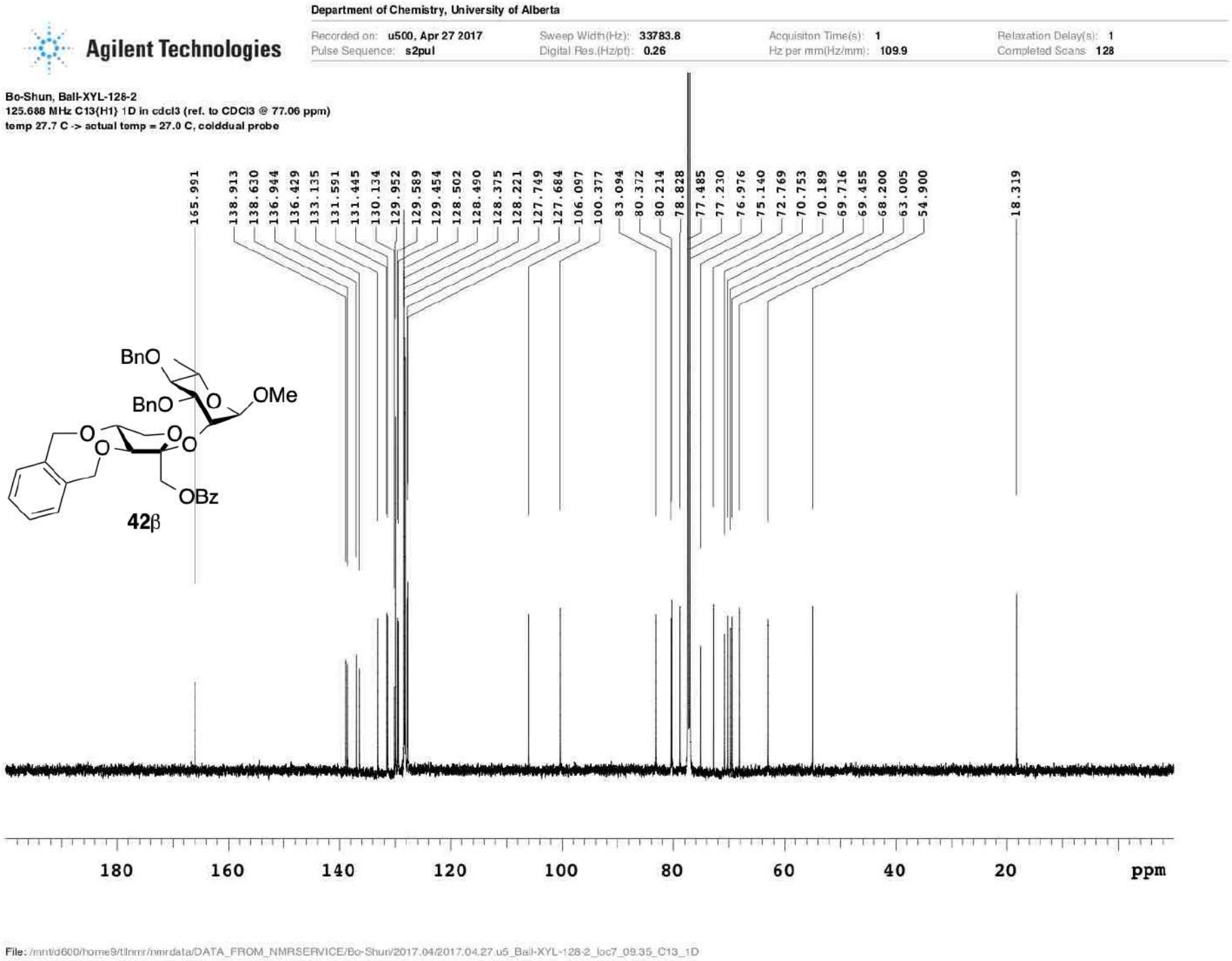
166.191
138.879
138.852
137.232
135.573
133.044
131.774
131.586
130.369
129.873
129.754
129.567
128.532
128.450
128.238
127.914
127.761
127.592
108.990
101.072
88.637
80.082
79.894
79.094
77.482
77.227
76.973
75.301
72.291
69.885
69.425
69.202
68.158
64.667
54.788
18.183



42α

180 160 140 120 100 80 60 40 20 ppm

File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.04/2017.04.27.u5_Ball-XYL-128-1_loc10_15.05_C13_1D

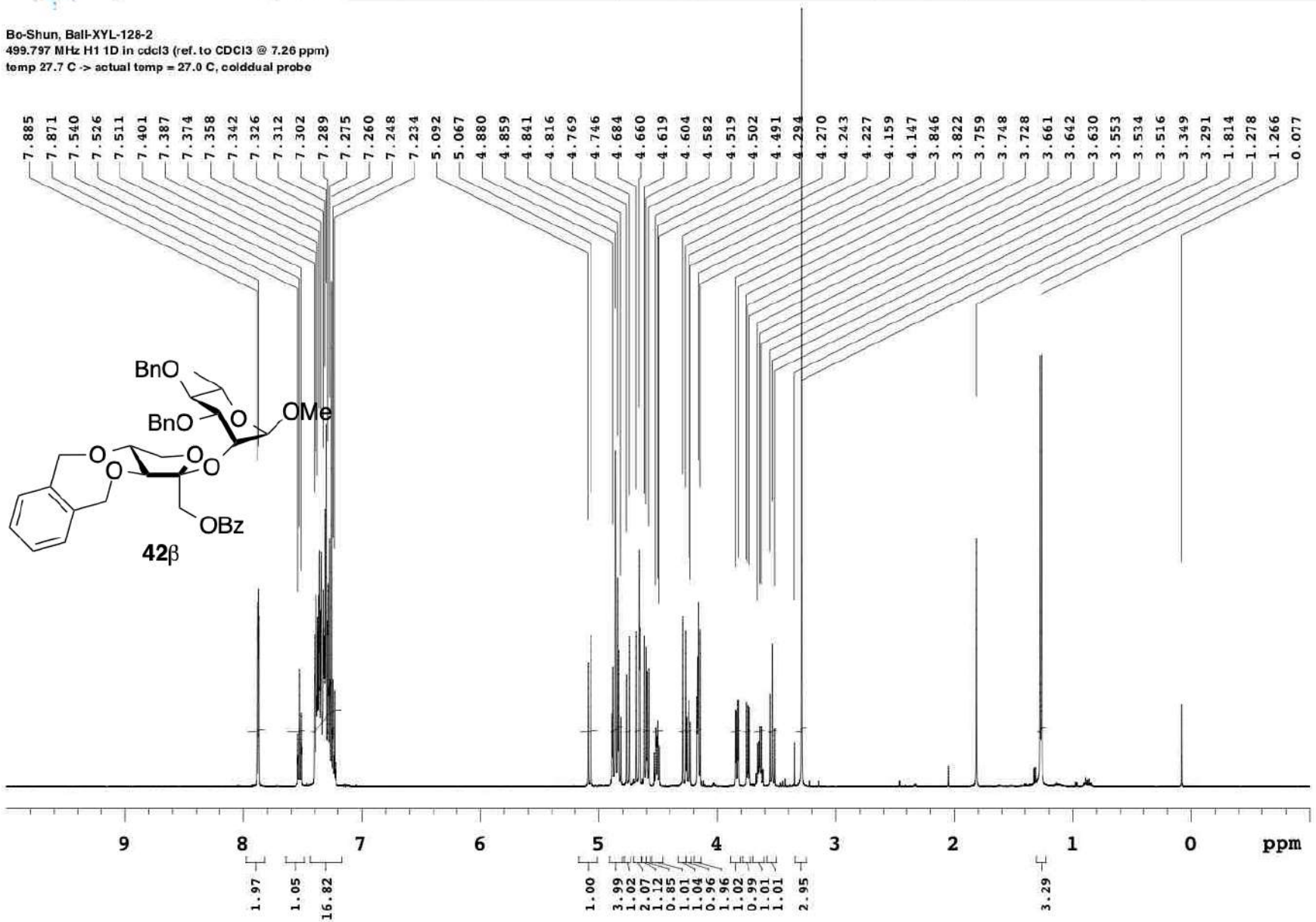

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Apr 27 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.9
Relaxation Delay(s): 1
Completed Scans 128
Bo-Shun, Ball-XYL-128-2
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
165.991
138.913
138.630
136.944
136.429
133.135
131.591
131.445
130.134
129.952
129.589
129.454
128.502
128.490
128.375
128.221
127.749
127.684
106.097
100.377
83.094
80.372
80.214
78.828
77.485
77.230
76.976
75.140
72.769
70.753
70.189
69.716
69.455
68.200
63.005
54.900
18.319
BnO
BnO
O
OMe
O
O
O
O
OBz
42β
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.04/2017.04.27.u5_Ball-XYL-128-2_loc7_09.35_C13_1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	u500, Apr 27 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.91	Completed Scans	16

Bo-Shun, Ball-XYL-128-2
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



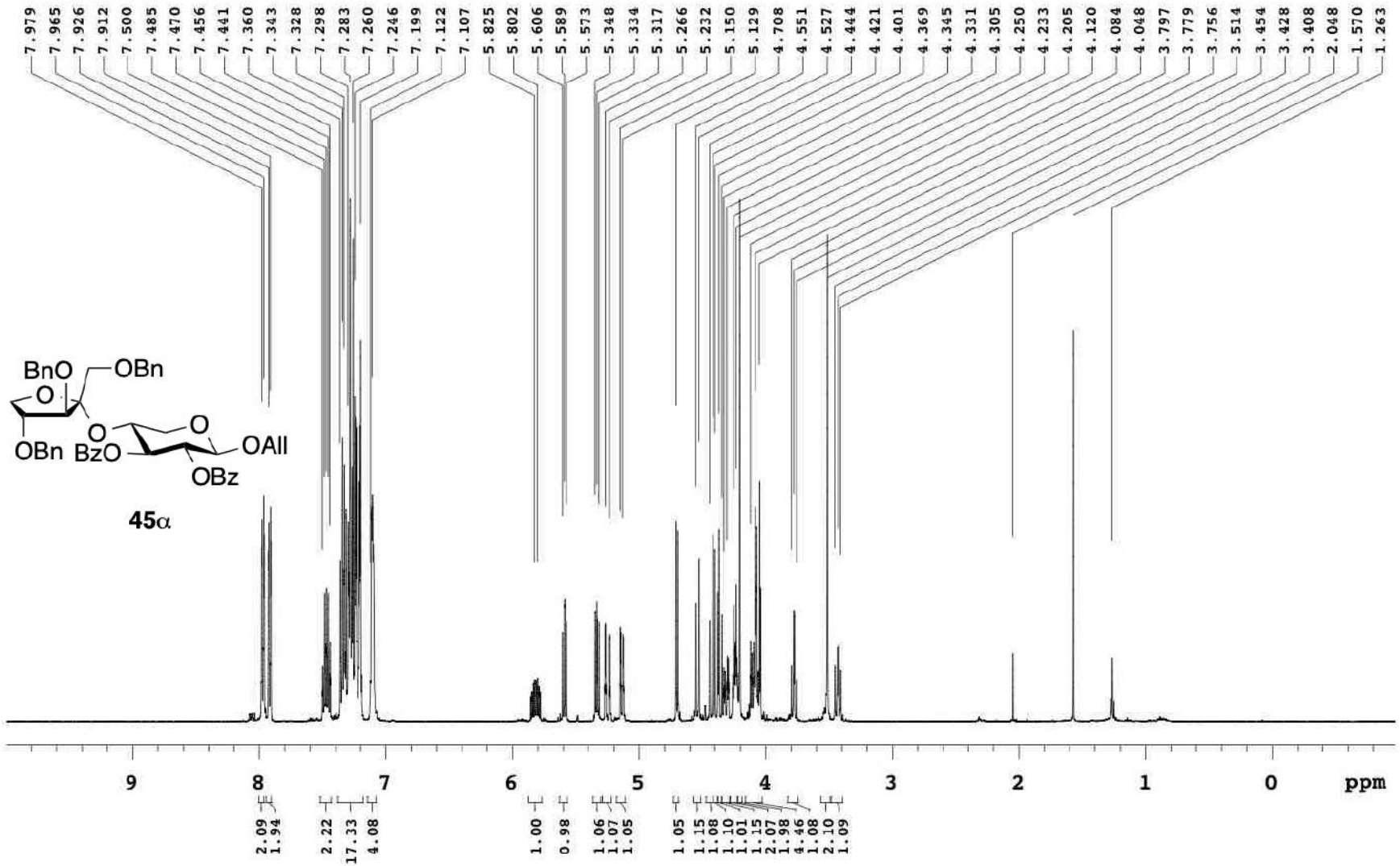
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.04/2017.04.27.u5_Ball-XYL-128-2_loc7_09.33_H1_1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	u500, Jan 12 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.82	Completed Scans	16

Bo-Shun, Ball-XYL-077-1
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.12.u5_Ball-XYL-077-1_loc7_13.37_H1_1D

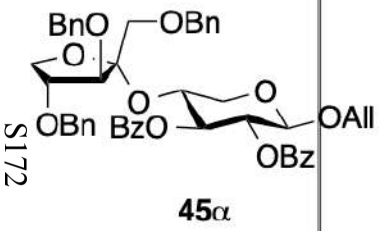
Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	u500, Jan 12 2017	Sweep Width(Hz):	33783.8	Acquisiton Time(s):	1	Relaxation Delay(s):	1
Pulse Sequence:	s2pul	Digital Res.(Hz/pt):	0.26	Hz per mm(Hz/mm):	109.81	Completed Scans	128

Bo-Shun, Ball-XYL-077-1
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe

165.747 165.513 138.174 138.043 138.018 133.898 133.186 133.149 130.054 129.995 129.939 129.888 128.600 128.473 128.459 128.399 127.964 127.944 127.919 127.821 127.790 127.710 127.620 117.640 108.985 99.883 88.578 82.085 77.484 77.230 76.976 73.526 72.983 72.779 72.179 71.537 70.380 69.783 69.112 68.468 65.103



45α

180 160 140 120 100 80 60 40 20 ppm

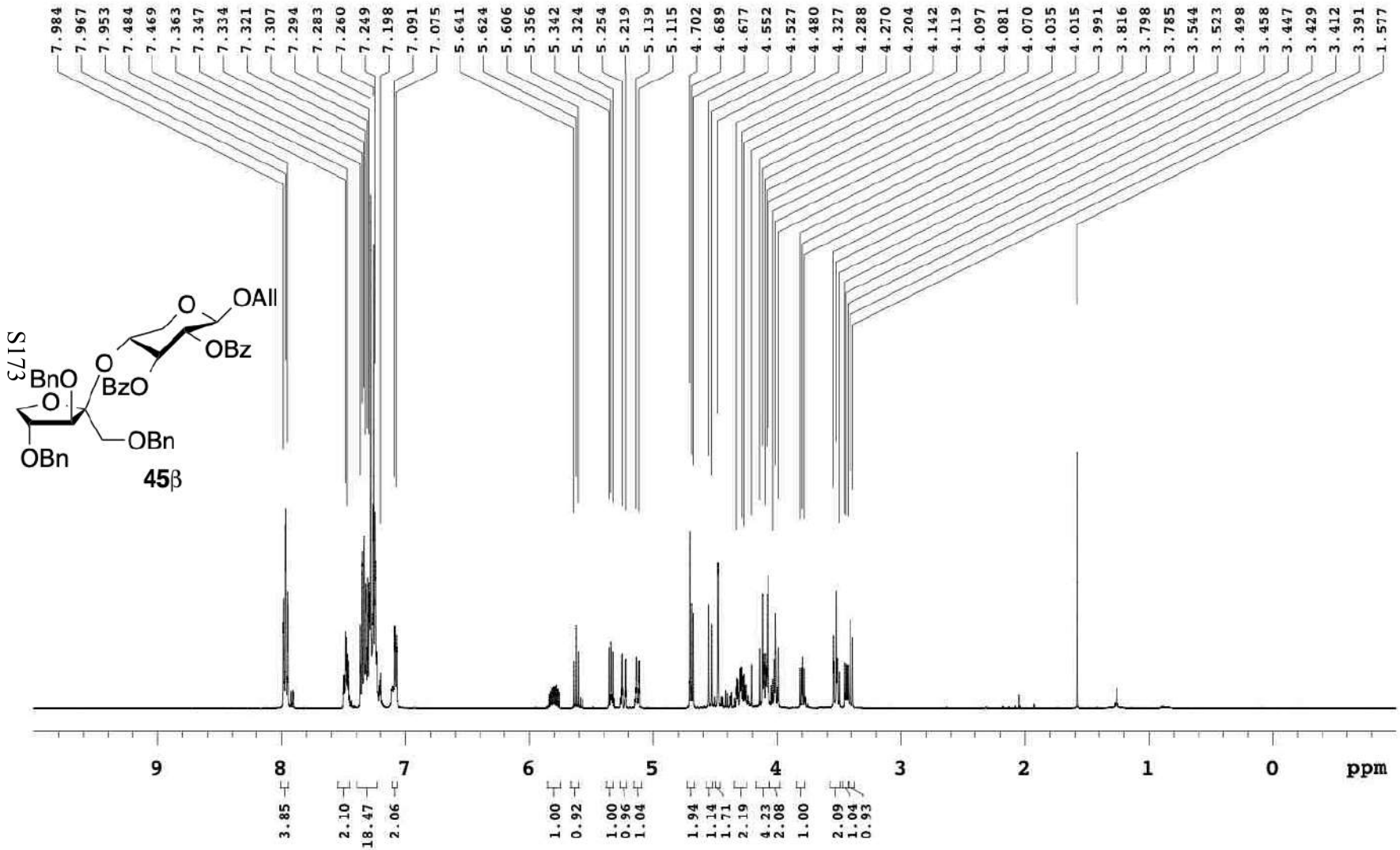
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.12.u5_Ball-XYL-077-1_loc7_13.39_C13_1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	u500, Jan 12 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.89	Completed Scans	16

Bo-Shun, Ball-XYL-077-2
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.12.u5_Ball-XYL-077-2_loc8_14.03_H1_1D

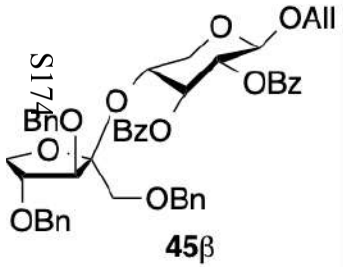
Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	u500, Jan 12 2017	Sweep Width(Hz):	33783.8	Acquisiton Time(s):	1	Relaxation Delay(s):	1
Pulse Sequence:	s2pul	Digital Res.(Hz/pt):	0.26	Hz per mm(Hz/mm):	109.92	Completed Scans	128

Bo-Shun, Ball-XYL-077-2
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe

165.654 165.541 138.711 138.060 137.697 133.805 133.280 133.226 130.068 130.015 129.736 128.636 128.601 128.565 128.515 128.480 128.413 128.115 128.015 127.992 127.921 127.843 127.709 127.666 117.676 105.342 100.134 83.979 82.547 77.484 77.229 76.935 73.724 73.347 72.555 72.163 71.948 70.654 69.928 69.528 68.127 65.324



45β

180 160 140 120 100 80 60 40 20 ppm

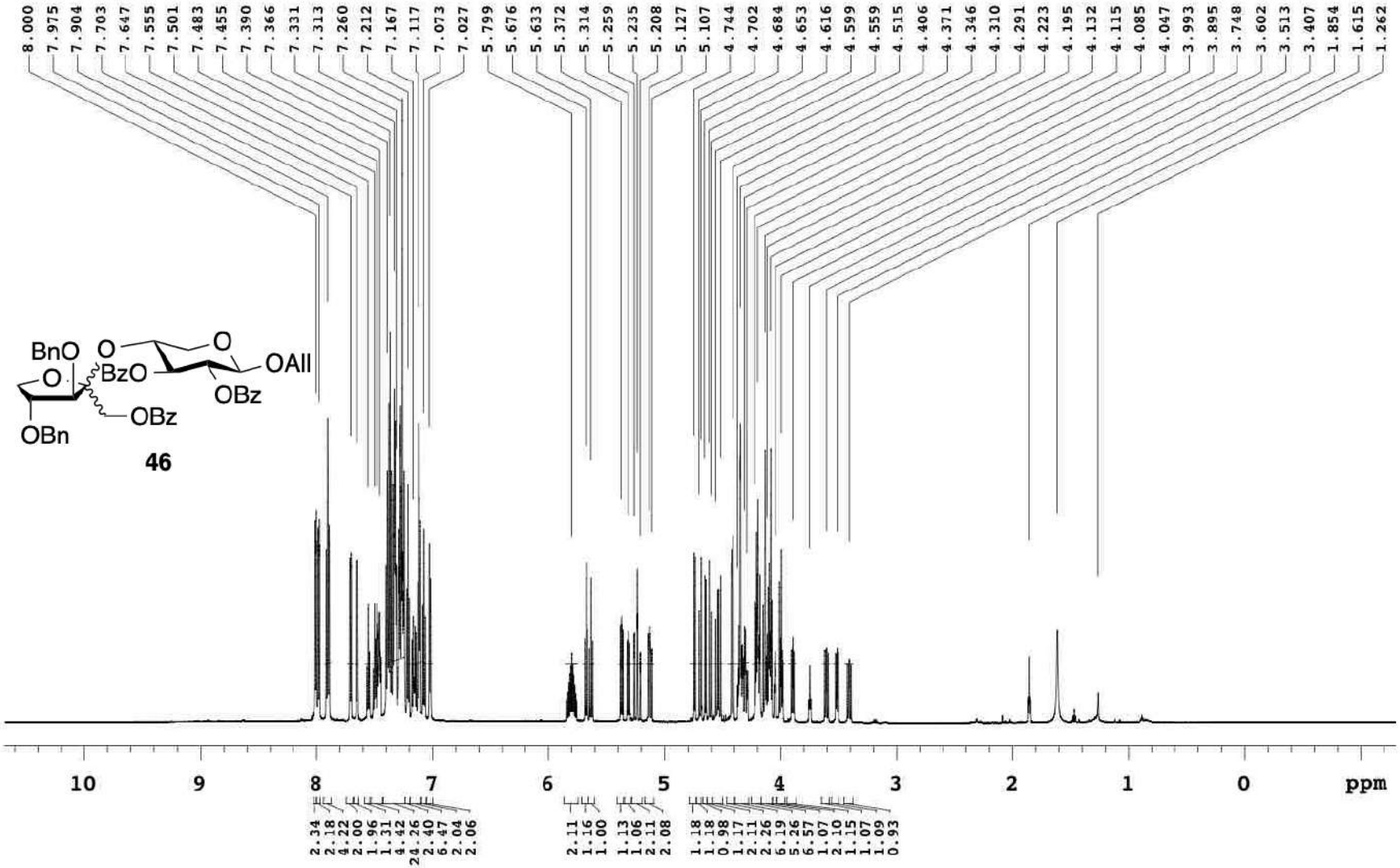
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.01/2017.01.12.u5_Ball-XYL-077-2_loc8_14.05_C13_1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	v700, Sep 5 2018	Sweep Width(Hz):	8389.26	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.13	Hz per mm(Hz/mm):	34.95	Completed Scans	8

Bo-Shun, Ball-XYL-072
699.762 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe



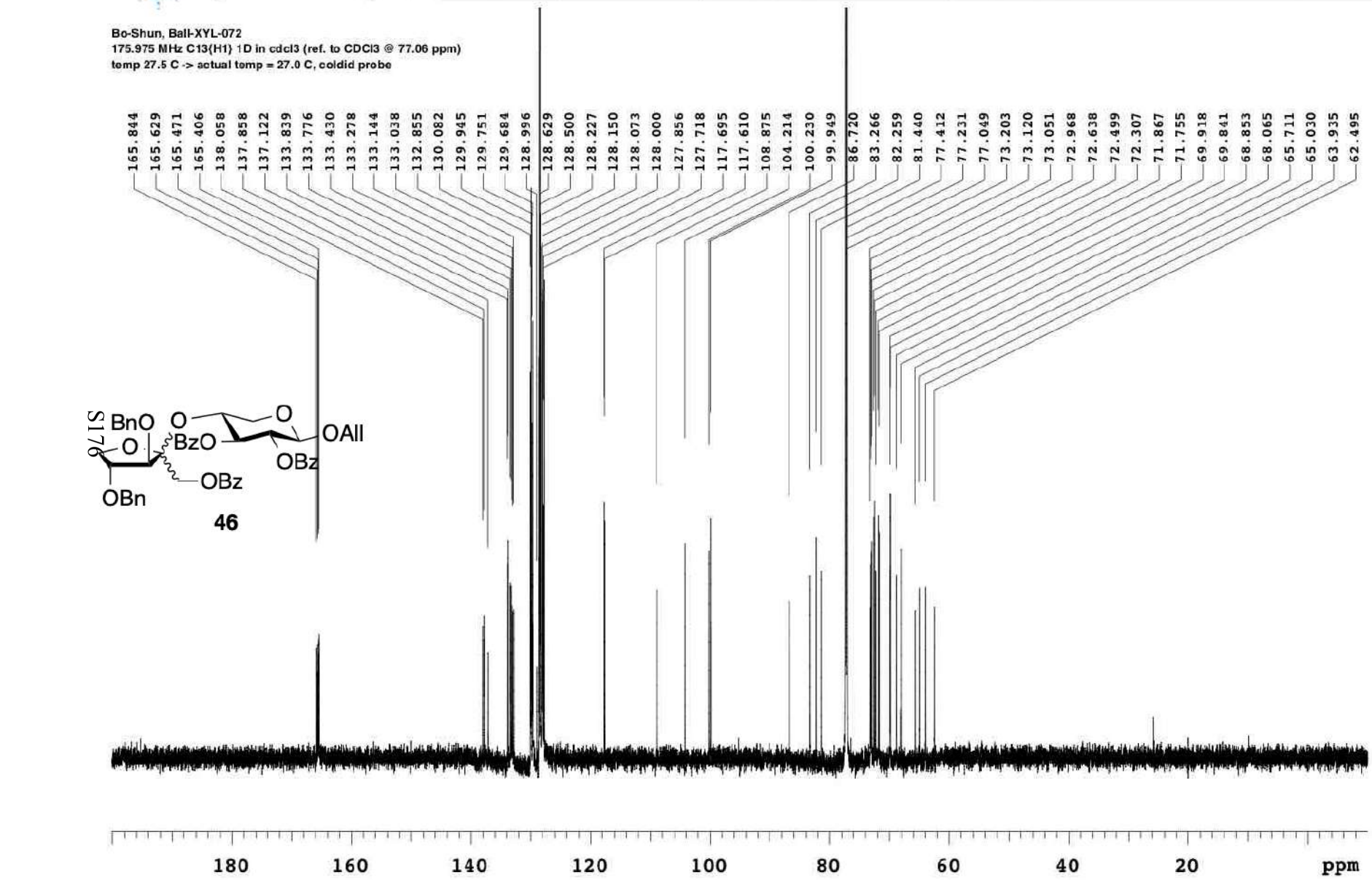
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2018.09/2018.09.05.v7_Ball-XYL-072_loc8_20.52_H1_1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on: v700, Sep 5 2018 | Sweep Width(Hz): 48076.9 | Acquisiton Time(s): 1 | Relaxation Delay(s): 1
Pulse Sequence: s2pul | Digital Res.(Hz/pt): 0.37 | Hz per mm(Hz/mm): 153.95 | Completed Scans 256

Bo-Shun, Ball-XYL-072
175.975 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe



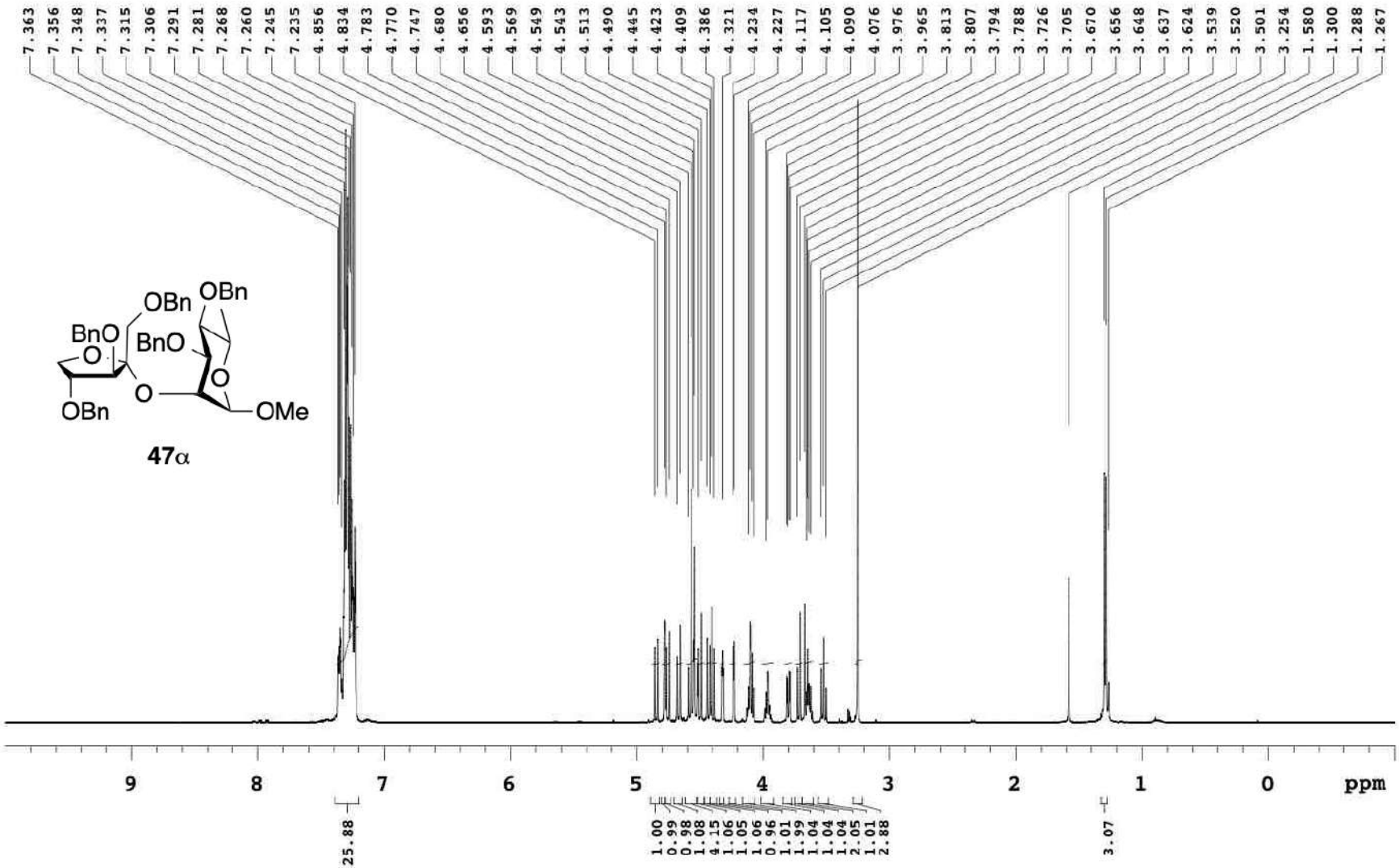
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2018.09/2018.09.05.v7_Ball-XYL-072_loc8_20.53_C13_1D

Department of Chemistry, University of Alberta

Agilent Technologies

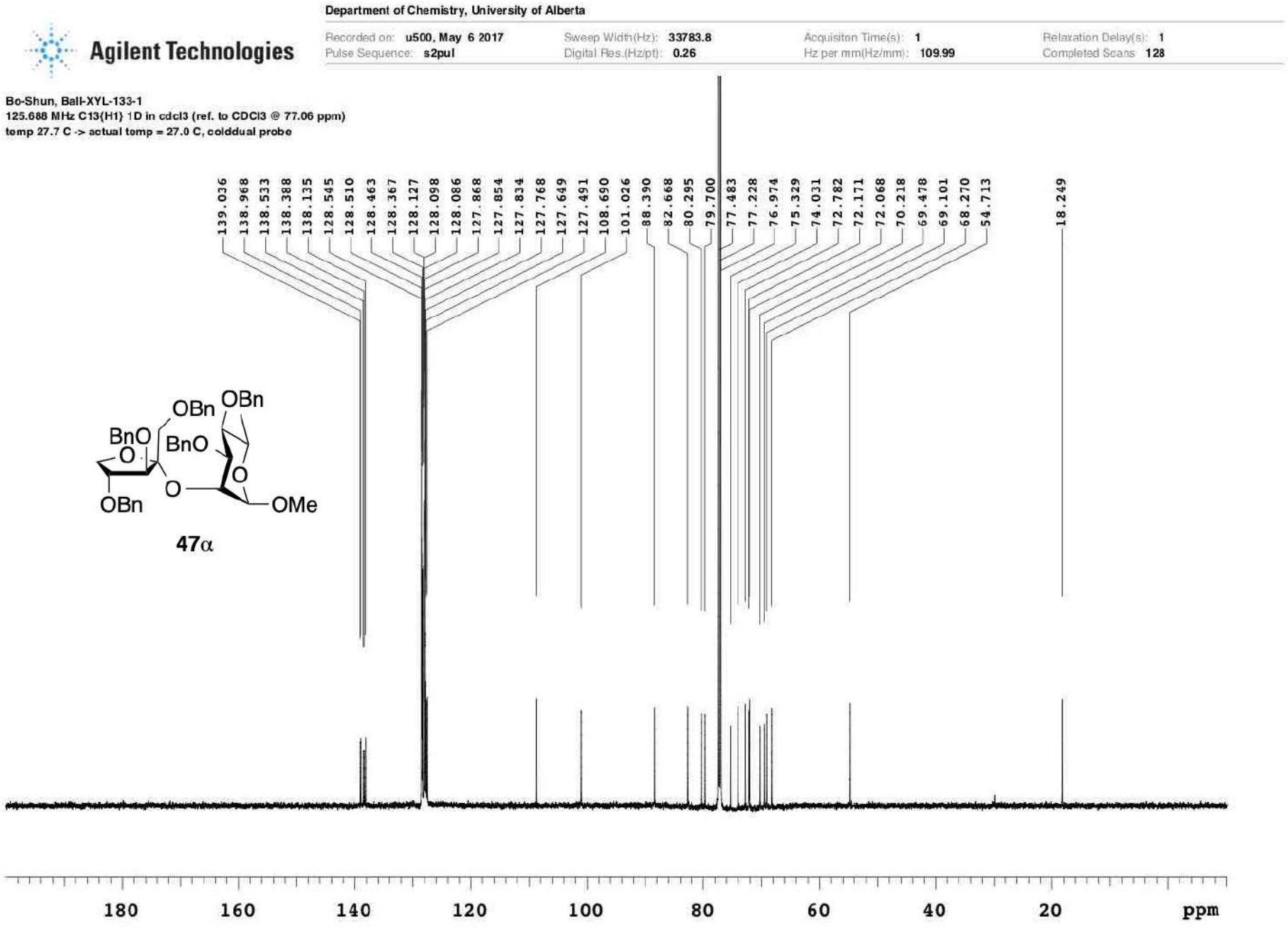
Recorded on:	u500, May 6 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.91	Completed Scans	16

Bo-Shun, Ball-XYL-133-1
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



47α

File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.05/2017.05.6.u5_Ball-XYL-133-1_loc5_12.06_H1_1D

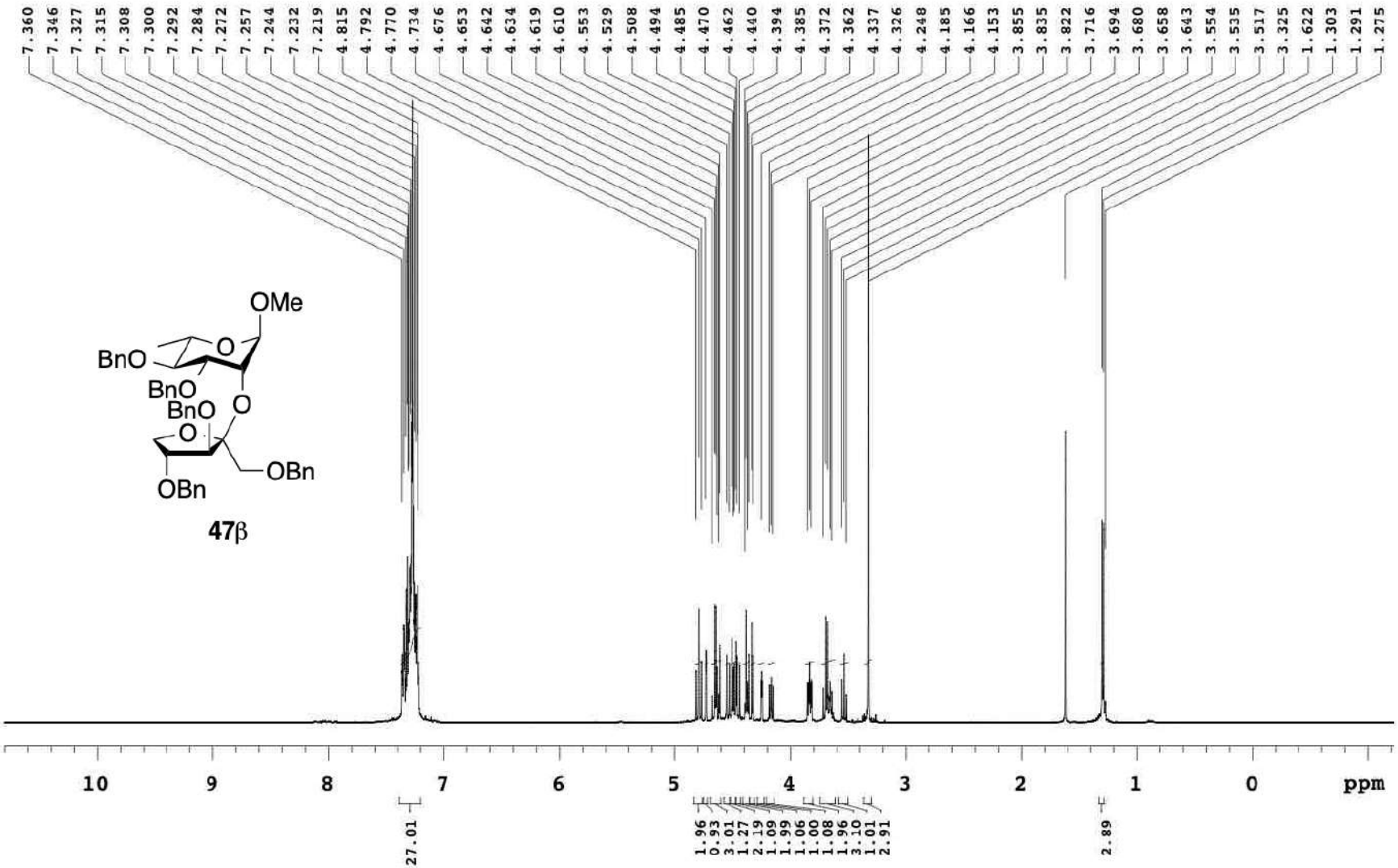

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, May 6 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.99
Relaxation Delay(s): 1
Completed Scans 128
Bo-Shun, Ball-XYL-133-1
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
139.036
138.968
138.533
138.388
138.135
128.545
128.510
128.463
128.367
128.127
128.098
128.086
127.868
127.854
127.834
127.768
127.649
127.491
108.650
101.026
88.390
82.668
80.295
79.700
77.483
77.228
76.974
75.329
74.031
72.782
72.171
72.068
70.218
69.478
69.101
68.270
54.713
18.249
OBn
OBn
BnO
BnO
O
O
OBn
OMe
47α
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.05/2017.05.6.u5_Ball-XYL-133-1_loc5_12.08_C13_1D

Department of Chemistry, University of Alberta

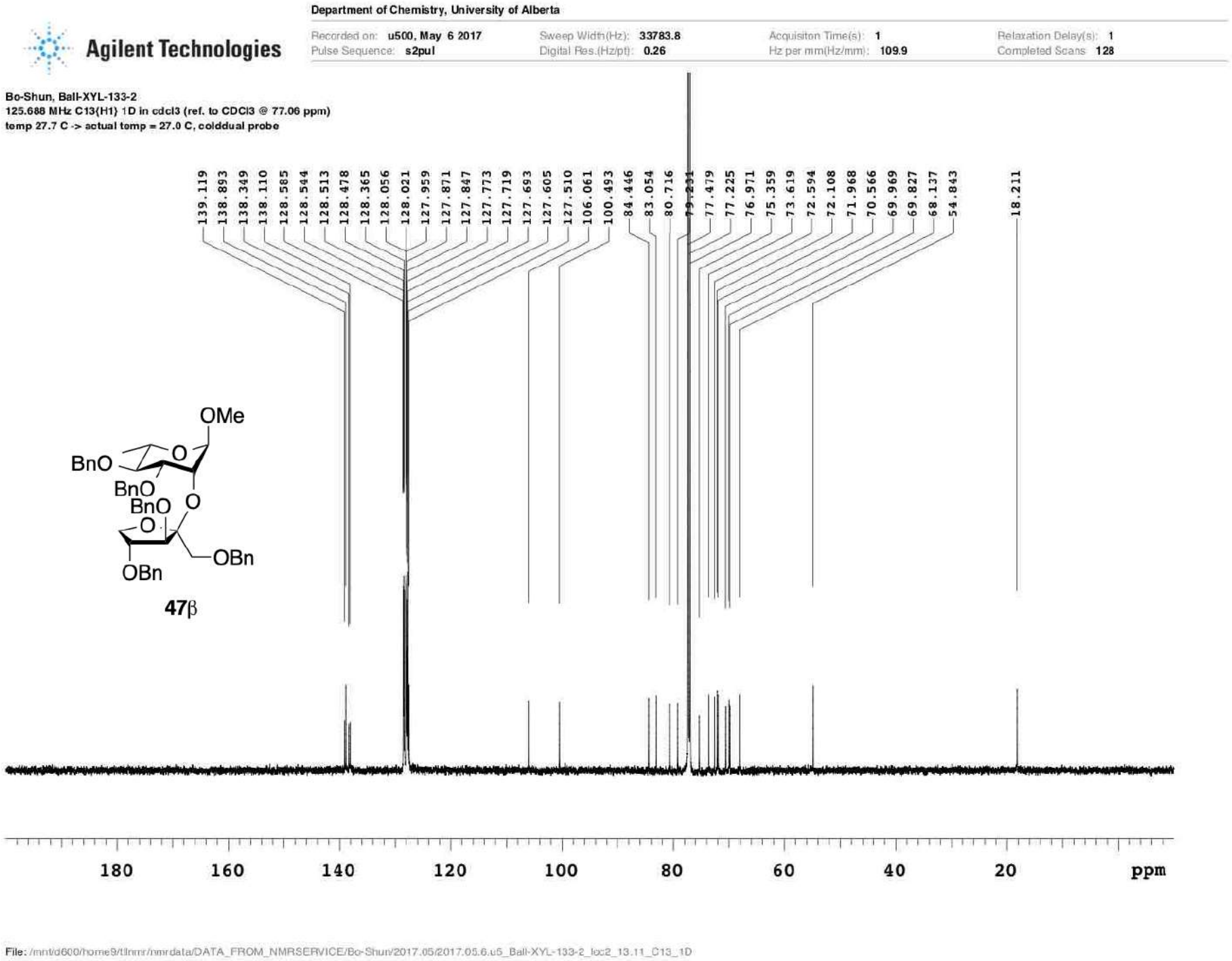
Agilent Technologies

Recorded on:	u500, May 6 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	25.04	Completed Scans	16

Bo-Shun, Ball-XYL-133-2
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.05/2017.05.6.u5_Ball-XYL-133-2_1cc2_13.09_H1_1D

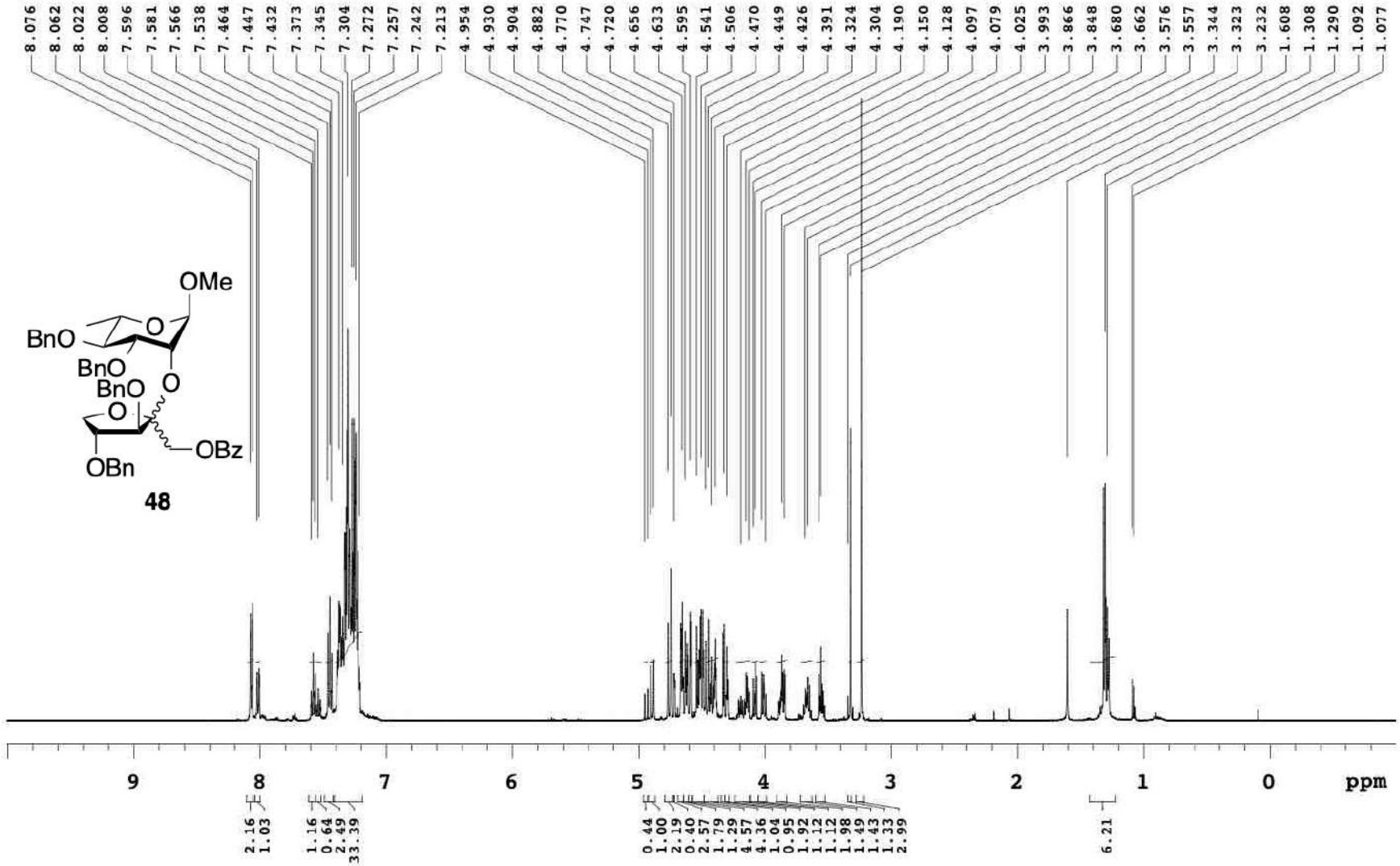

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, May 6 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.9
Relaxation Delay(s): 1
Completed Scans 128
Bo-Shun, Ball-XYL-133-2
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
139.119
138.893
138.349
138.110
128.585
128.544
128.513
128.478
128.365
128.056
128.021
127.959
127.871
127.847
127.773
127.719
127.693
127.605
127.510
106.061
100.493
84.446
83.054
80.716
79.231
77.479
77.225
76.971
75.359
73.619
72.594
72.108
71.968
70.566
69.969
69.827
68.137
54.843
18.211
OMe
BnO
BnO
BnO
O
O
O
OBn
OBn
47β
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.05/2017.05.6.u5_Ball-XYL-133-2_loc2_13.11_C13_1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	u500, May 3 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.91	Completed Scans	16

Bo-Shun, Ball-XYL-131
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.05/2017.05.3.u5_Ball-XYL-131_loc3_15.47_H1_1D

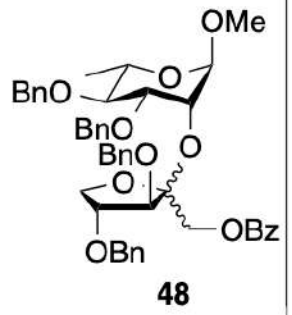
Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	u500, May 3 2017	Sweep Width(Hz):	33783.8	Acquisiton Time(s):	1	Relaxation Delay(s):	1
Pulse Sequence:	s2pul	Digital Res.(Hz/pt):	0.26	Hz per mm(Hz/mm):	109.9	Completed Scans	128

Bo-Shun, Ball-XYL-131
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe

166.214 166.108 138.931 138.851 138.621 138.537 138.102 138.036 133.190 130.276 130.048 129.972 128.655 128.612 128.481 128.434 128.198 128.100 127.989 127.880 127.765 127.667 127.605 107.984 105.244 101.054 100.516 88.484 84.665 83.186 82.007 80.858 80.546 79.396 78.873 77.478 77.224 76.969 75.327 73.073 72.718 72.566 72.271 72.185 72.086 70.517 70.355 70.224 69.646 68.263 68.210 64.350 63.770 54.846 54.797 18.241 18.189



48

180 160 140 120 100 80 60 40 20 ppm

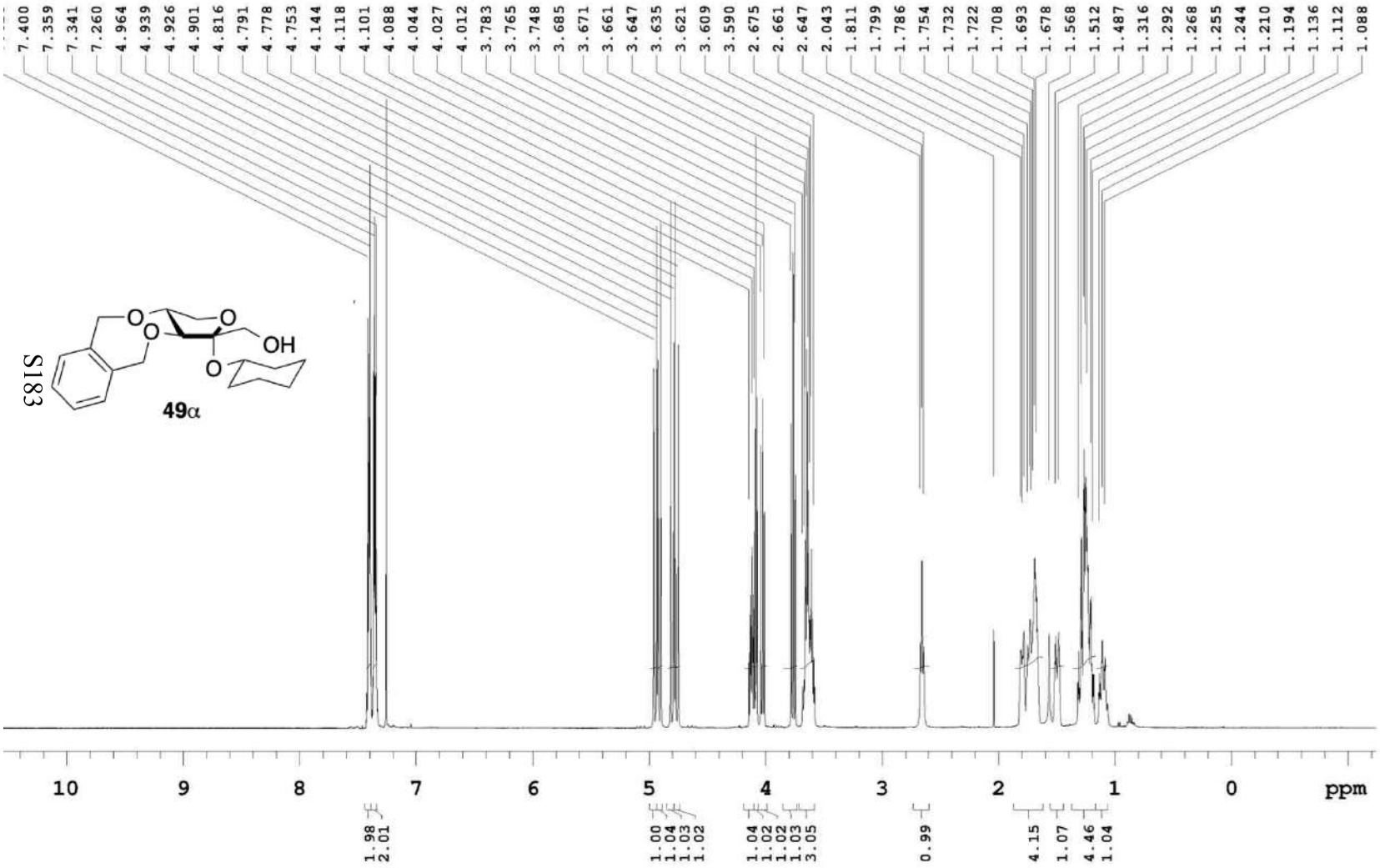
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.05/2017.05.3.u5_Ball-XYL-131_loc3_15.49_C13_1D

Department of Chemistry, University of Alberta

Agilent Technologies

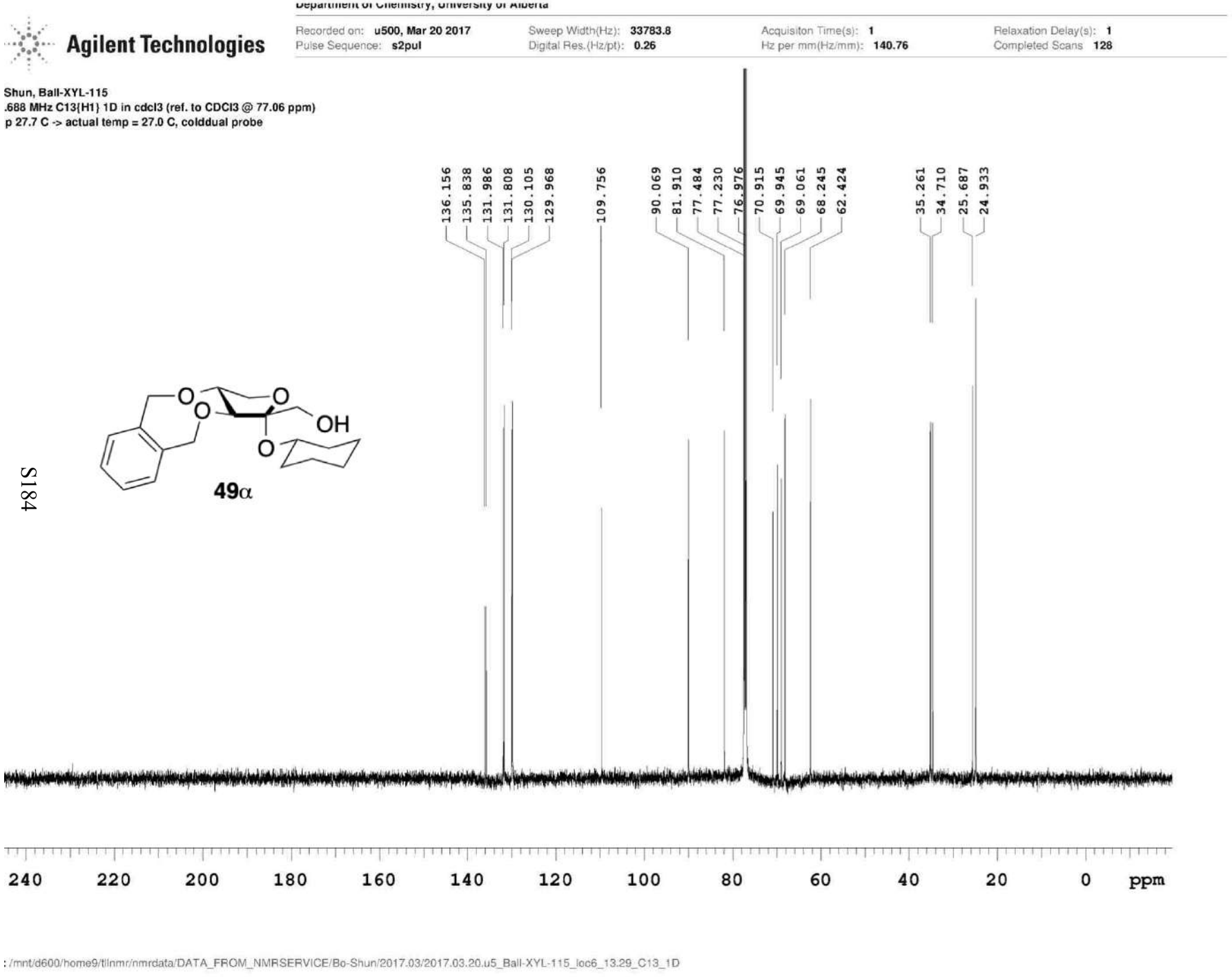
Recorded on:	u500, Mar 20 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	25.04	Completed Scans	16

ihun, Ball-XYL-115
797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
27.7 C -> actual temp = 27.0 C, colddual probe



49α

/mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.03/2017.03.20.u5_Ball-XYL-115_loc6_13.27_H1_1D

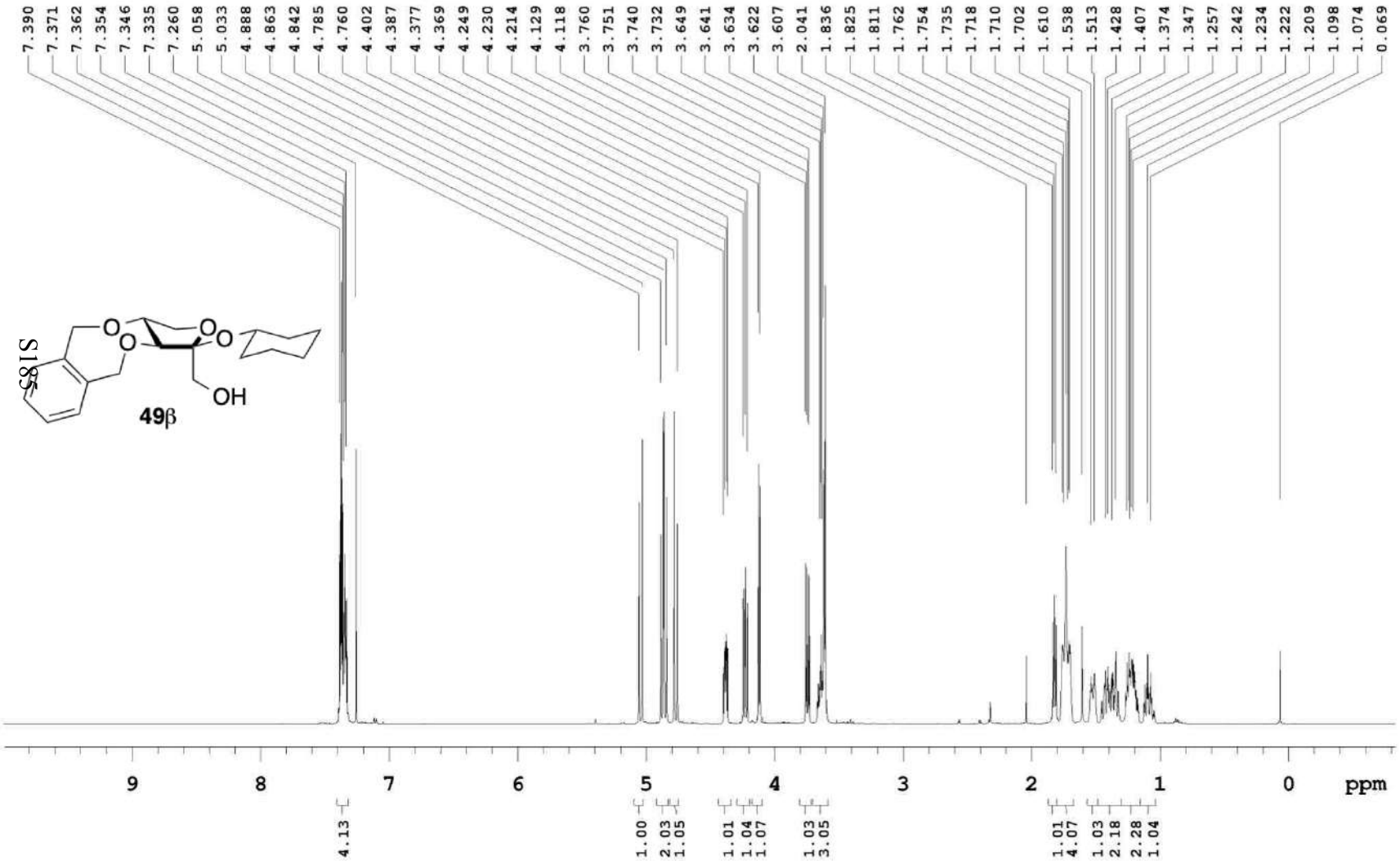

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Mar 20 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 140.76
Relaxation Delay(s): 1
Completed Scans 128
Shun, Ball-XYL-115
.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
p 27.7 C -> actual temp = 27.0 C, colddual probe
136.156
135.838
131.986
131.808
130.105
129.968
109.756
90.069
81.910
77.484
77.230
76.976
70.915
69.945
69.061
68.245
62.424
35.261
34.710
25.687
24.933
O
O
O
O
OH
49α
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm
: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.03/2017.03.20.u5_Ball-XYL-115_loc6_13.29_C13_1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on: u500, Mar 6 2017	Sweep Width(Hz): 6009.62	Acquisiton Time(s): 5	Relaxation Delay(s): 0.1
Pulse Sequence: PRESAT	Digital Res.(Hz/pt): 0.09	Hz per mm(Hz/mm): 22.54	Completed Scans 16

Bo-Shun, Ball-XYL-110
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



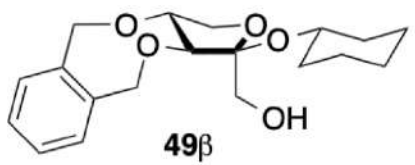
File: /mnt/d600/home9/fllnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017/03/2017-03-6-u5_Ball-XYL-110_loc8_11-54_H1_1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on: u500, Mar 6 2017	Sweep Width(Hz): 33783.8	Acquisiton Time(s): 1	Relaxation Delay(s): 1
Pulse Sequence: s2pul	Digital Res.(Hz/pt): 0.26	Hz per mm(Hz/mm): 140.76	Completed Scans 128

ihun, Ball-XYL-110
588 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
27.7 C -> actual temp = 27.0 C, colddual probe



49β

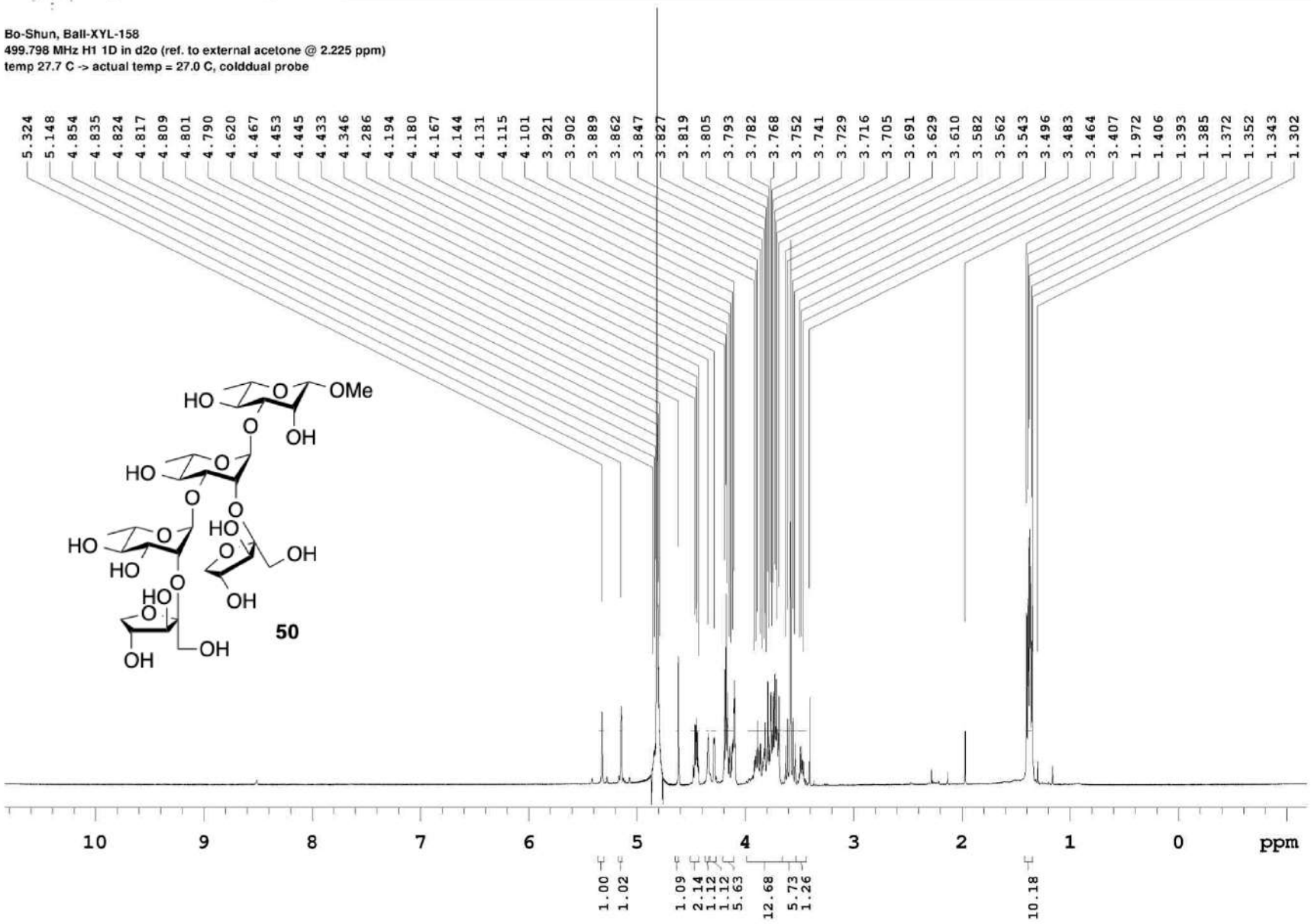
/mnt/d600/home9/tllnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.03/2017.03.6.u5 Ball-XYL-110 loc8 11.55 C13 1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on: u500, Nov 6 2017 | Sweep Width(Hz): 6009.62 | Acquisiton Time(s): 3 | Relaxation Delay(s): 2
Pulse Sequence: PRESAT | Digital Res.(Hz/pt): 0.09 | Hz per mm(Hz/mm): 25.04 | Completed Scans 32

Bo-Shun, Ball-XYL-158
499.798 MHz H1 1D in d2o (ref. to external acetone @ 2.225 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe

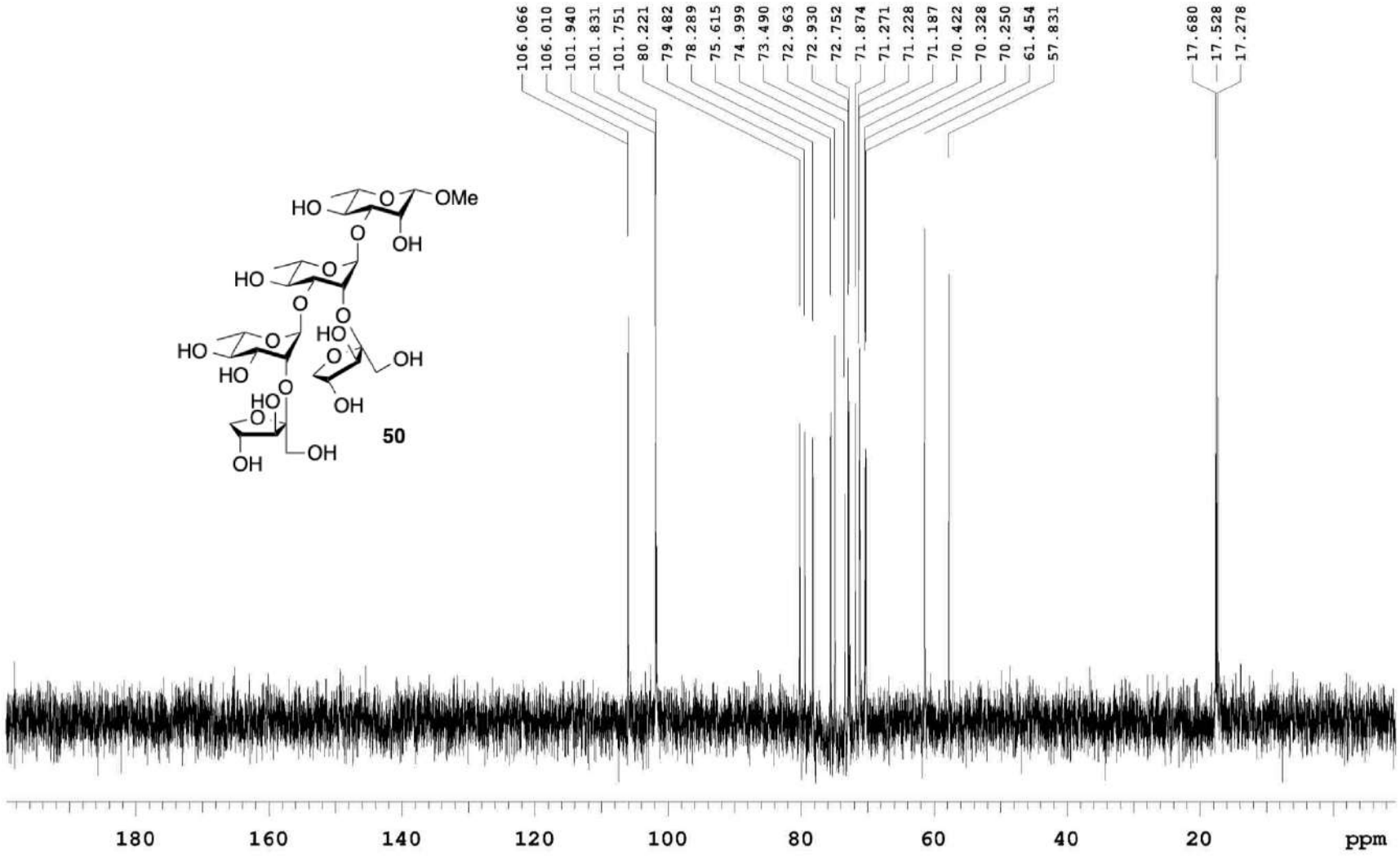


File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.11/2017.11.06.u5_Ball-XYL-158_loc8_10.01_H1_1D

Agilent Technologies

Recorded on: u500, Nov 15 2017	Sweep Width(Hz): 33783.8	Acquisiton Time(s): 1	Relaxation Delay(s): 1
Pulse Sequence: s2pul	Digital Res.(Hz/pt): 0.26	Hz per mm(Hz/mm): 109.4	Completed Scans 5892

Bo-Shun, Ball-XYL-158
125.688 MHz C13{H1} 1D in d2o (ref. to external acetone @ 31.07 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



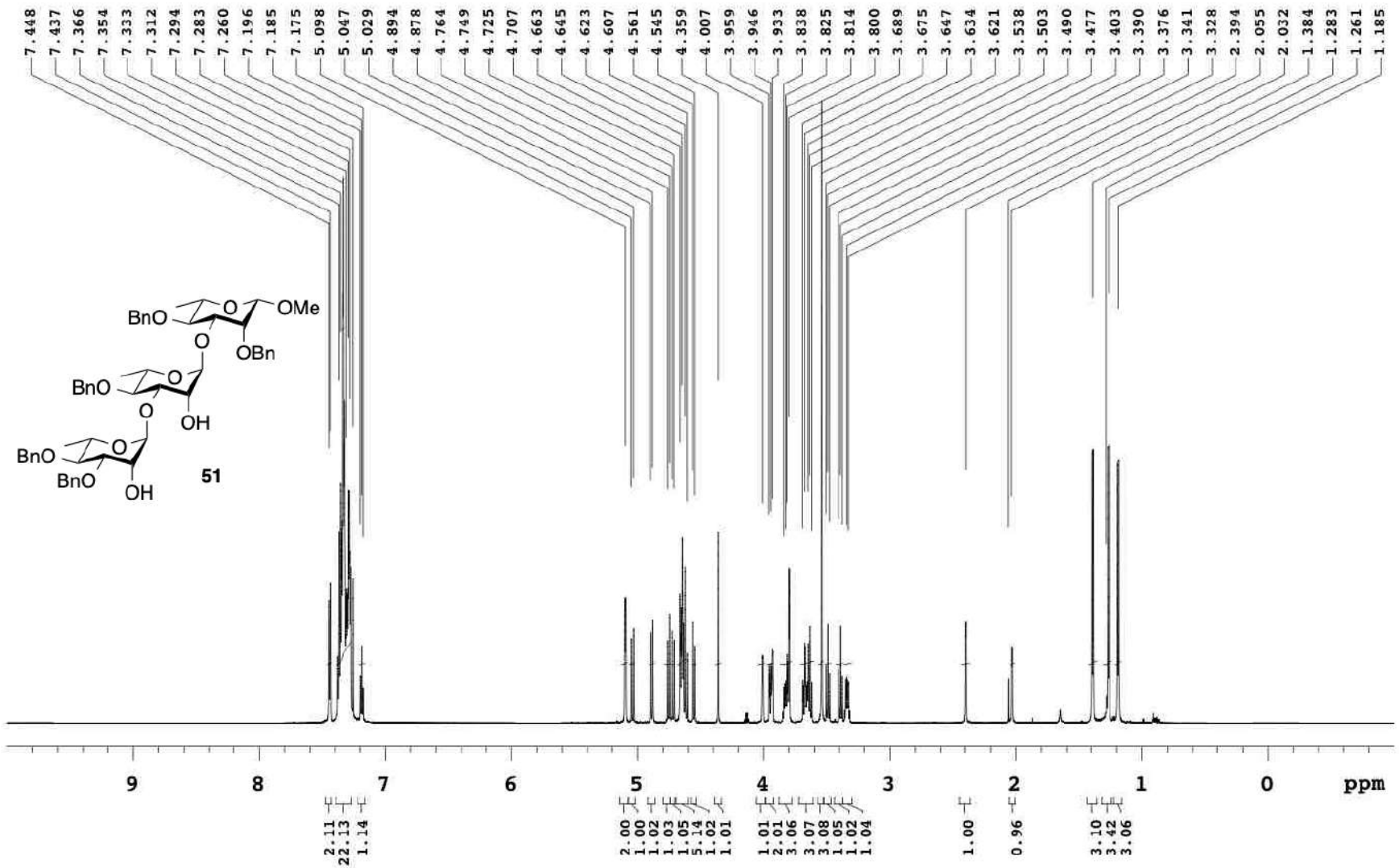
File: /mnt/d600/home9/tlinmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.11/2017.11.15.u5_Ball-XYL-158_loc11_04.03_C13_1D

Department of Chemistry, University of Alberta

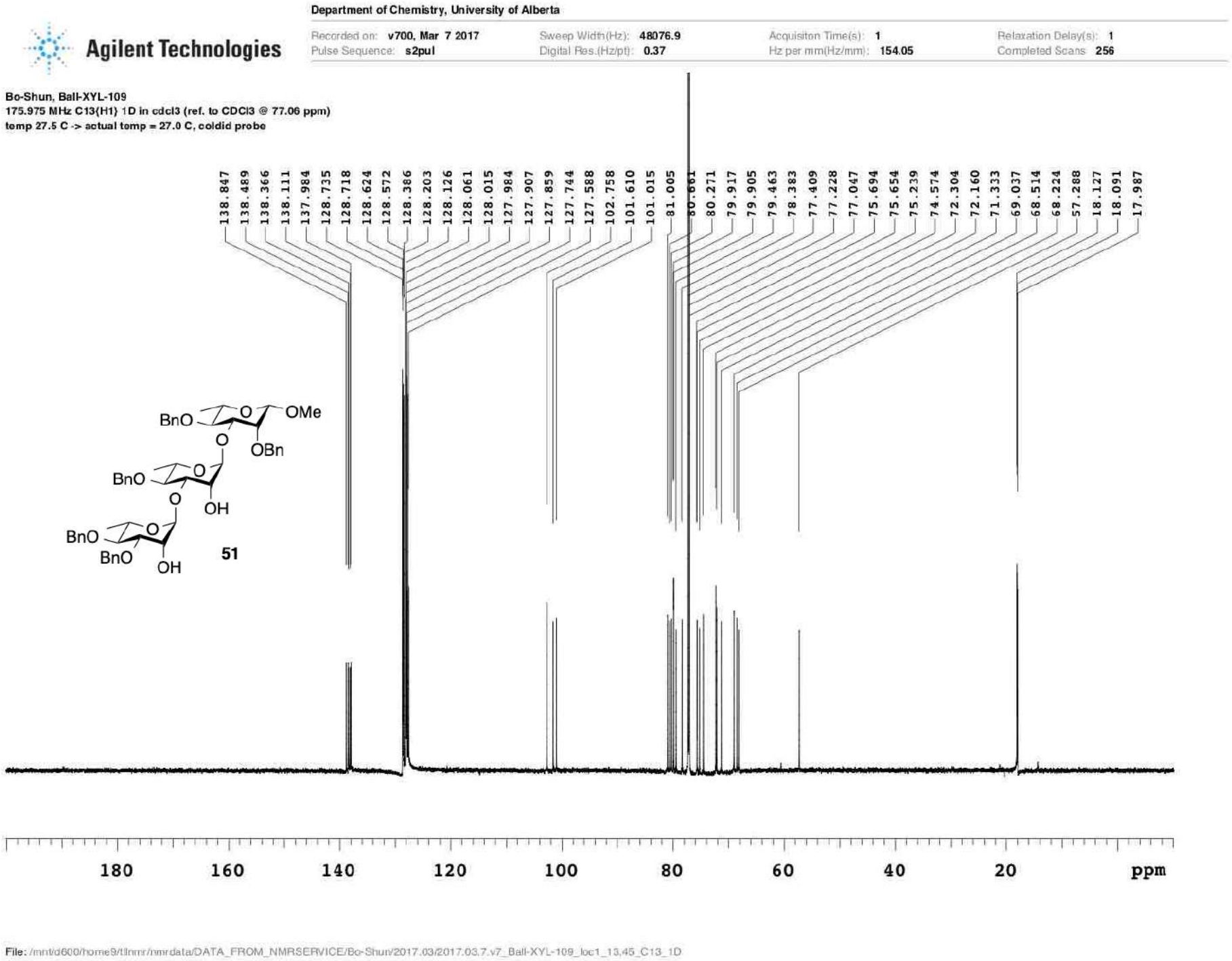
Agilent Technologies

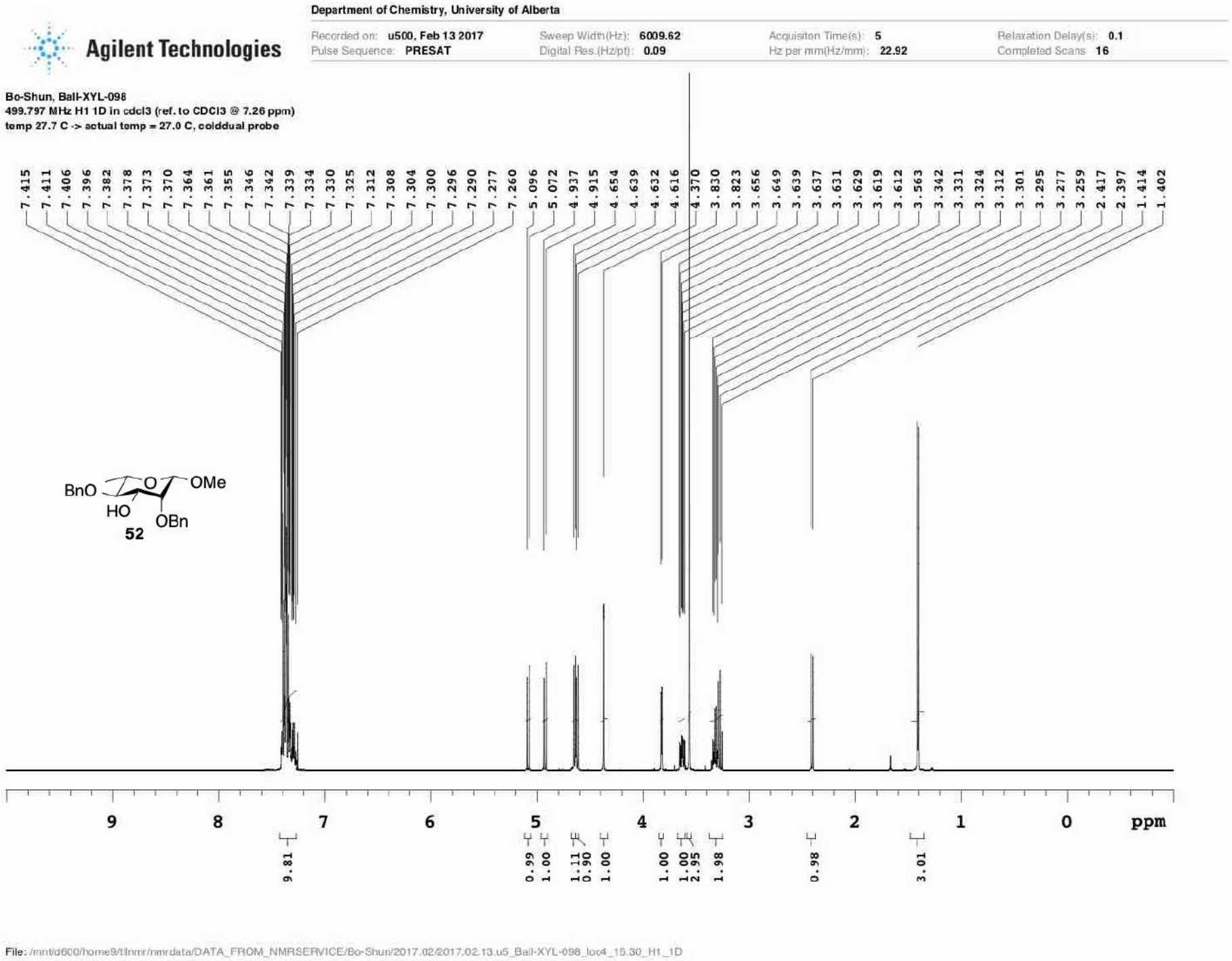
Recorded on:	v700, Mar 7 2017	Sweep Width(Hz):	8389.26	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.13	Hz per mm(Hz/mm):	32.07	Completed Scans	16

Bo-Shun, Ball-XYL-109
699.762 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.03/2017.03.7.v7_Ball-XYL-109_loc1_13.43_H1_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: v700, Mar 7 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 48076.9
Digital Res.(Hz/pt): 0.37
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 154.05
Relaxation Delay(s): 1
Completed Scans 256
Bo-Shun, Ball-XYL-109
175.975 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe
138.847
138.489
138.366
138.111
137.984
128.735
128.718
128.624
128.572
128.386
128.203
128.126
128.061
128.015
127.984
127.907
127.859
127.744
127.588
102.758
101.610
101.015
81.005
80.661
80.271
79.917
79.905
79.463
78.383
77.409
77.228
77.047
75.694
75.654
75.239
74.574
72.304
72.160
71.333
69.037
68.514
68.224
57.288
18.127
18.091
17.987
BnO
O
OMe
OBn
BnO
O
OH
BnO
BnO
OH
51
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.03/2017.03.7.v7_Ball-XYL-109_loc1_13,45_C13_1D

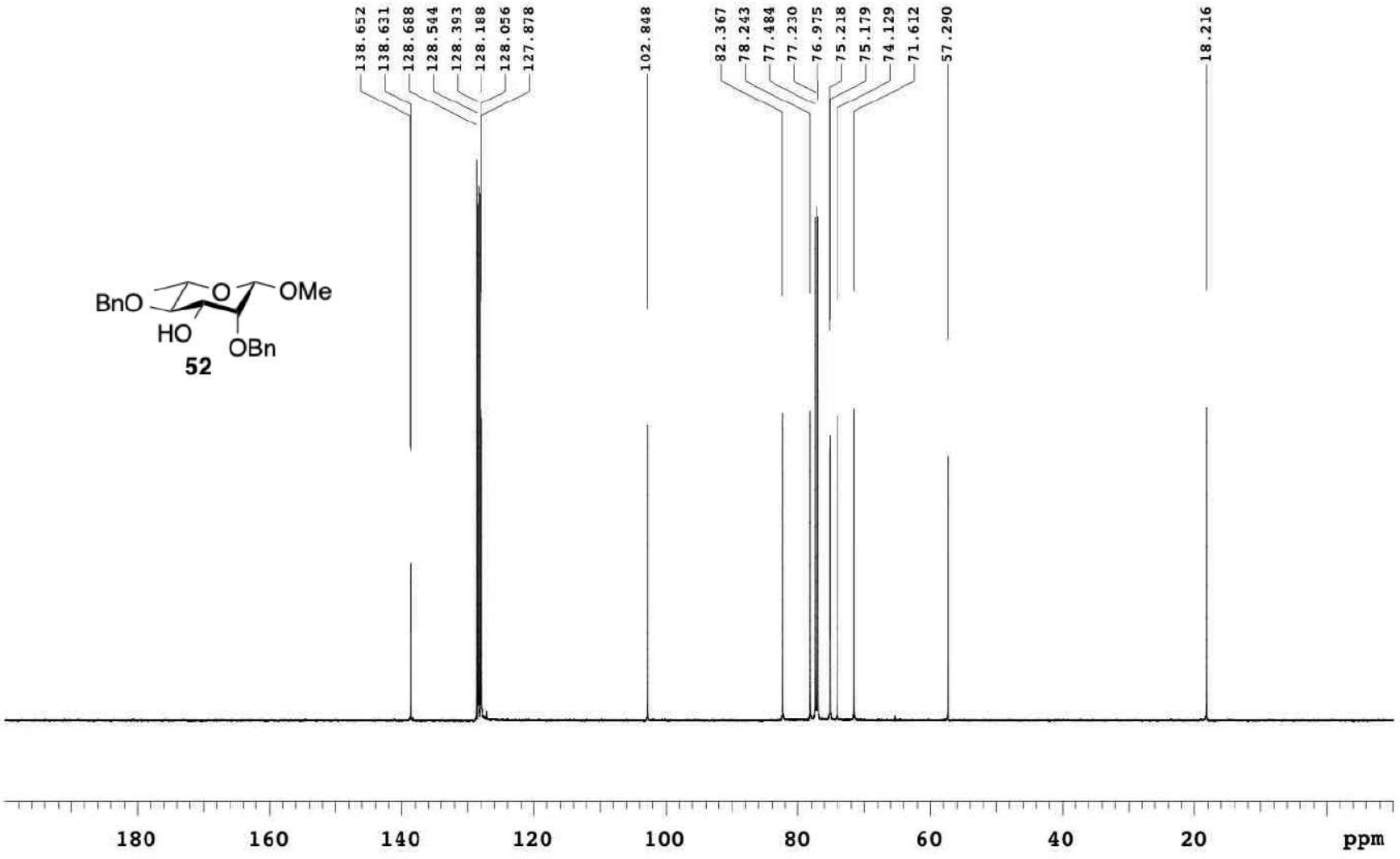

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Feb 13 2017
Pulse Sequence: PRESAT
Sweep Width(Hz): 6009.62
Digital Res.(Hz/pt): 0.09
Acquisiton Time(s): 5
Hz per mm(Hz/mm): 22.92
Relaxation Delay(s): 0.1
Completed Scans 16
Bo-Shun, Ball-XYL-098
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
7.415 7.411 7.406 7.396 7.382 7.378 7.373 7.370 7.364 7.361 7.355 7.346 7.342 7.339 7.334 7.330 7.325 7.312 7.308 7.304 7.300 7.296 7.290 7.277 7.260
5.096 5.072 4.937 4.915 4.654 4.639 4.632 4.616 4.370
3.830 3.823 3.656 3.649 3.639 3.637 3.631 3.629 3.619 3.612 3.563 3.342 3.331 3.324 3.312 3.301 3.295 3.277 3.259
2.417 2.397 1.414 1.402
BnO
O
OMe
HO
OBn
52
9 8 7 6 5 4 3 2 1 0 ppm
9.81
0.99 1.00
1.11 0.90 1.00
1.00 1.00 2.95 1.98
0.98
3.01
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.13.u5_Ball-XYL-098_loc4_15.30_H1_1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	u500, Feb 13 2017	Sweep Width(Hz):	33783.8	Acquisiton Time(s):	1	Relaxation Delay(s):	1
Pulse Sequence:	s2pul	Digital Res.(Hz/pt):	0.26	Hz per mm(Hz/mm):	109.97	Completed Scans	128

Bo-Shun, Ball-XYL-098
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



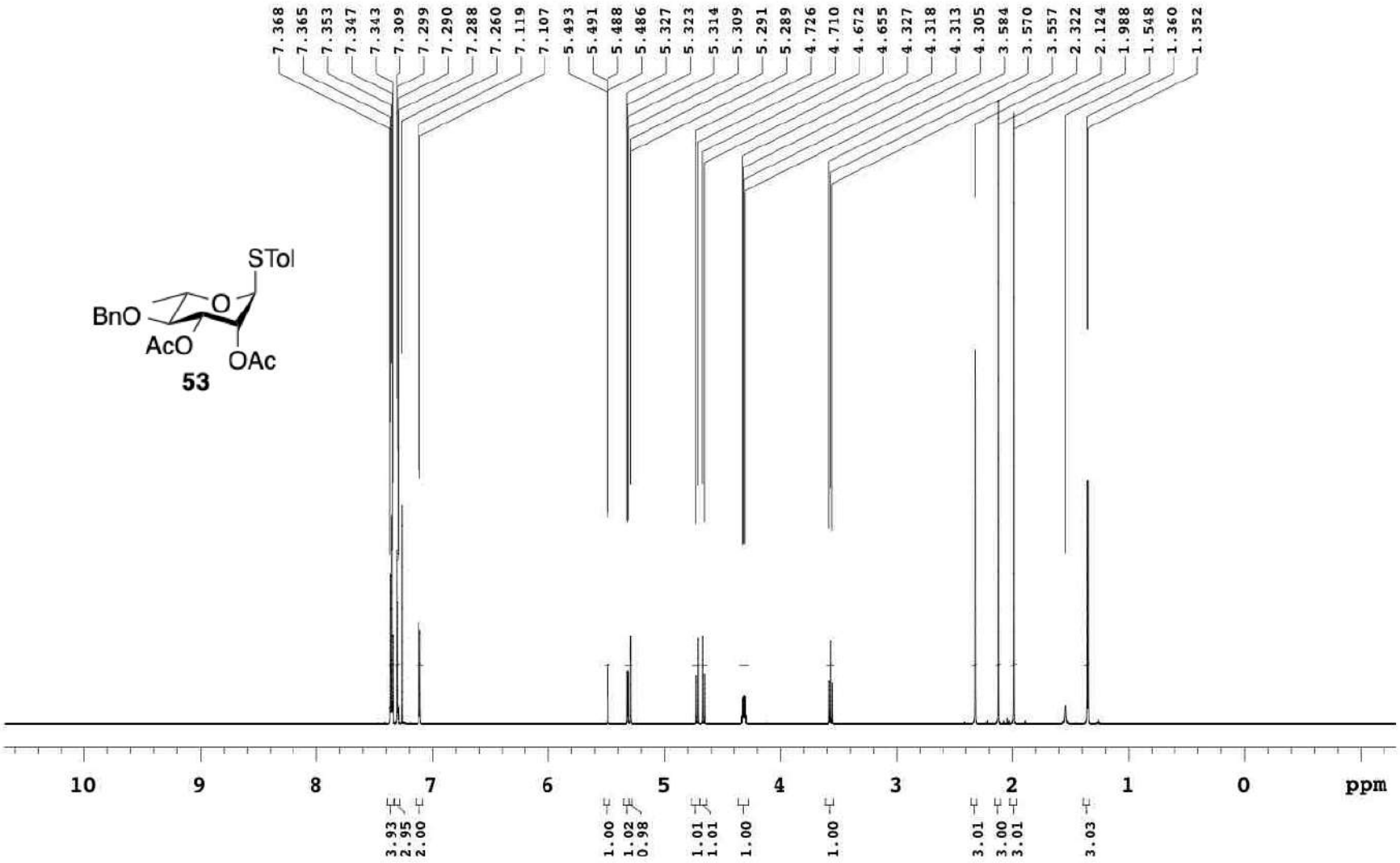
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.13.u5_Ball-XYL-098_loc4_15.31_C13_1D

Agilent Technologies

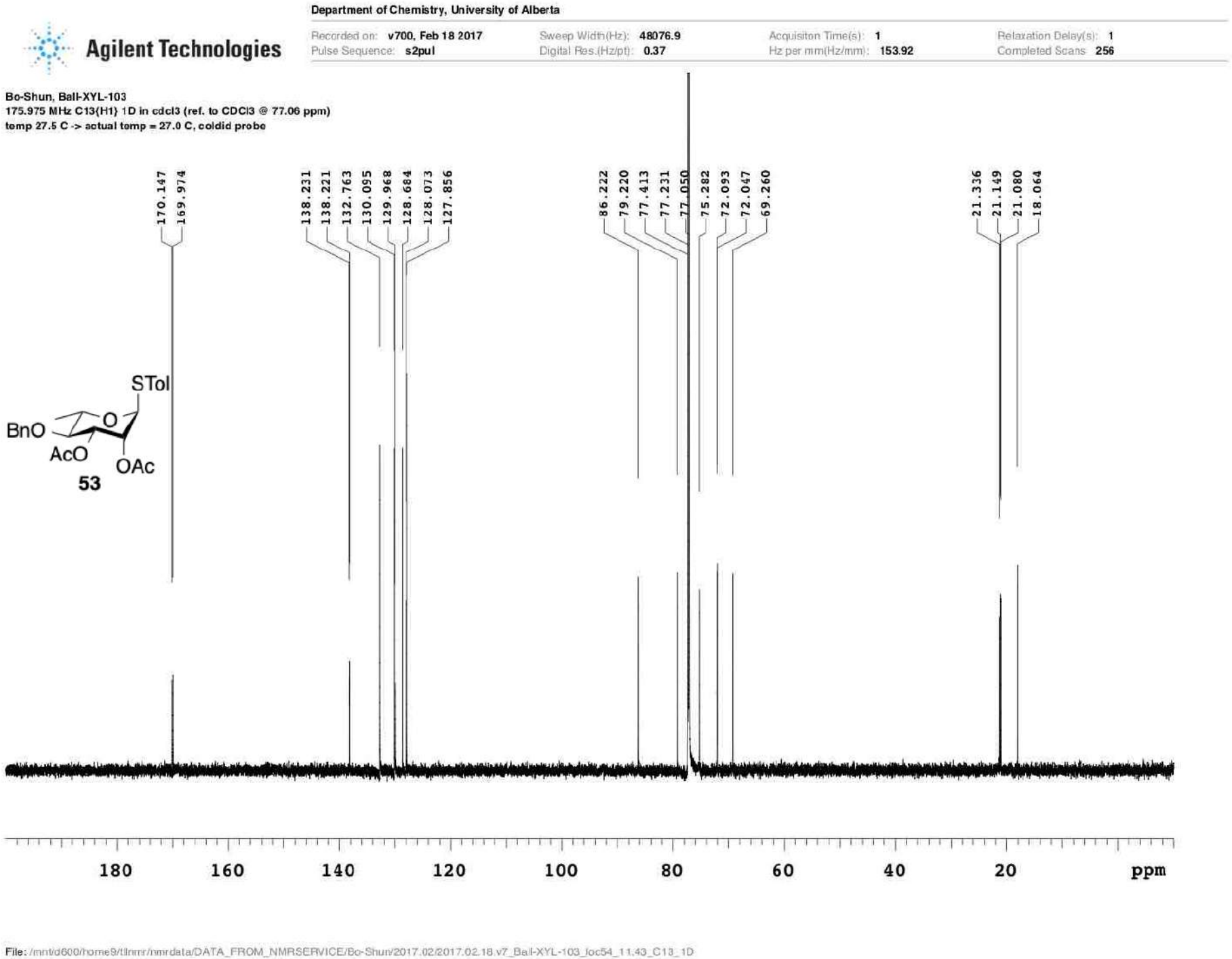
Department of Chemistry, University of Alberta

Recorded on:	v700, Feb 18 2017	Sweep Width(Hz):	8389.26	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.13	Hz per mm(Hz/mm):	34.95	Completed Scans	16

Bo-Shun, Ball-XYL-103
699.762 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.18.v7_Ball-XYL-103_loc54_11.42_H1_1D

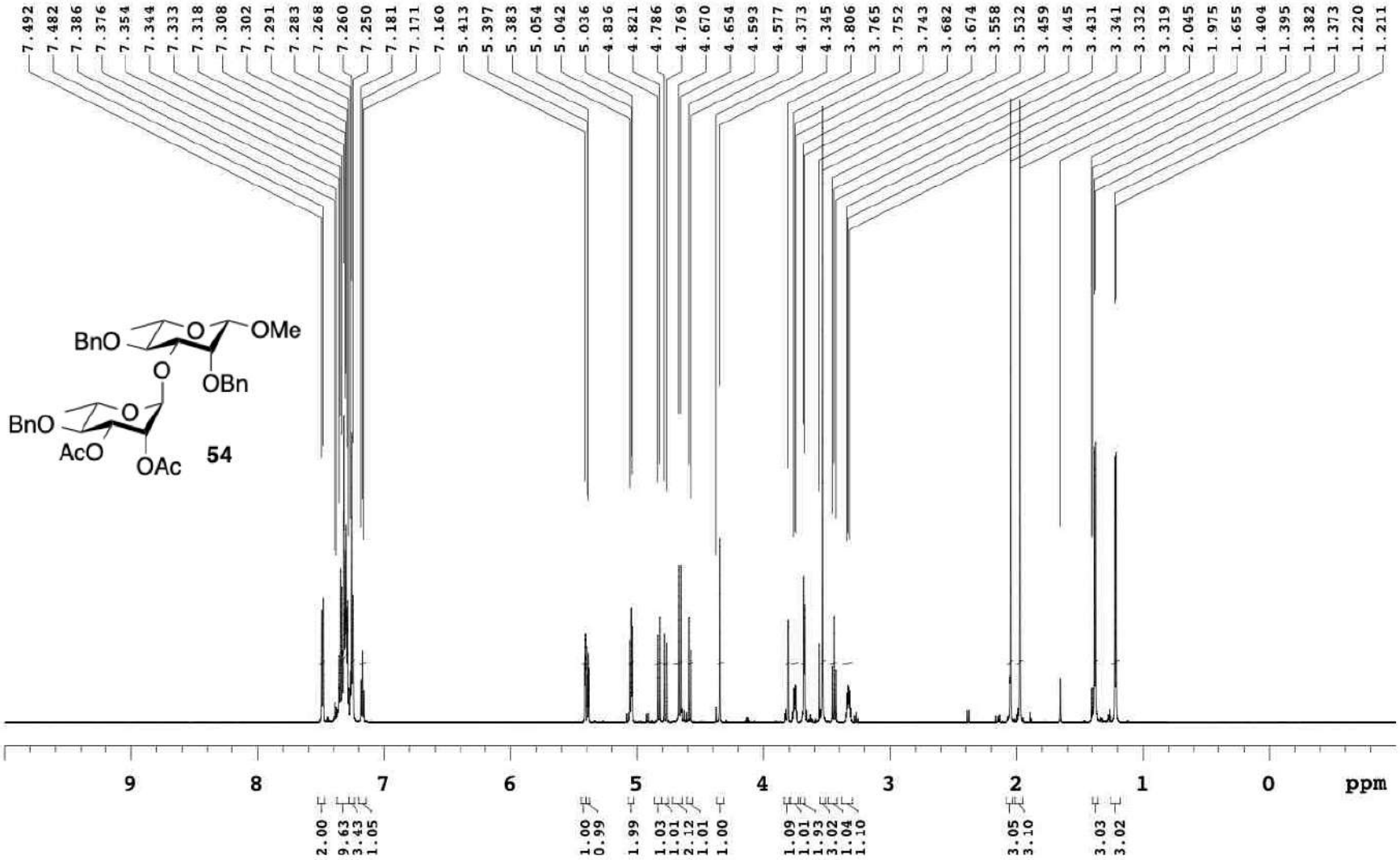

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: v700, Feb 18 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 48076.9
Digital Res.(Hz/pt): 0.37
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 153.92
Relaxation Delay(s): 1
Completed Scans 256
Bo-Shun, Ball-XYL-103
175.975 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe
170.147
169.974
138.231
138.221
132.763
130.095
129.968
128.684
128.073
127.856
86.222
79.220
77.413
77.231
77.050
75.282
72.093
72.047
69.260
21.336
21.149
21.080
18.064
STol
BnO
O
AcO
OAc
53
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.18.v7_Ball-XYL-103_loc54_11.43_C13_1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	v700, Feb 18 2017	Sweep Width(Hz):	8389.26	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.13	Hz per mm(Hz/mm):	32.07	Completed Scans	16

Bo-Shun, Ball-XYl-104
699.762 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe



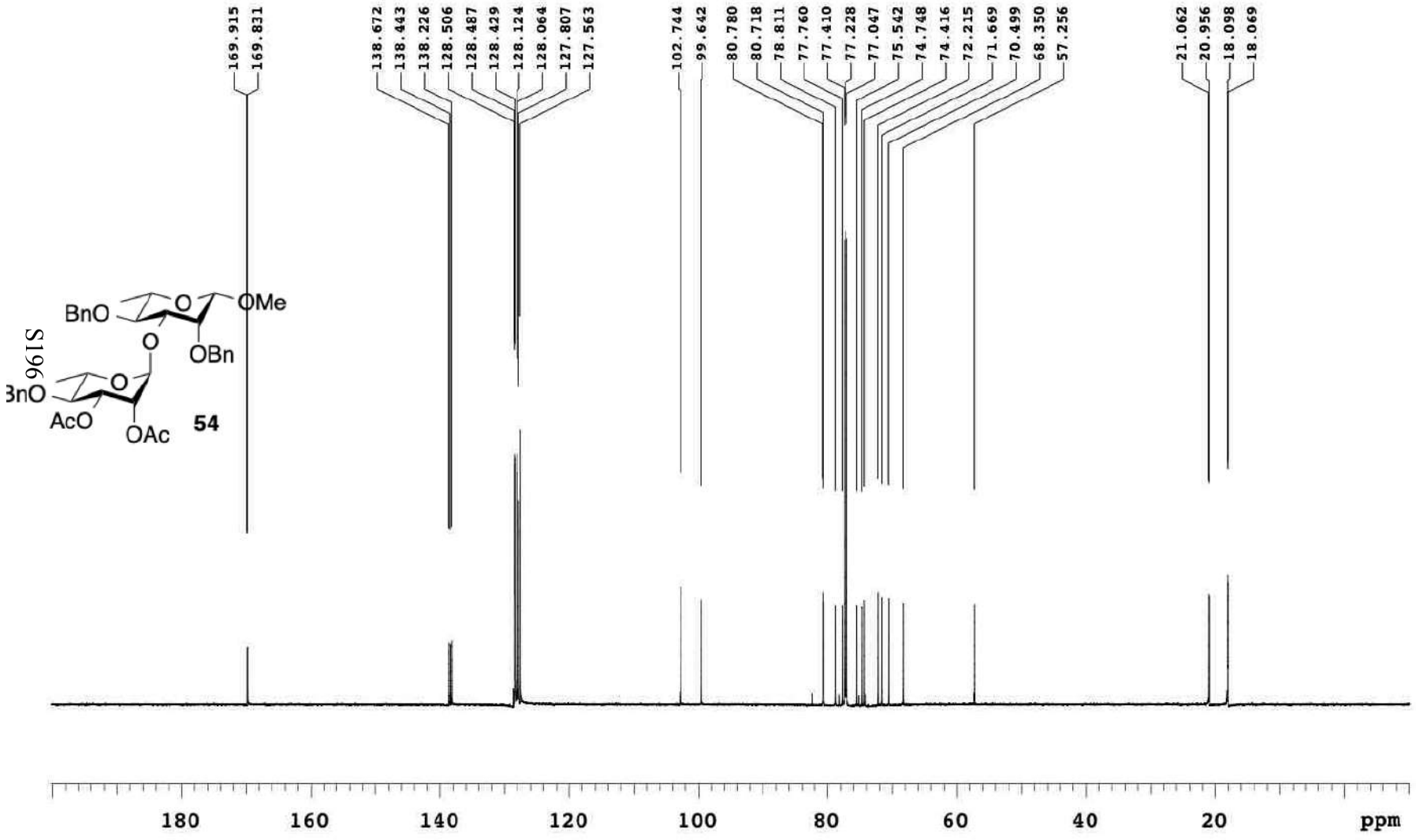
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.18.v7_Ball-XYl-104_loc51_21.07_H1_1D

Department of Chemistry, University of Alberta

Agilent Technologies

Recorded on:	v700, Feb 18 2017	Sweep Width(Hz):	48076.9	Acquisiton Time(s):	1	Relaxation Delay(s):	1
Pulse Sequence:	s2pul	Digital Res.(Hz/pt):	0.37	Hz per mm(Hz/mm):	154.05	Completed Scans	256

Bo-Shun, Ball-XYI-104
175.975 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe



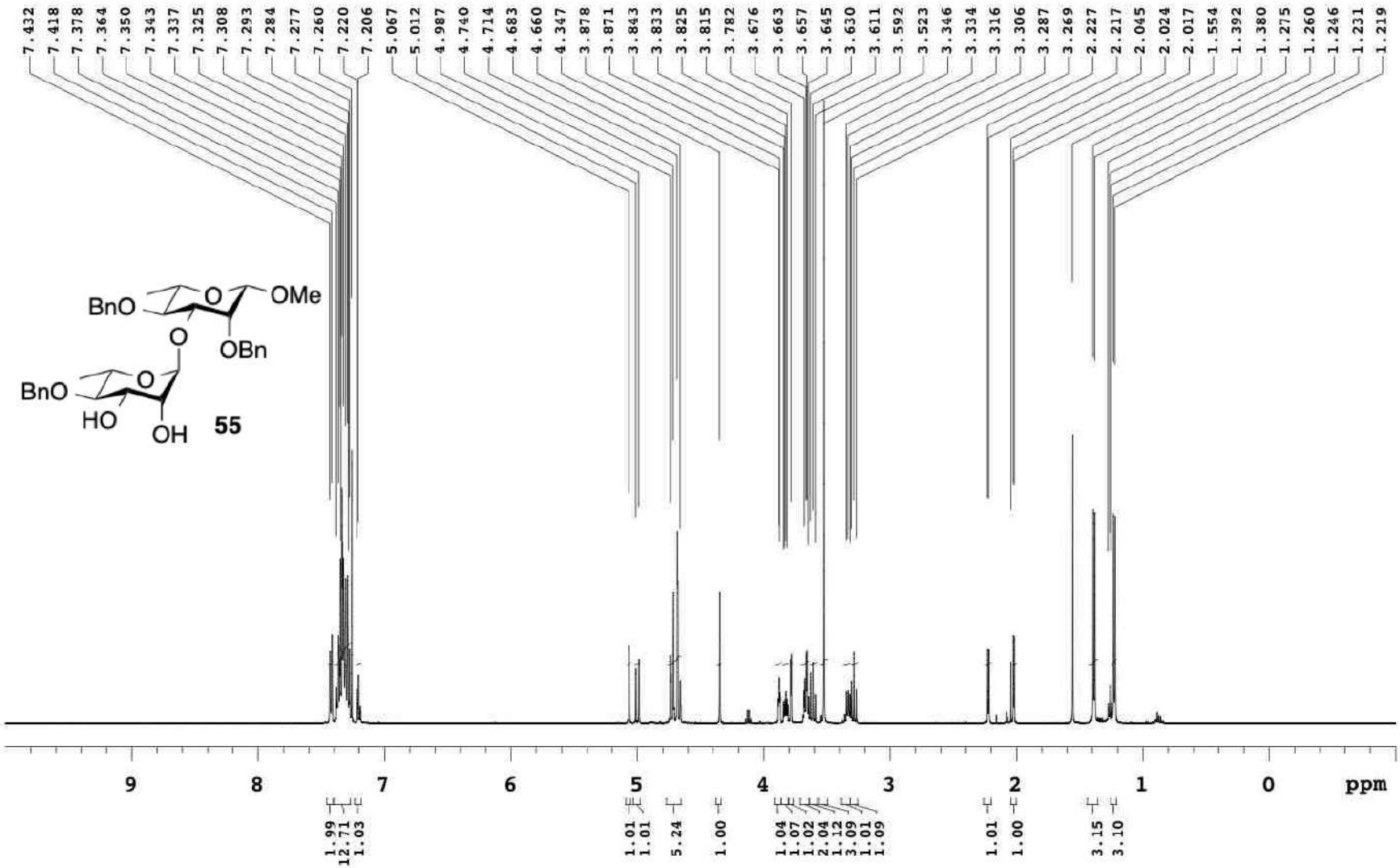
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.18.v7_Ball-XYI-104_loc51_21.09_C13_1D

Department of Chemistry, University of Alberta

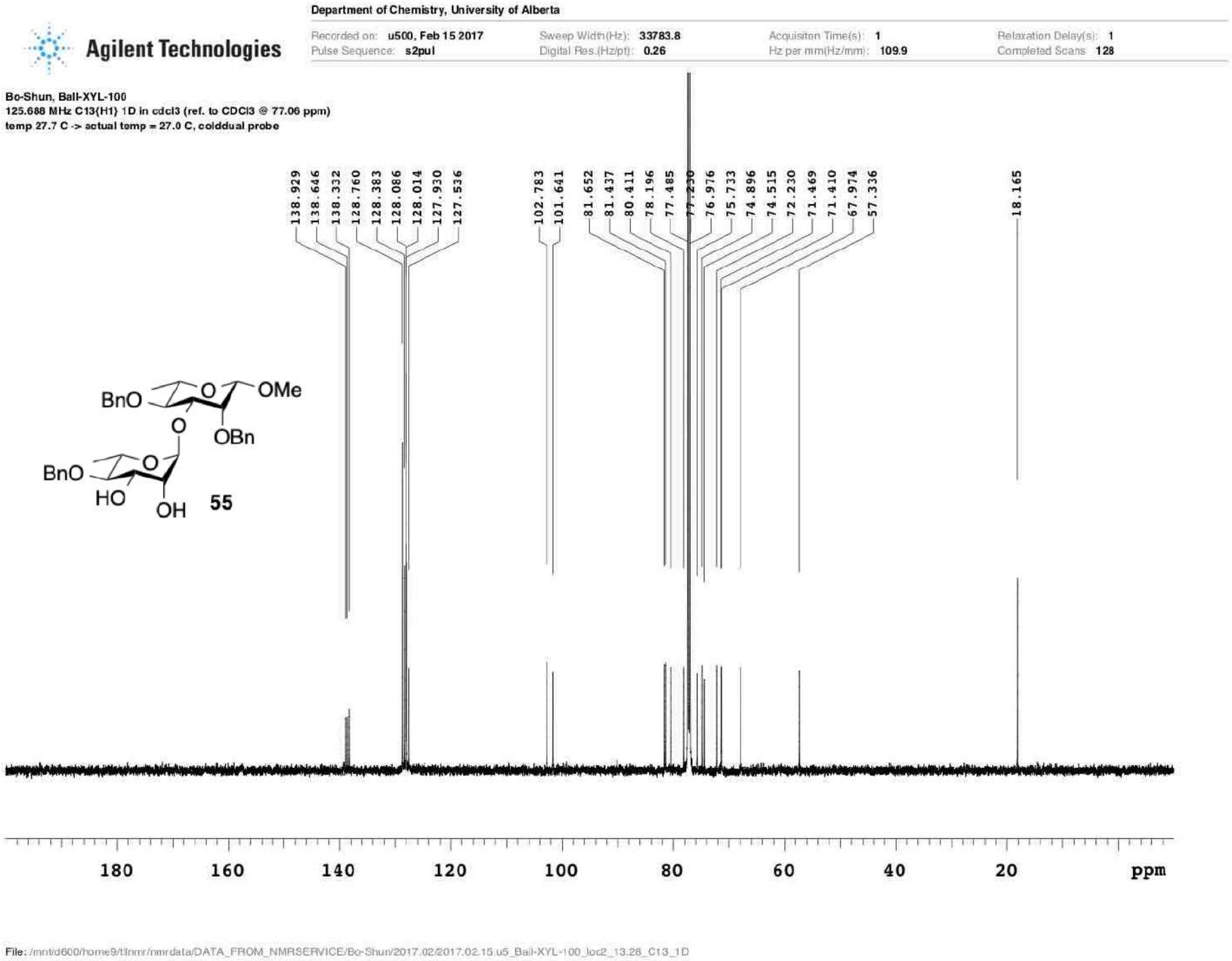
Agilent Technologies

Recorded on:	u500, Feb 15 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.91	Completed Scans	16

Bo-Shun, Ball-XYL-100
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.15.u5_Ball-XYL-100_loc2_13.26_H1_1D

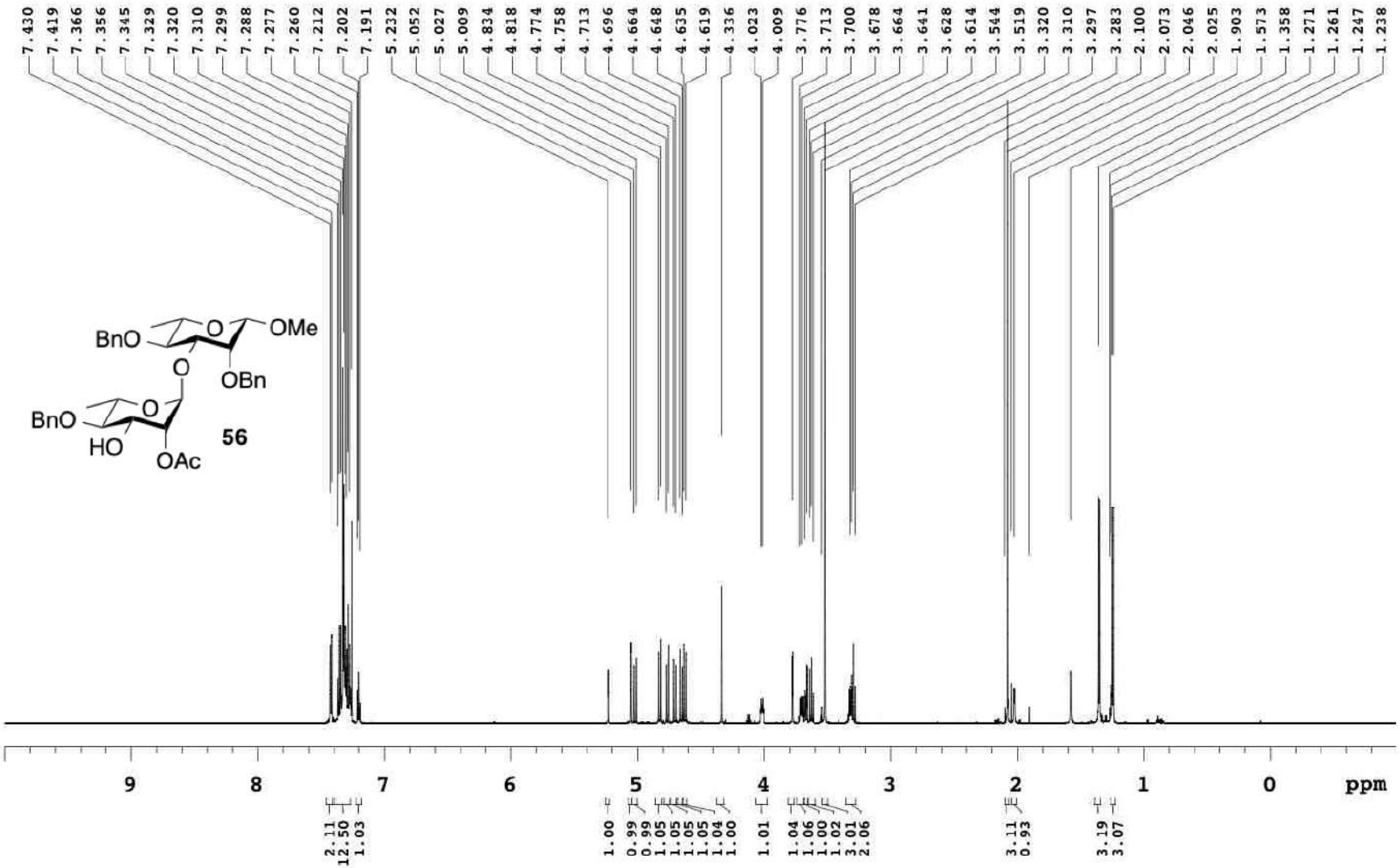

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Feb 15 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.9
Relaxation Delay(s): 1
Completed Scans 128
Bo-Shun, Ball-XYL-100
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
138.929
138.646
138.332
128.760
128.383
128.086
128.014
127.930
127.536
102.783
101.641
81.652
81.437
80.411
78.196
77.485
77.230
76.976
75.733
74.896
74.515
72.230
71.469
71.410
67.974
57.336
18.165
BnO
OMe
OBn
BnO
HO
OH
55
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.15.u5_Ball-XYL-100_loc2_13.28_C13_1D

Department of Chemistry, University of Alberta

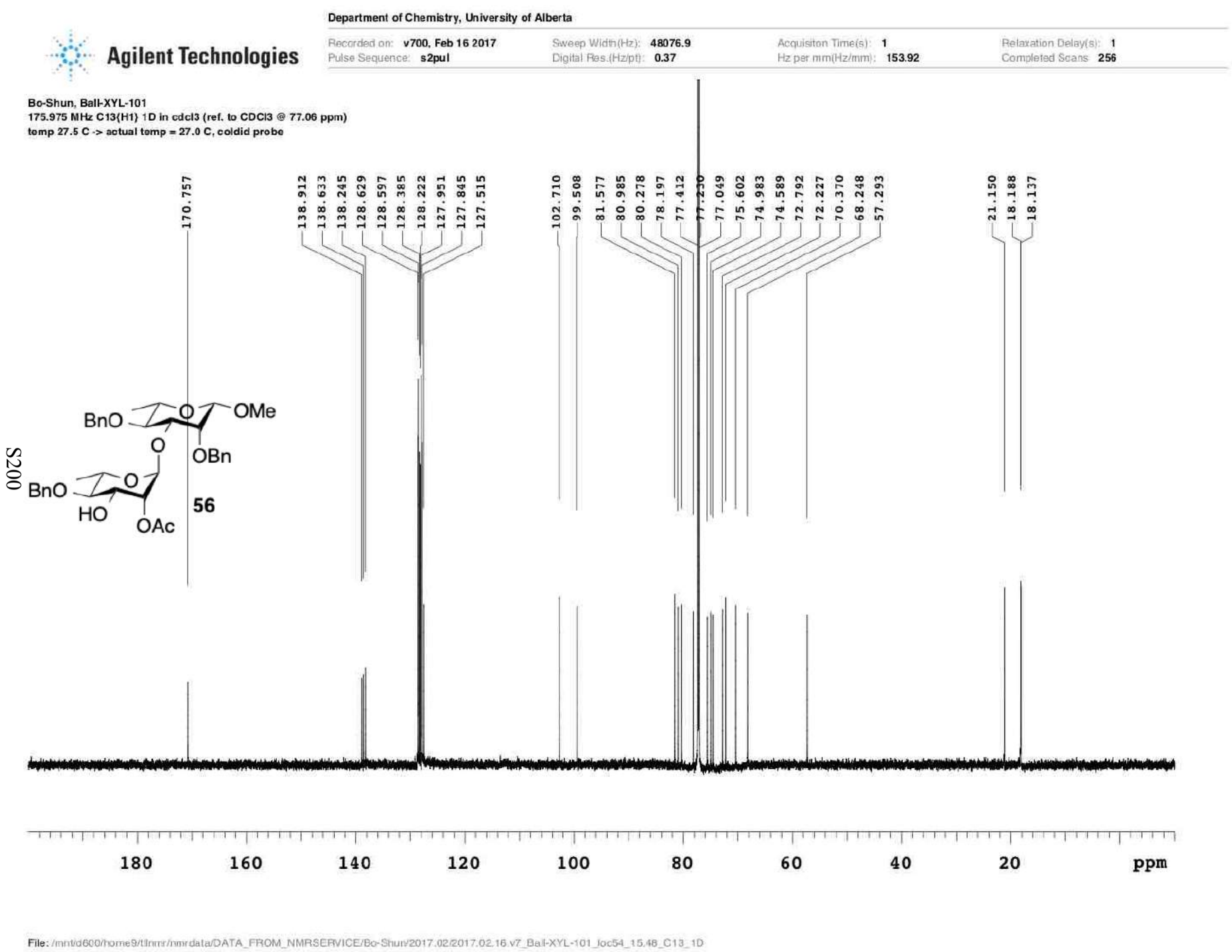
Agilent Technologies

Recorded on:	v700, Feb 16 2017	Sweep Width(Hz):	8389.26	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.13	Hz per mm(Hz/mm):	32.04	Completed Scans	16

Bo-Shun, Ball-XYL-101
699.762 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.16.v7_Ball-XYL-101_loc54_15.46_H1_1D

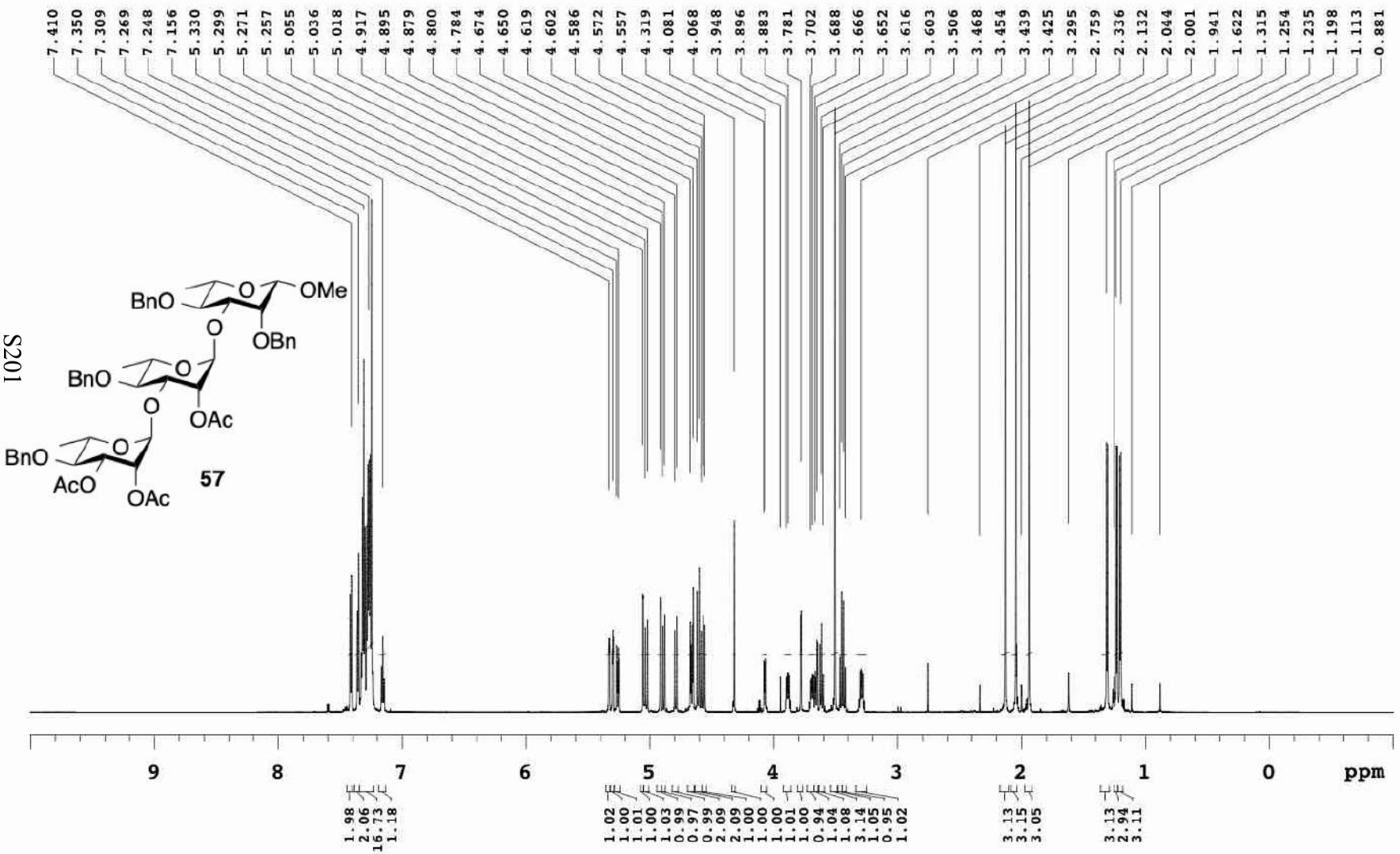

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: v700, Feb 16 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 48076.9
Digital Res.(Hz/pt): 0.37
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 153.92
Relaxation Delay(s): 1
Completed Scans 256
Bo-Shun, Ball-XYL-101
175.975 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe
170.757
138.912
138.633
138.245
128.629
128.597
128.385
128.222
127.951
127.845
127.515
102.710
99.508
81.577
80.985
80.278
78.197
77.412
77.230
77.049
75.602
74.983
74.589
72.792
72.227
70.370
68.248
57.293
21.150
18.188
18.137
BnO
O
OMe
OBn
O
BnO
O
HO
OAc
56
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.16.v7_Ball-XYL-101_loc54_15.48_C13_1D

Department of Chemistry, University of Alberta

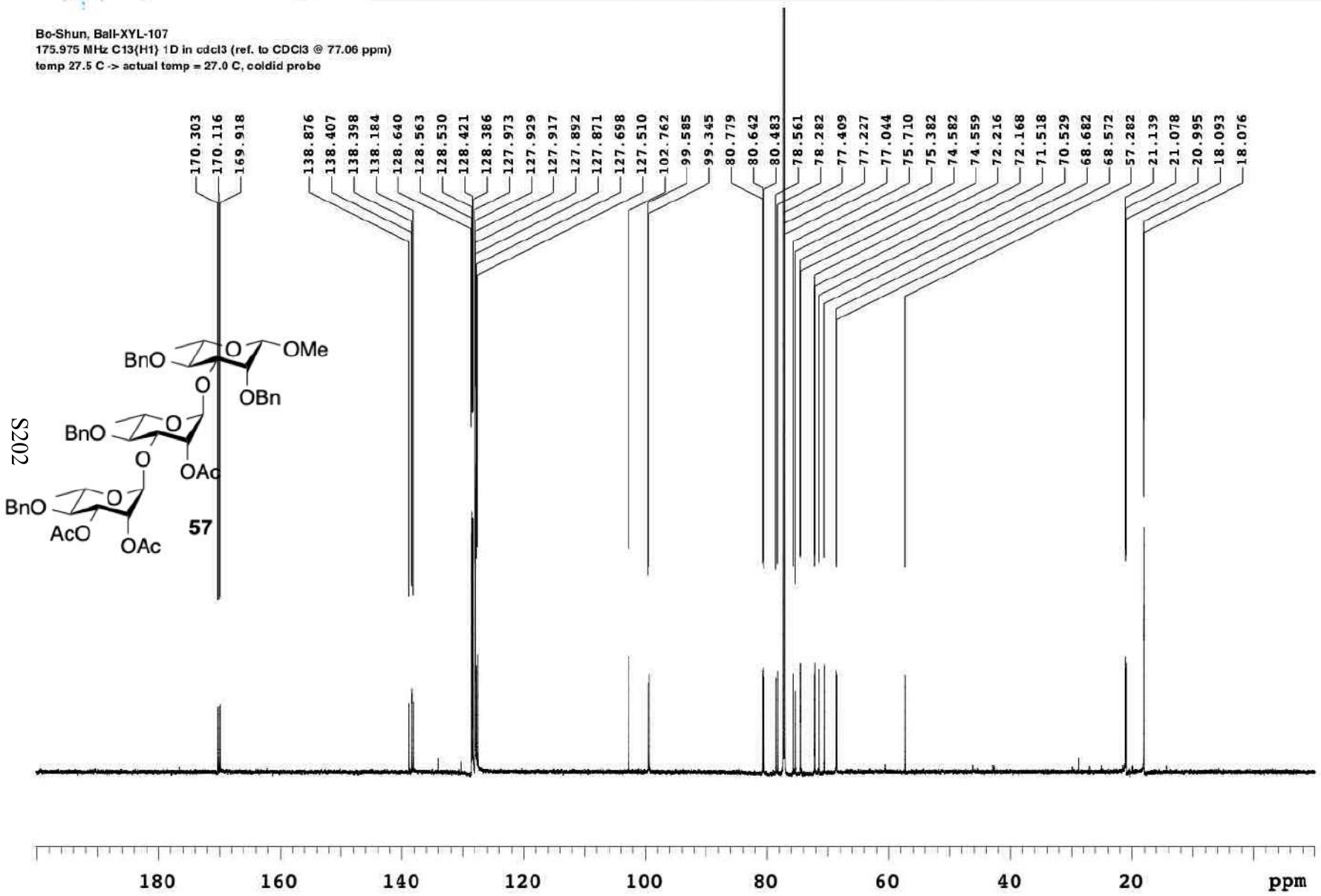
Agilent Technologies

Recorded on:	v700, Mar 3 2017	Sweep Width(Hz):	8389.26	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.13	Hz per mm(Hz/mm):	32.09	Completed Scans	16

Bo-Shun, Ball-XYL-107
699.762 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.03/2017.03.3.v7_Ball-XYL-107_loc5_11.47_H1_1D

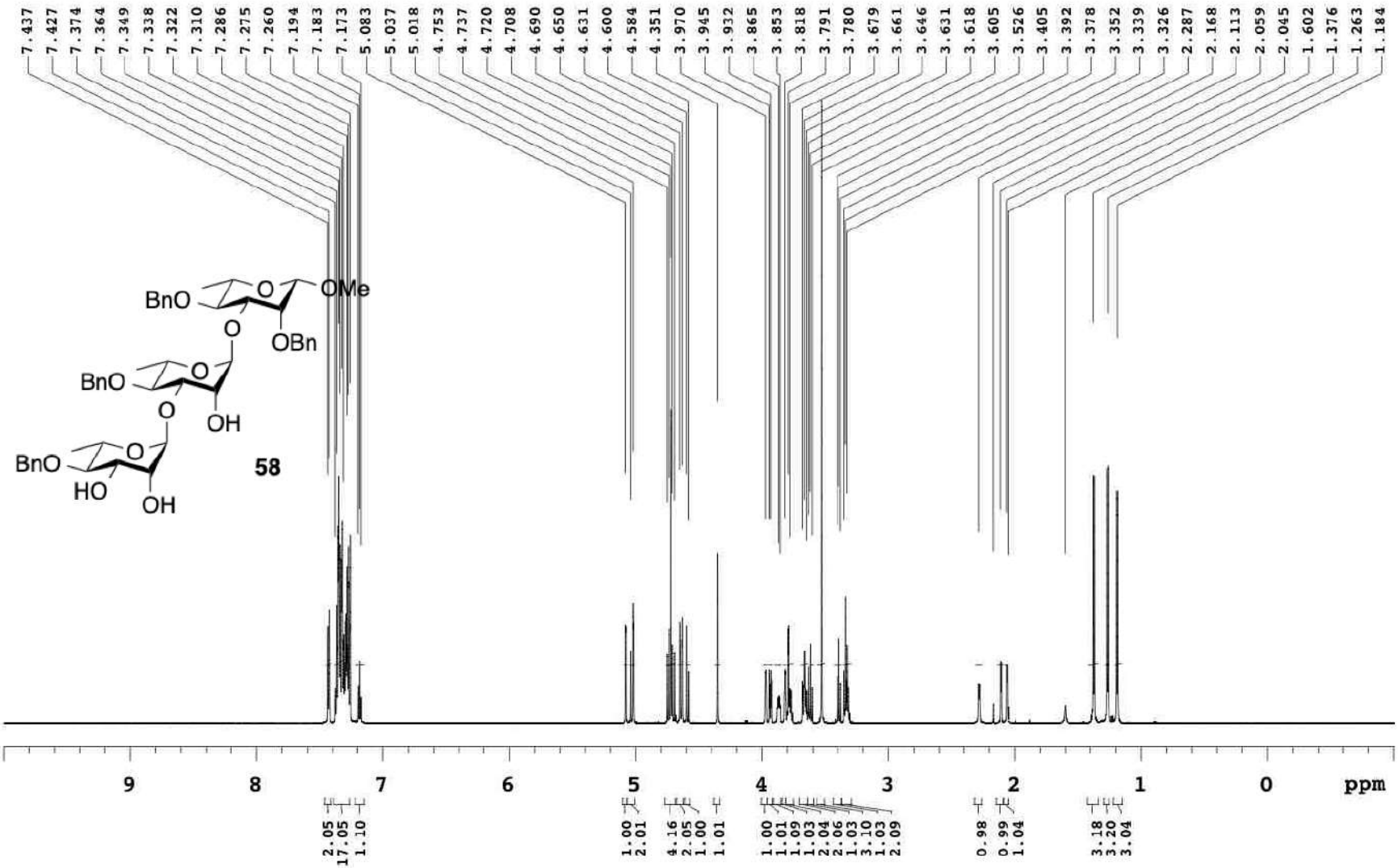

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: v700, Mar 3 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 48076.9
Digital Res.(Hz/pt): 0.37
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 154.05
Relaxation Delay(s): 1
Completed Scans 256
Bo-Shun, Ball-XYL-107
175.975 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe
170.303
170.116
169.918
138.876
138.407
138.398
138.184
128.640
128.563
128.530
128.421
128.386
127.973
127.929
127.917
127.892
127.871
127.698
127.510
102.762
99.585
99.345
80.779
80.642
80.483
78.561
78.282
77.409
77.227
77.044
75.710
75.382
74.582
74.559
72.216
72.168
71.518
70.529
68.682
68.572
57.282
21.139
21.078
20.995
18.093
18.076
BnO
O
OMe
OBn
BnO
O
OAc
BnO
O
AcO
OAc
57
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.03/2017.03.3.v7_Ball-XYL-107_loc5_11.49_C13_1D

Agilent Technologies

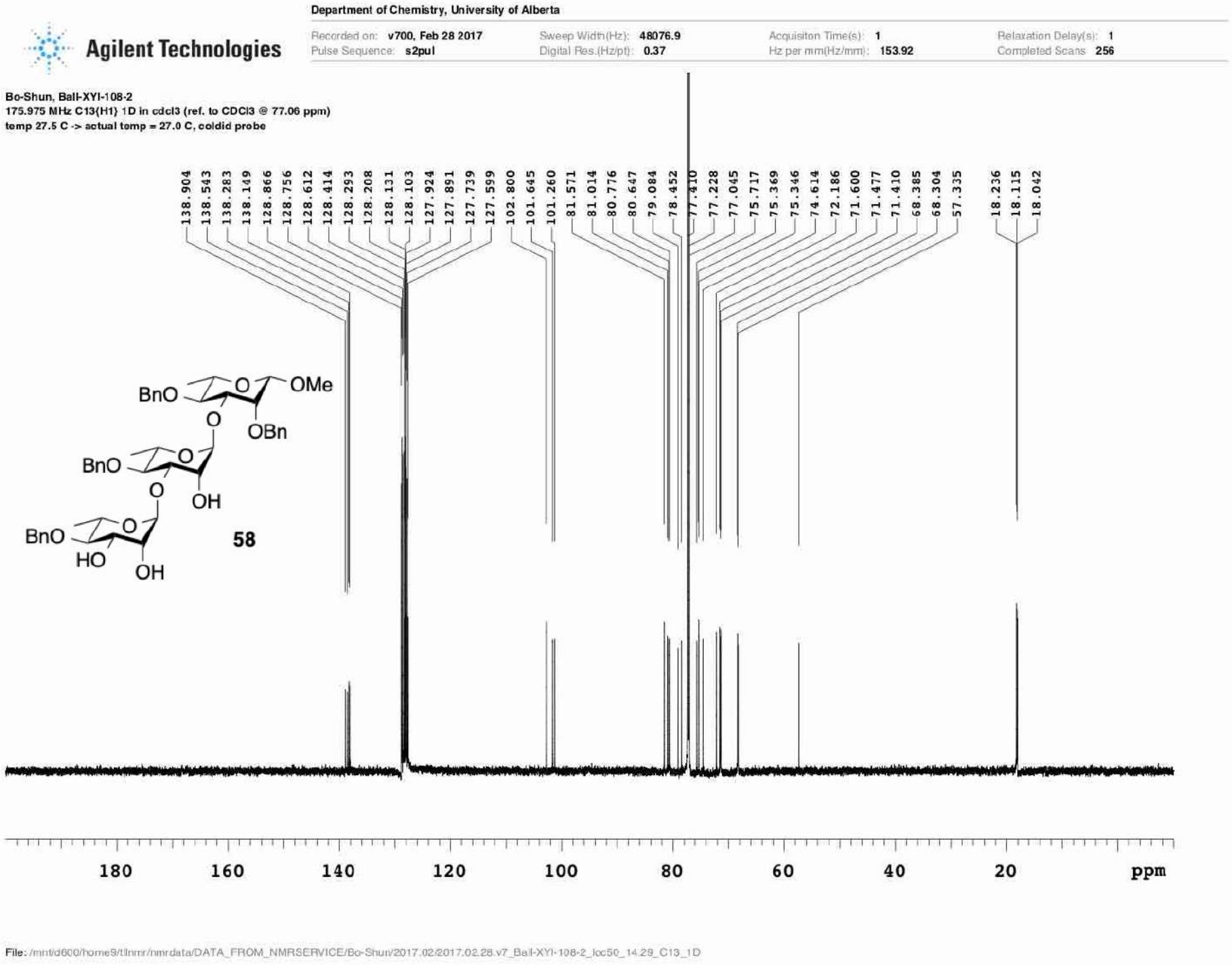
Department of Chemistry, University of Alberta

Recorded on:	v700, Feb 28 2017	Sweep Width(Hz):	8389.26	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.13	Hz per mm(Hz/mm):	32.09	Completed Scans	16

Bo-Shun, Ball-XYl-108-2
699.762 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe



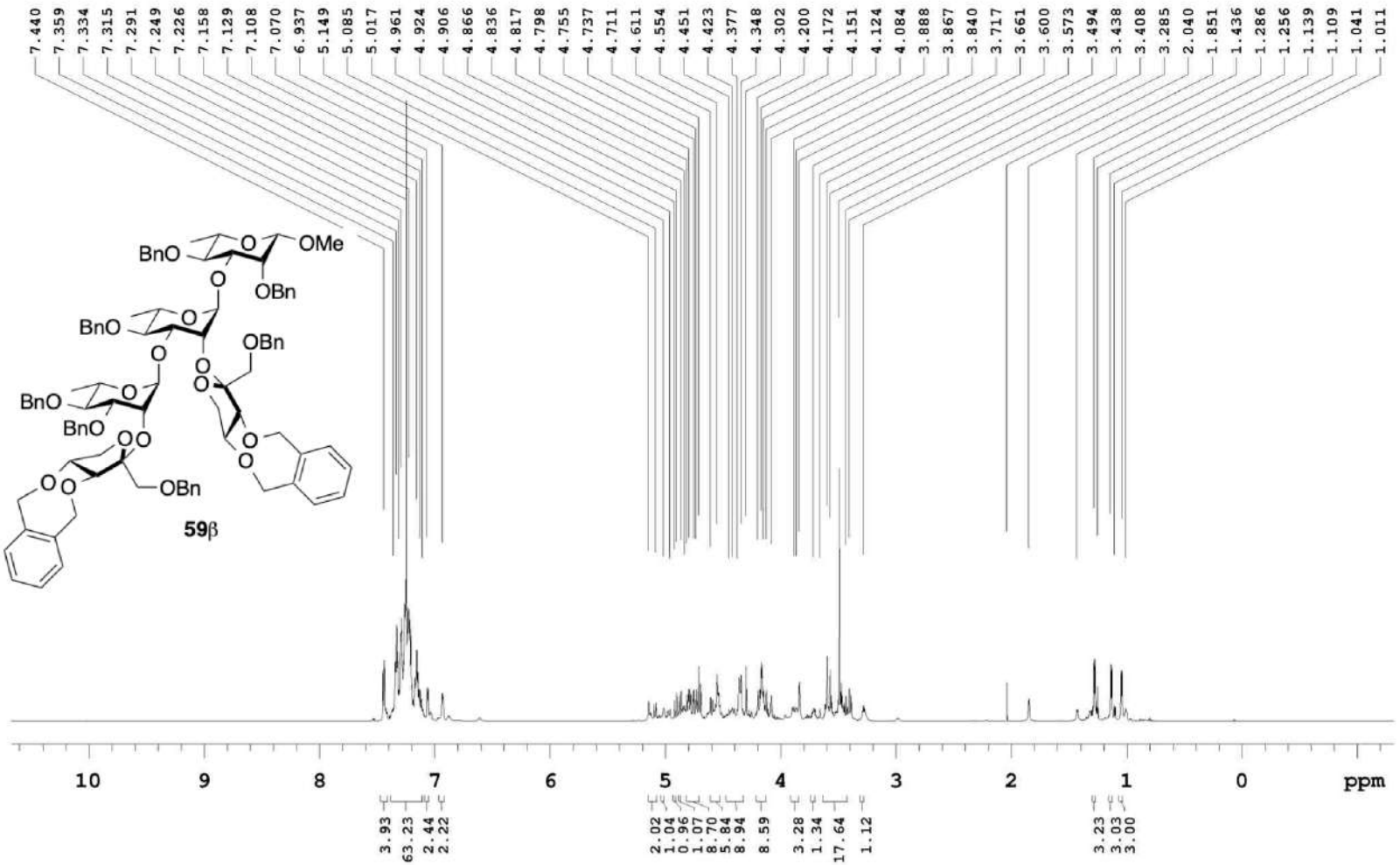
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.28.v7_Ball-XYl-108-2_lcc50_14.28_H1_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: v700, Feb 28 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 48076.9
Digital Res.(Hz/pt): 0.37
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 153.92
Relaxation Delay(s): 1
Completed Scans 256
Bo-Shun, Ball-XYl-108-2
175.975 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe
138.904
138.543
138.283
138.149
128.866
128.756
128.612
128.414
128.293
128.208
128.131
128.103
127.924
127.891
127.739
127.599
102.800
101.645
101.260
81.571
81.014
80.776
80.647
79.084
78.452
77.410
77.228
77.045
75.717
75.369
75.346
74.614
72.186
71.600
71.477
71.410
68.385
68.304
57.335
18.236
18.115
18.042
BnO
O
OMe
OBn
BnO
O
OH
BnO
O
HO
OH
58
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.02/2017.02.28.v7_Ball-XYl-108-2_lcc50_14.29_C13_1D

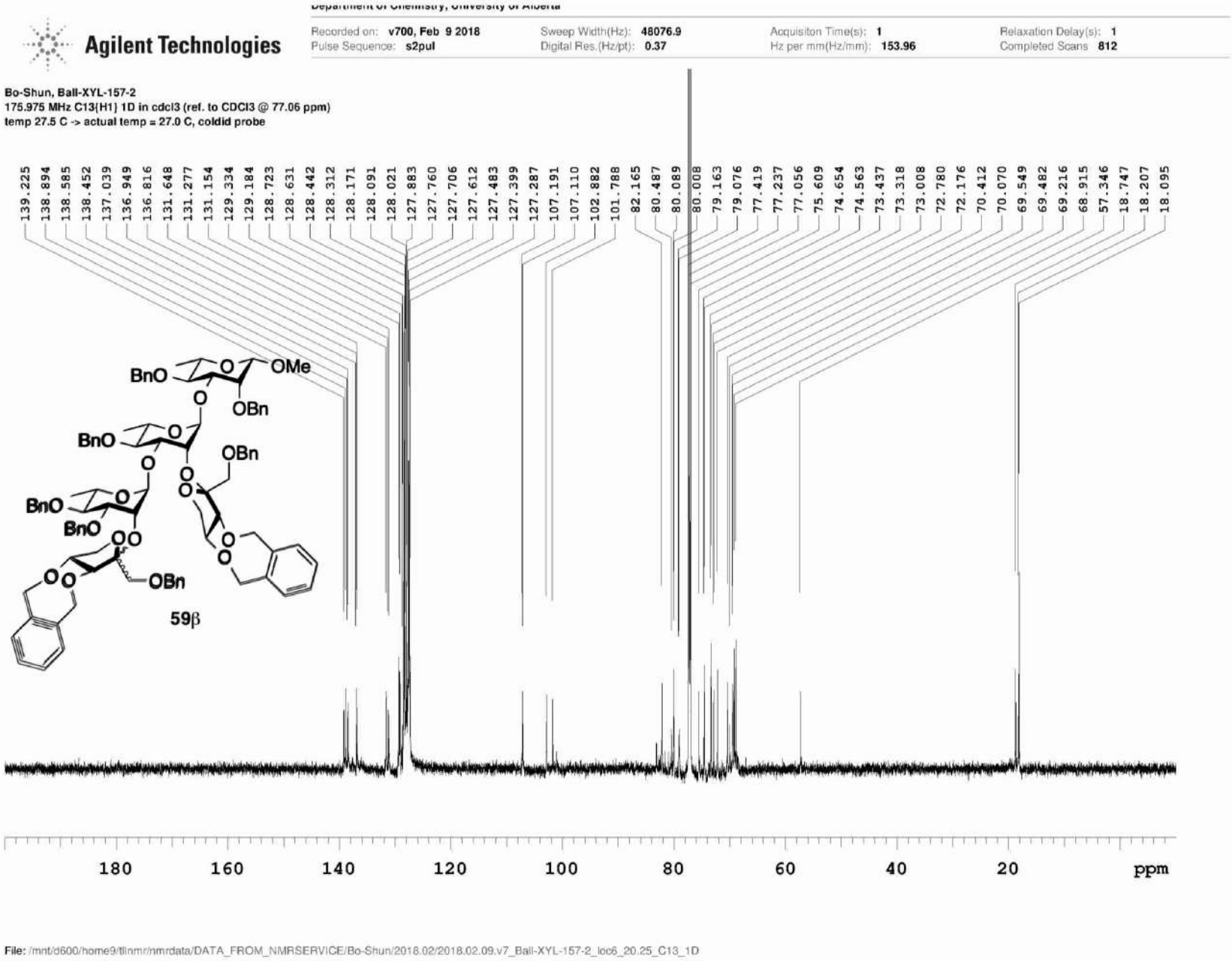
Agilent Technologies

Recorded on: v700, Feb 9 2018	Sweep Width(Hz): 8389.26	Acquisiton Time(s): 5	Relaxation Delay(s): 0.1
Pulse Sequence: PRESAT	Digital Res.(Hz/pt): 0.13	Hz per mm(Hz/mm): 34.95	Completed Scans 32

Bo-Shun, Ball-XYL-157-2
699.762 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2018.02/2018.02.09.v7_Ball-XYL-157-2_loc6_20.22_H1_1D

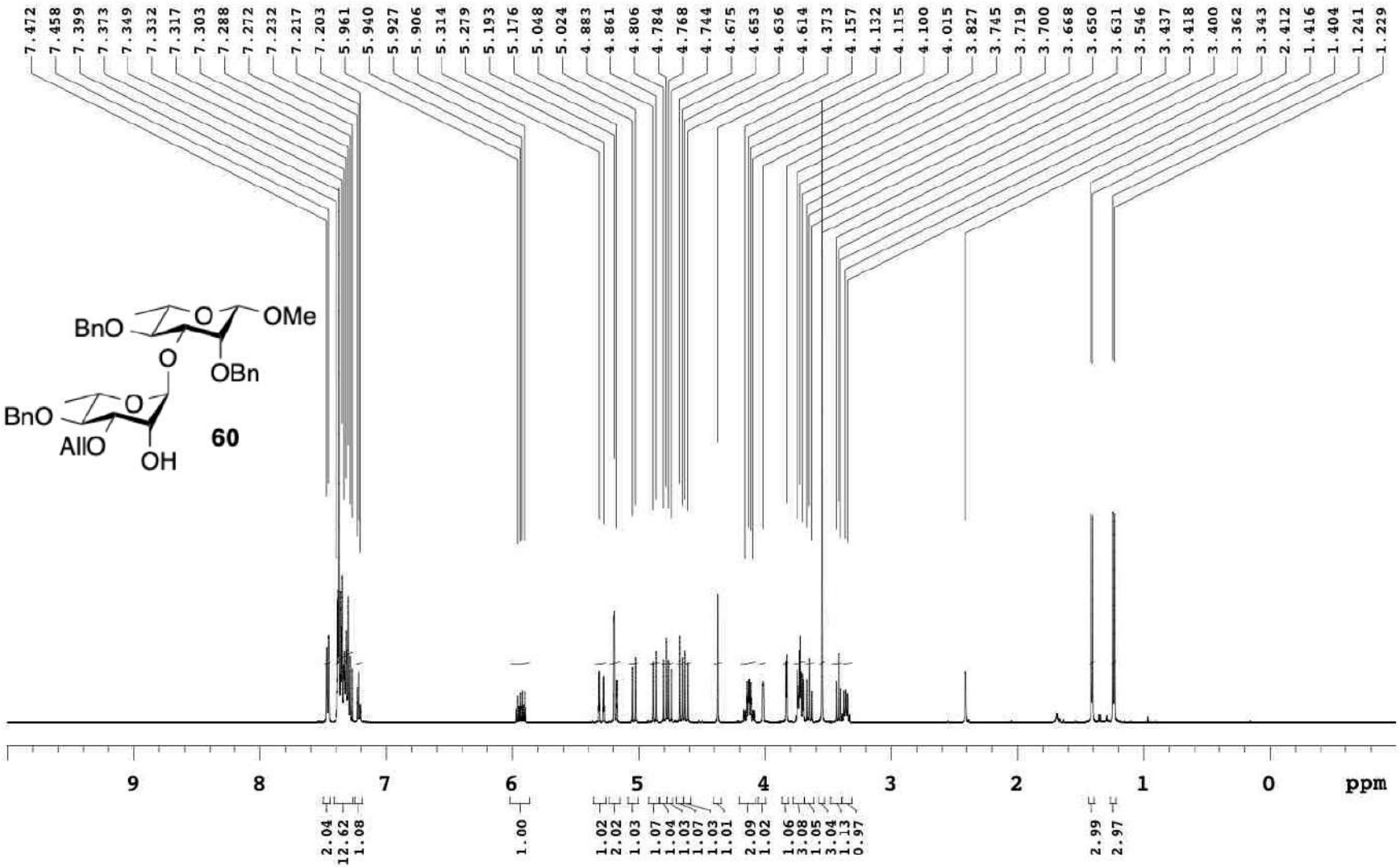

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: v700, Feb 9 2018
Pulse Sequence: s2pul
Sweep Width(Hz): 48076.9
Digital Res.(Hz/pt): 0.37
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 153.96
Relaxation Delay(s): 1
Completed Scans 812
Bo-Shun, Ball-XYL-157-2
175.975 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe
139.225
138.894
138.585
138.452
137.039
136.949
136.816
131.648
131.277
131.154
129.334
129.184
128.723
128.631
128.442
128.312
128.171
128.091
128.021
127.883
127.760
127.706
127.612
127.483
127.399
127.287
107.191
107.110
102.882
101.788
82.165
80.487
80.089
80.008
79.163
79.076
77.419
77.237
77.056
75.609
74.654
74.563
73.437
73.318
73.008
72.780
72.176
70.412
70.070
69.549
69.482
69.216
68.915
57.346
18.747
18.207
18.095
BnO
OMe
OBn
BnO
OBn
BnO
BnO
OBn
59β
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2018.02/2018.02.09.v7_Ball-XYL-157-2_loc6_20.25_C13_1D

Department of Chemistry, University of Alberta

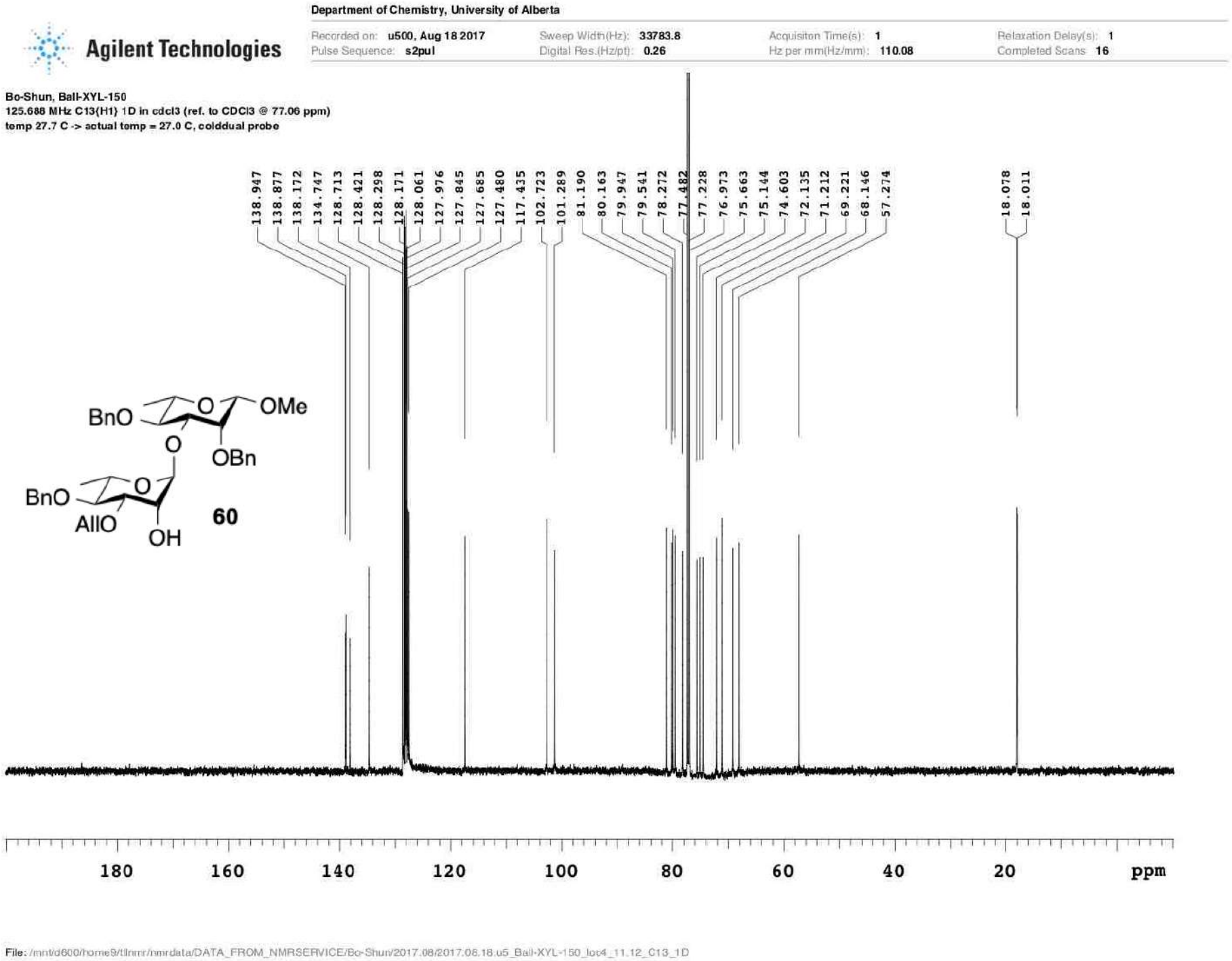
Agilent Technologies

Recorded on:	u500, Aug 18 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.91	Completed Scans	8

Bo-Shun, Ball-XYL-150
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.08/2017.08.18.u5_Ball-XYL-150_loc4_11.11_H1_1D

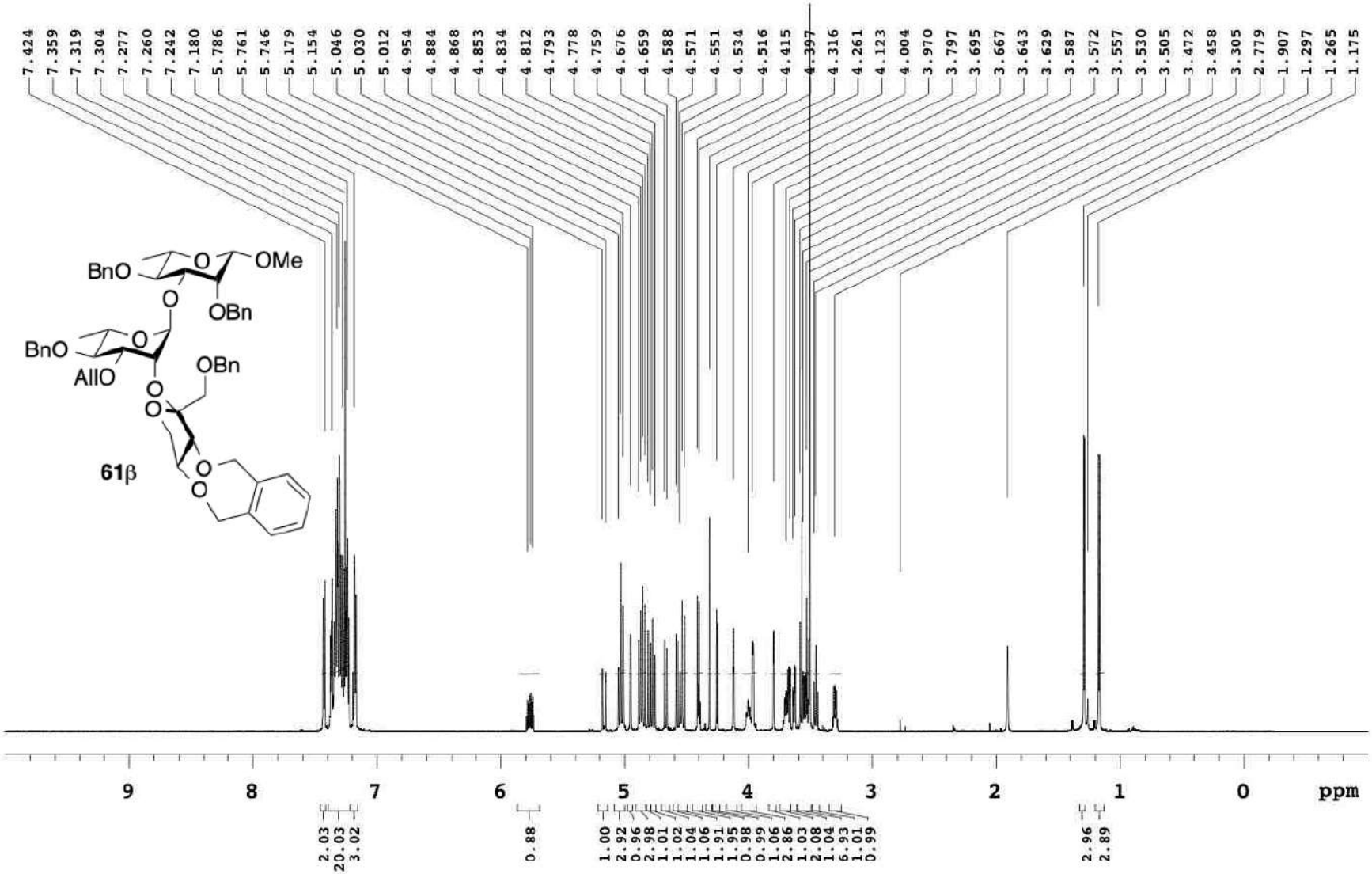

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Aug 18 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 110.08
Relaxation Delay(s): 1
Completed Scans 16
Bo-Shun, Ball-XYL-150
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
138.947
138.877
138.172
134.747
128.713
128.421
128.298
128.171
128.061
127.976
127.845
127.685
127.480
117.435
102.723
101.289
81.190
80.163
79.947
79.541
78.272
77.482
77.228
76.973
75.663
75.144
74.603
72.135
71.212
69.221
68.146
57.274
18.078
18.011
BnO
O
OMe
O
OBn
BnO
O
AllO
OH
60
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.08/2017.08.18.u5_Ball-XYL-150_loc4_11.12_C13_1D

Department of Chemistry, University of Alberta

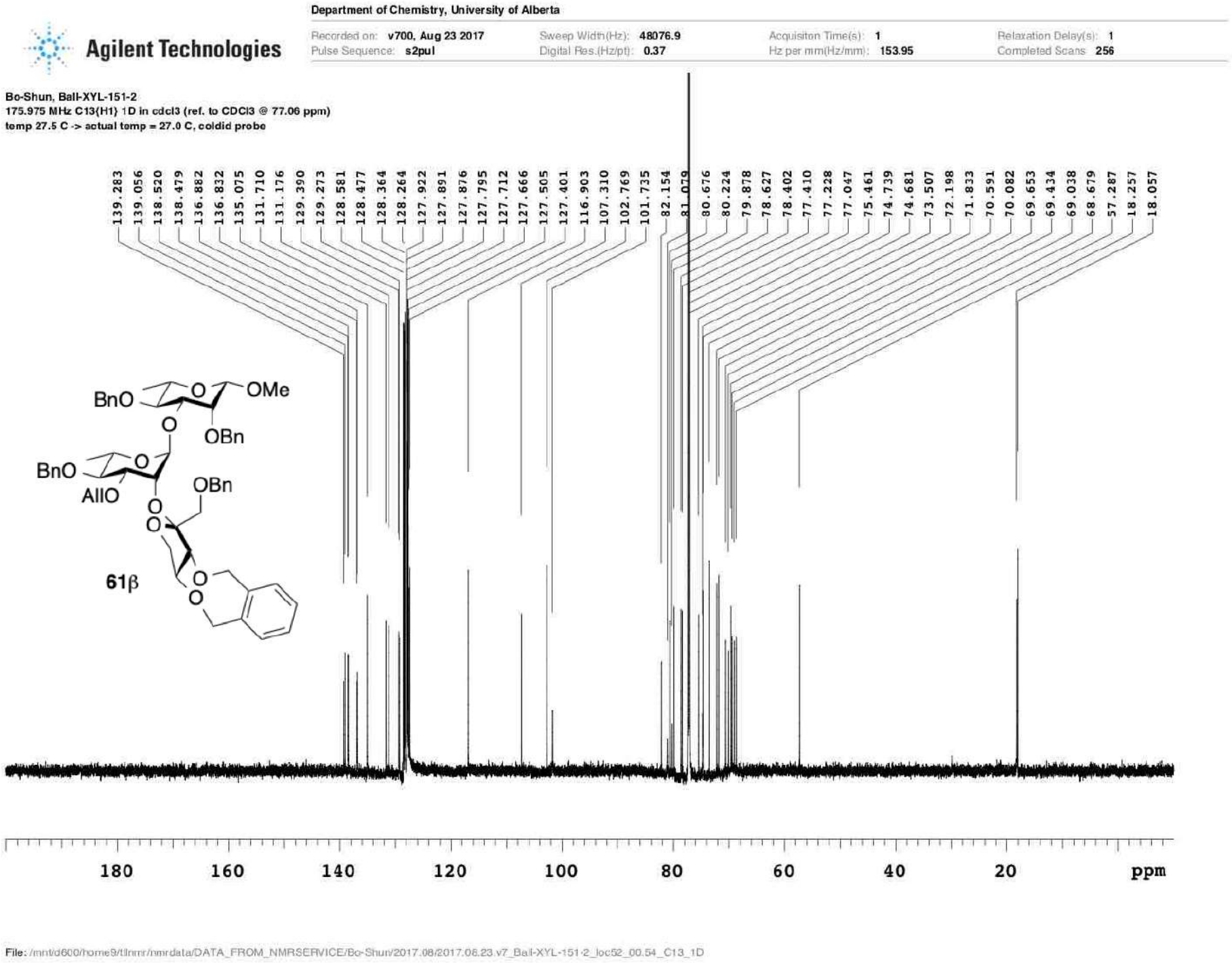
Agilent Technologies

Recorded on:	v700, Aug 23 2017	Sweep Width(Hz):	8389.26	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.13	Hz per mm(Hz/mm):	32.07	Completed Scans	8

Bo-Shun, Ball-XYL-151-2
699.762 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.08/2017.08.23.v7_Ball-XYL-151-2_loc52_00.53_H1_1D

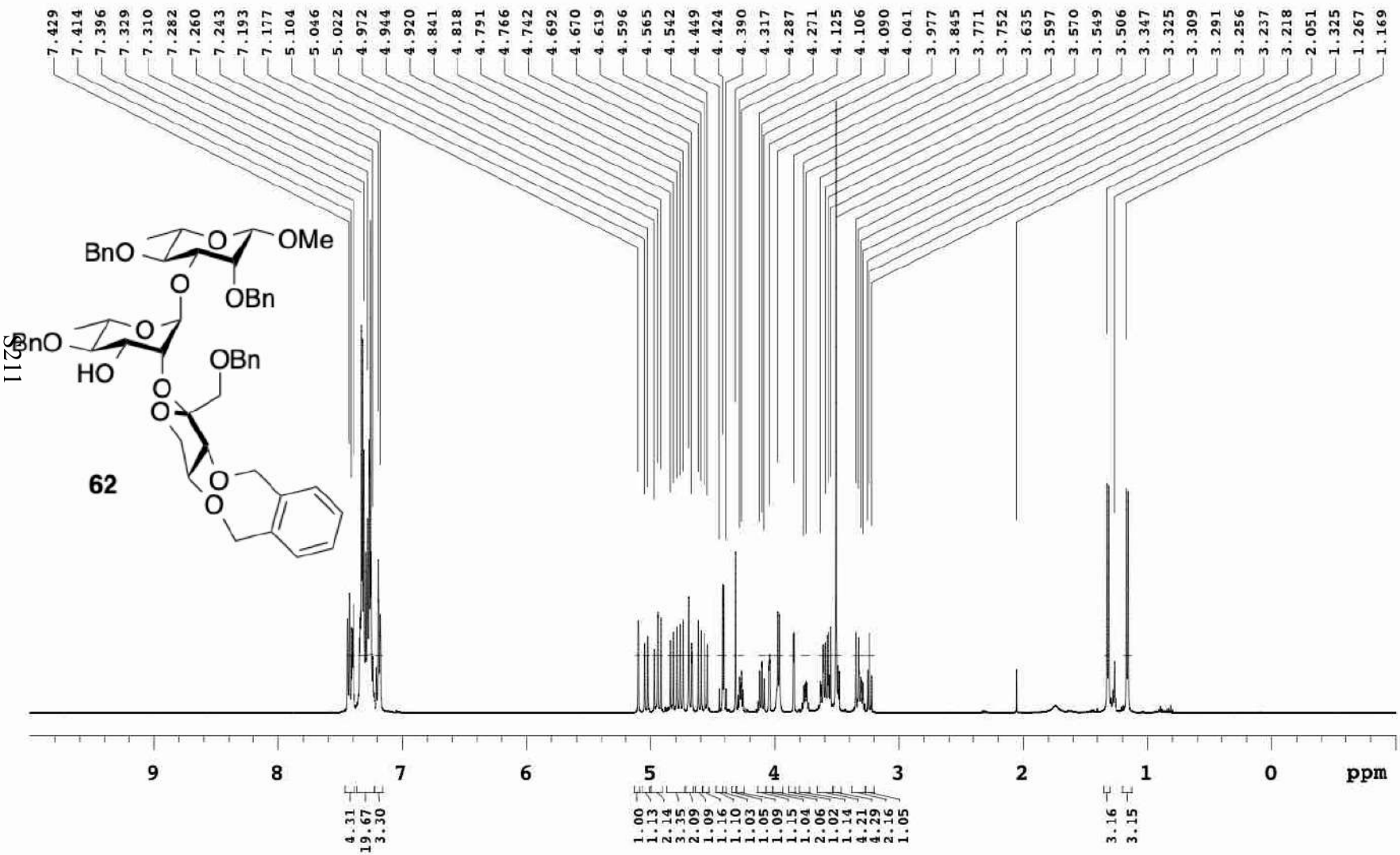

Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: v700, Aug 23 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 48076.9
Digital Res.(Hz/pt): 0.37
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 153.95
Relaxation Delay(s): 1
Completed Scans 256
Bo-Shun, Ball-XYL-151-2
175.975 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe
139.283
139.056
138.520
138.479
136.882
136.832
135.075
131.710
131.176
129.390
129.273
128.581
128.477
128.364
128.264
127.922
127.891
127.876
127.795
127.712
127.666
127.505
127.401
116.903
107.310
102.769
101.735
82.154
81.029
80.676
80.224
79.878
78.627
78.402
77.410
77.228
77.047
75.461
74.739
74.681
73.507
72.198
71.833
70.591
70.082
69.653
69.434
69.038
68.679
57.287
18.257
18.057
BnO
OMe
OBn
BnO
AllO
OBn
61β
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.08/2017.08.23.v7_Ball-XYL-151-2_loc52_00.54_C13_1D

Department of Chemistry, University of Alberta

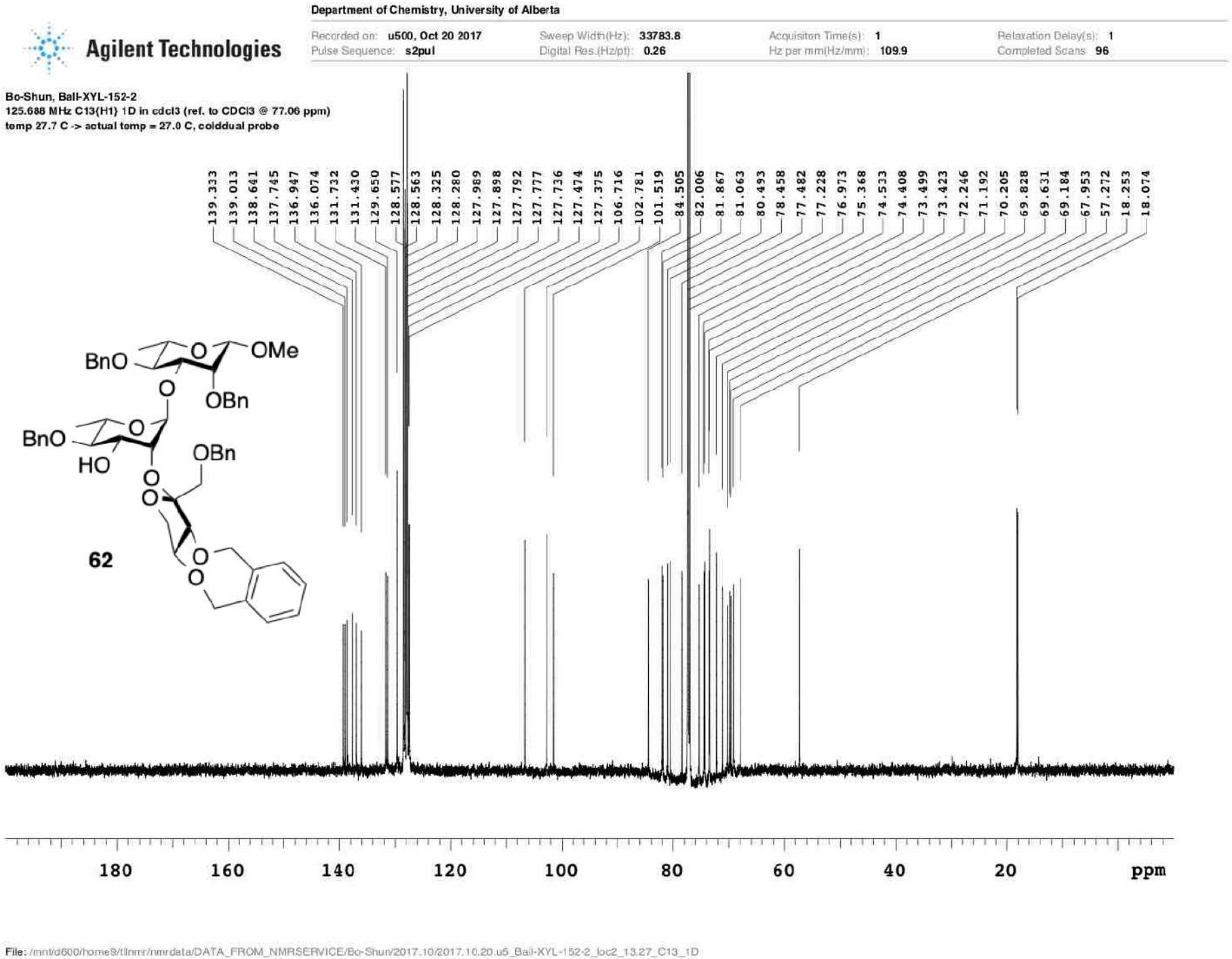
Agilent Technologies

Recorded on:	u500, Oct 20 2017	Sweep Width(Hz):	6009.62	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.09	Hz per mm(Hz/mm):	22.91	Completed Scans	8

Bo-Shun, Ball-XYL-152-2
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.10/2017.10.20.u5_Ball-XYL-152-2_loc2_13.26_H1_1D


Department of Chemistry, University of Alberta
Agilent Technologies
Recorded on: u500, Oct 20 2017
Pulse Sequence: s2pul
Sweep Width(Hz): 33783.8
Digital Res.(Hz/pt): 0.26
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 109.9
Relaxation Delay(s): 1
Completed Scans 96
Bo-Shun, Ball-XYL-152-2
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe
139.333
139.013
138.641
137.745
136.947
136.074
131.732
131.430
129.650
128.577
128.563
128.325
128.280
127.989
127.898
127.792
127.777
127.736
127.474
127.375
106.716
102.781
101.519
84.505
82.006
81.867
81.063
80.493
78.458
77.482
77.228
76.973
75.368
74.533
74.408
73.499
73.423
72.246
71.192
70.205
69.828
69.631
69.184
67.953
57.272
18.253
18.074
BnO
O
OMe
OBn
BnO
O
HO
OBn
O
O
O
O
62
180
160
140
120
100
80
60
40
20
ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.10/2017.10.20.u5_Ball-XYL-152-2_loc2_13.27_C13_1D

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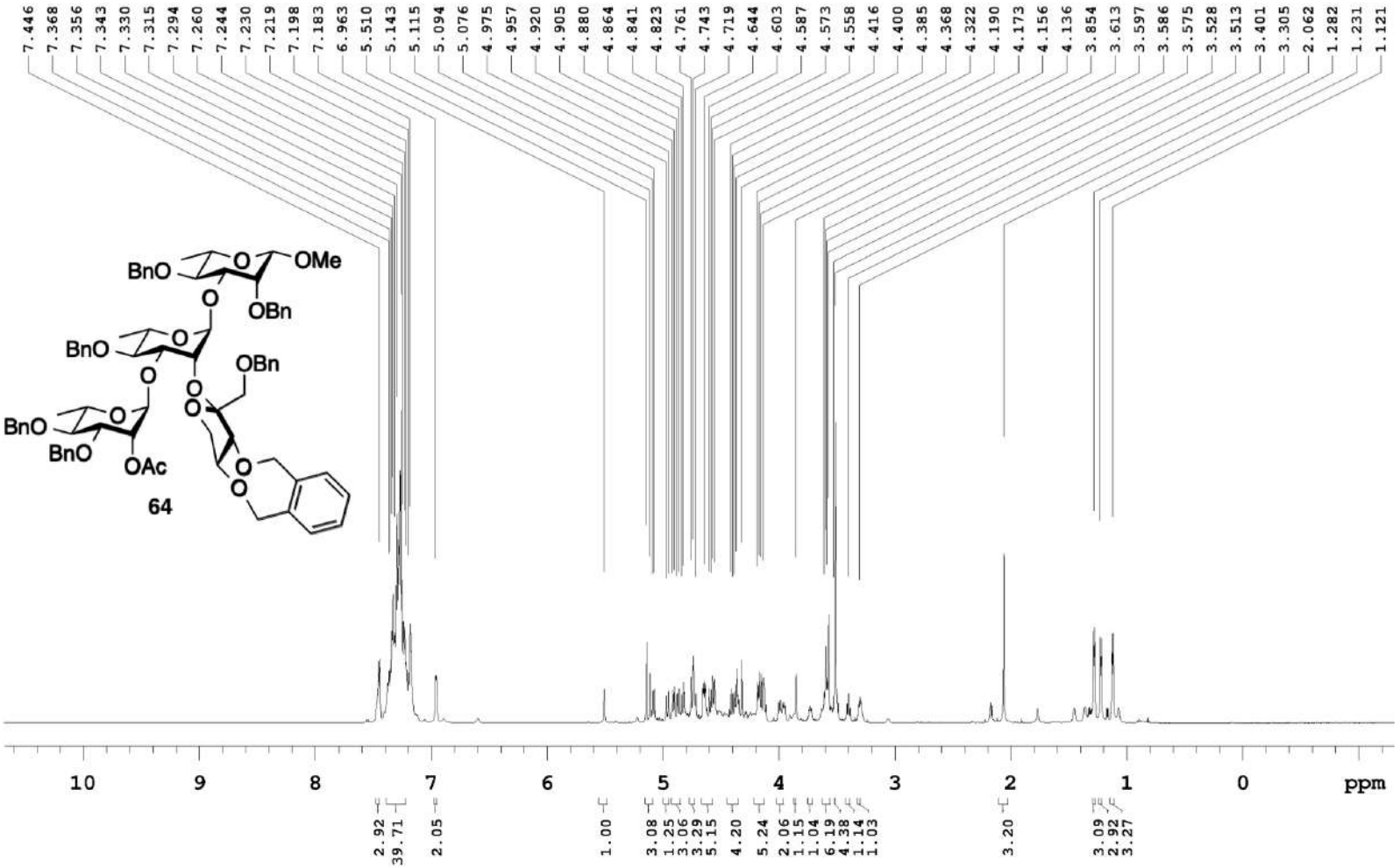
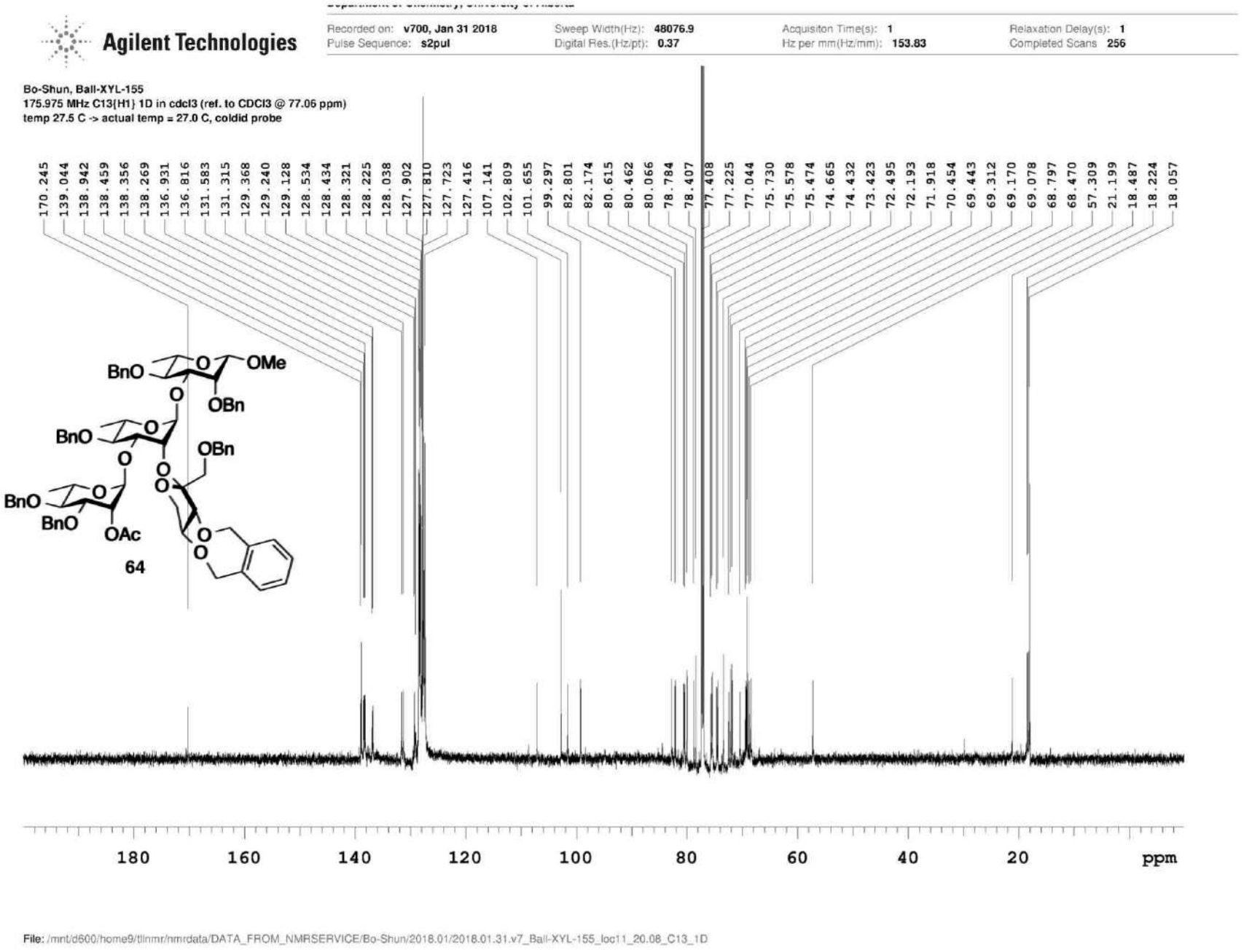
Recorded on:	v700, Jan 31 2018	Sweep Width(Hz):	8389.26	Acquisiton Time(s):	5	Relaxation Delay(s):	0.1
Pulse Sequence:	PRESAT	Digital Res.(Hz/pt):	0.13	Hz per mm(Hz/mm):	34.95	Completed Scans	8

Bo-Shun, Ball-XYL-155
699.762 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe



File: /mnt/d600/home9/tlinmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2018.01/2018.01.31.v7_Ball-XYL-155_loc11_20.07_H1_1D


Agilent Technologies
Recorded on: v700, Jan 31 2018
Pulse Sequence: s2pul
Sweep Width(Hz): 48076.9
Digital Res.(Hz/pt): 0.37
Acquisiton Time(s): 1
Hz per mm(Hz/mm): 153.83
Relaxation Delay(s): 1
Completed Scans 256
Bo-Shun, Ball-XYL-155
175.975 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.5 C -> actual temp = 27.0 C, coldid probe
170.245 139.044 138.942 138.459 138.356 138.269 136.931 136.816 131.583 131.315 129.368 129.240 129.128 128.534 128.434 128.321 128.225 128.038 127.902 127.810 127.723 127.416 107.141 102.809 101.655 99.297 82.801 82.174 80.615 80.462 80.066 78.784 78.407 77.408 77.225 77.044 75.730 75.578 75.474 74.665 74.432 73.423 72.495 72.193 71.918 70.454 69.443 69.312 69.170 69.078 68.797 68.470 57.309 21.199 18.487 18.224 18.057
BnO
OMe
OBn
BnO
OBn
BnO
BnO
OAc
64
180 160 140 120 100 80 60 40 20 ppm
File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2018.01/2018.01.31.v7_Ball-XYL-155_loc11_20.08_C13_1D

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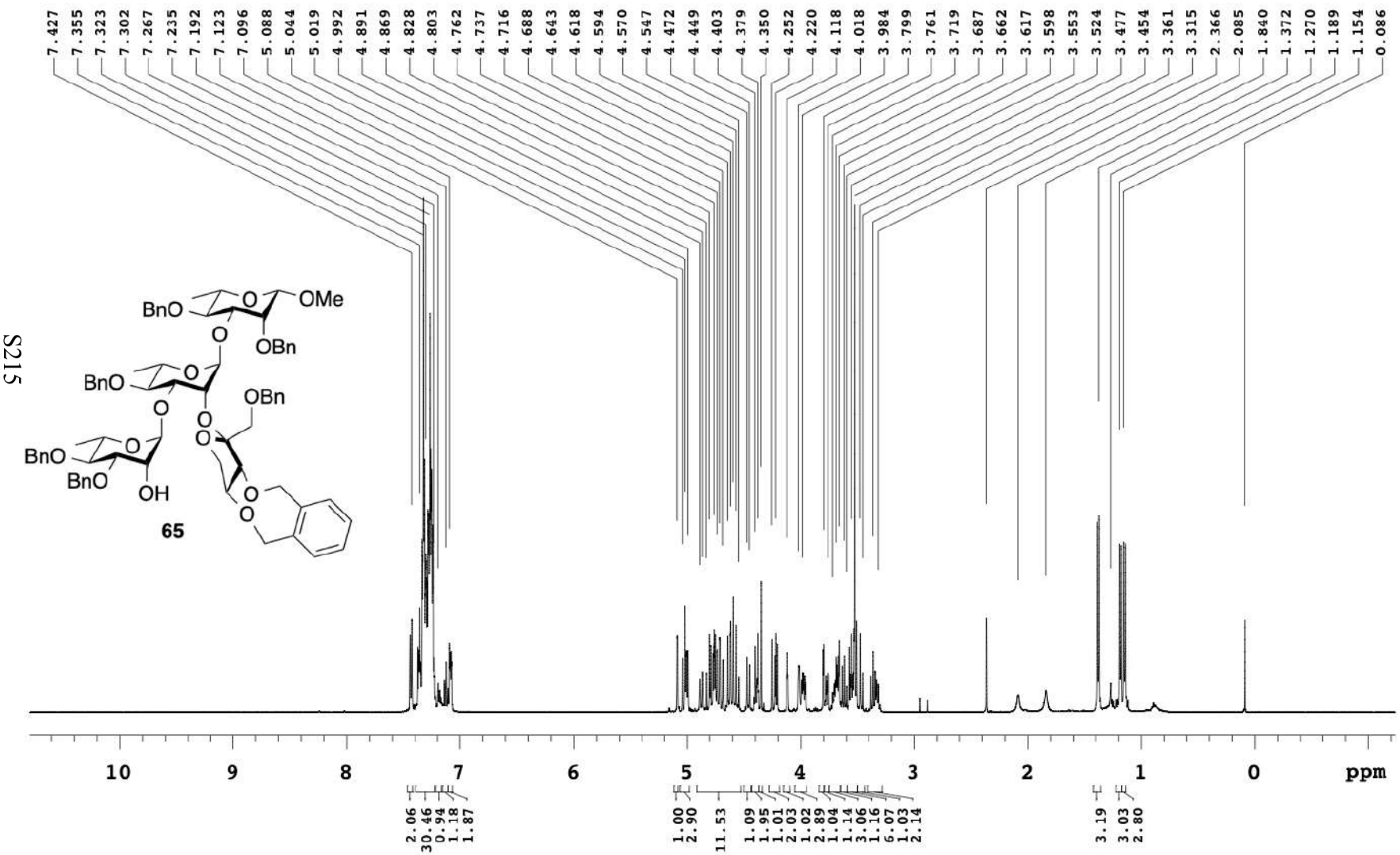
Recorded on: u500, Jun 3 2017	Sweep Width(Hz): 6009.62	Acquisiton Time(s): 5	Relaxation Delay(s): 0.1
Pulse Sequence: PRESAT	Digital Res.(Hz/pt): 0.09	Hz per mm(Hz/mm): 25.04	Completed Scans 8

Bo-Shun, Ball-XYL-135
499.797 MHz H1 1D in cdcl3 (ref. to CDCl3 @ 7.26 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.06/2017.06.03.u5_Ball-XYL-135_loc9_16.33_H1_1D

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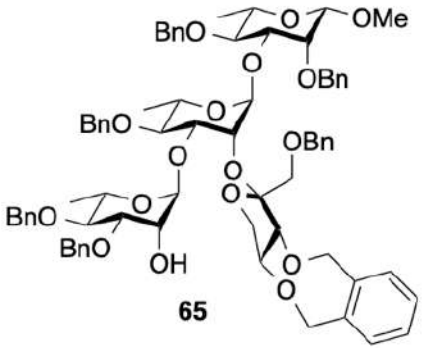
Recorded on:	u500, Jun 3 2017	Sweep Width(Hz):	33783.8	Acquisiton Time(s):	1	Relaxation Delay(s):	1
Pulse Sequence:	s2pul	Digital Res.(Hz/pt):	0.26	Hz per mm(Hz/mm):	104.68	Completed Scans	176

Bo-Shun, Ball-XYL-135
125.688 MHz C13{H1} 1D in cdcl3 (ref. to CDCl3 @ 77.06 ppm)
temp 27.7 C -> actual temp = 27.0 C, colddual probe

138.909 138.659 138.569 138.413 138.124 136.904 136.721 131.678 131.214 129.407 129.309 129.241 128.753 128.573 128.499 128.452 128.380 128.279 128.169 128.107 128.041 127.867 127.787 127.627 127.551 107.265 102.850 101.715 101.650 82.141 81.028 80.915 80.269 80.012 78.630 78.435 77.481 77.227 76.973 75.767 75.281 75.100 74.553 73.332 72.785 72.170 71.581 70.523 70.100 69.507 69.421 68.923 68.273 57.323 18.363 18.119 17.986



65

180 160 140 120 100 80 60 40 20 ppm

File: /mnt/d600/home9/tlnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2017.06/2017.06.03.u5_Ball-XYL-135_loc9_16.34_C13_1D

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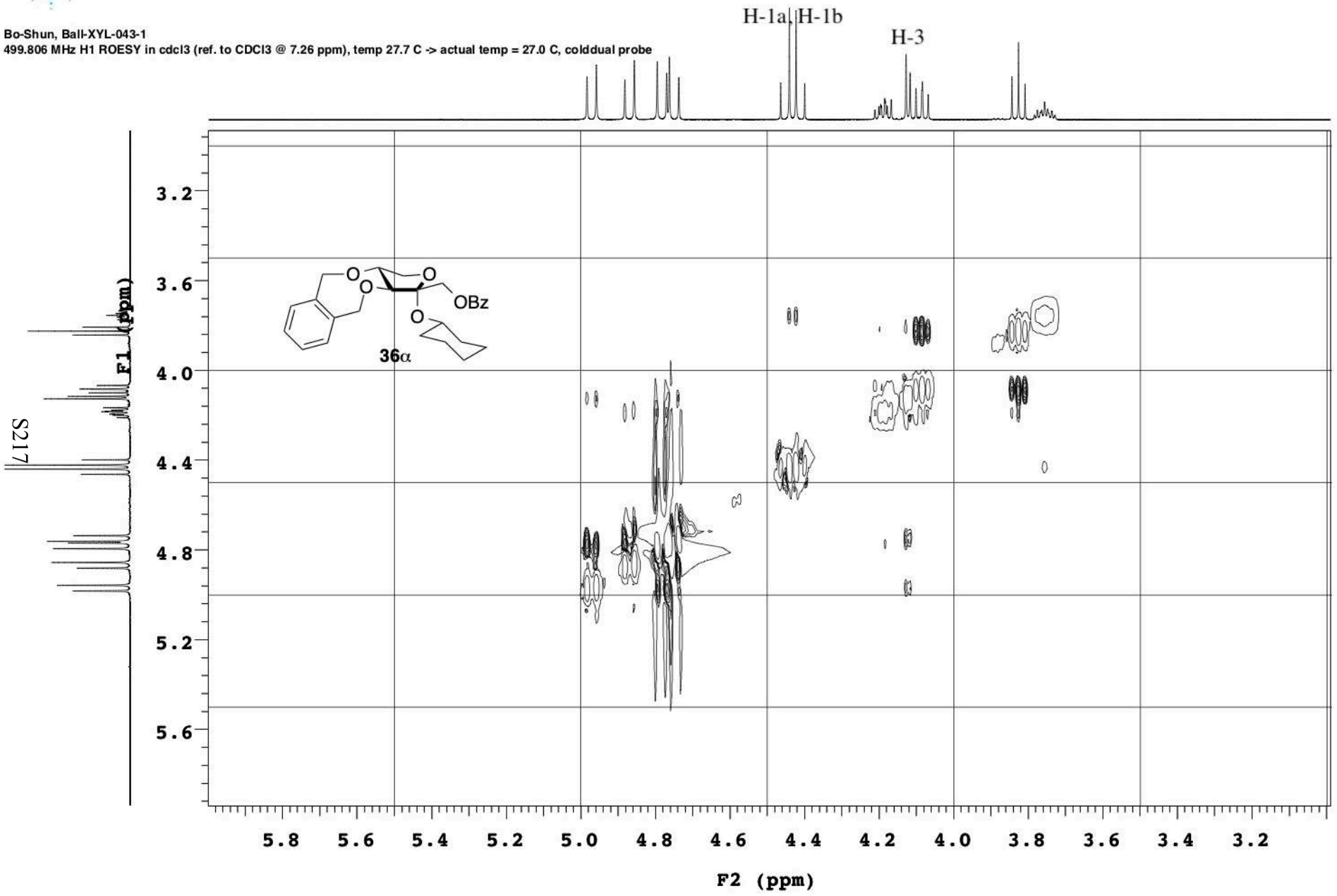
Recorded on: u500, Jun 24 2016 | Sweep Width F2lF1(Hz): 6009.62 l 6009.62 | Acquisiton Time(s): 1 | Relaxation Delay(s): 1
Pulse Sequence: ROESY | Digital Res. F2lF1(Hz/pt): 1.47 l 11.74 | Hz per mm F2lF1(Hz/mm): 6.41 l 10.39 | No. of Scans|Increments 8 l 170

Bo-Shun, Ball-XYL-043-1
499.806 MHz H1 ROESY in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe

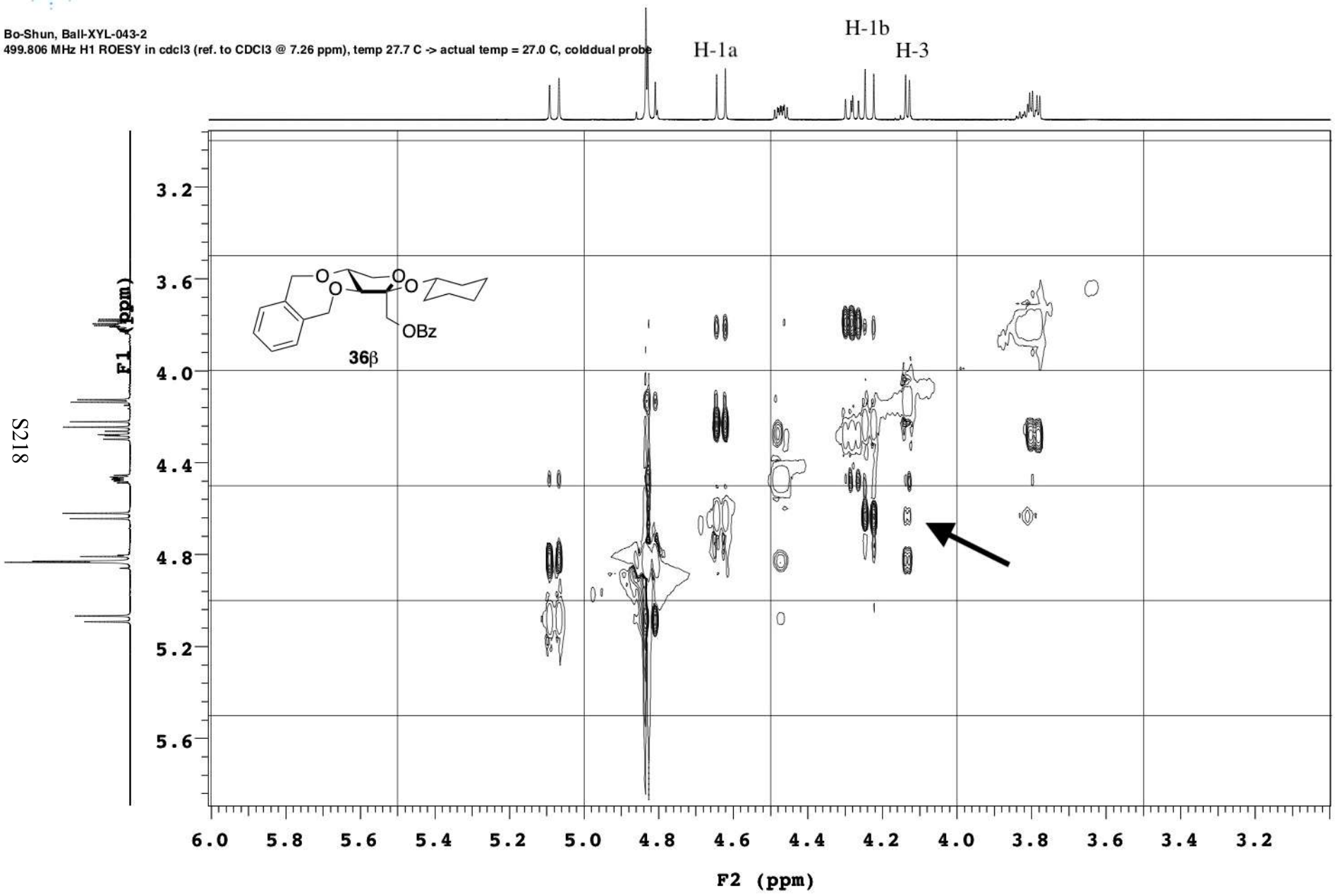


File: /mnt/d600/home9/tllnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.06/2016.06.24.u5_Ball-XYL-043-1_loc5_21.02_H1_ROESY

Agilent Technologies

Recorded on: u500, Jun 24 2016 | Sweep Width F2|F1(Hz): 6009.62 | 6009.62 | Acquisiton Time(s): 1 | Relaxation Delay(s): 1
Pulse Sequence: ROESY | Digital Res. F2|F1(Hz/pt): 1.47 | 11.74 | Hz per mm F2|F1(Hz/mm): 6.41 | 10.15 | No. of Scans|Increments 8 | 170

Bo-Shun, Ball-XYL-043-2
499.806 MHz H1 ROESY in cdcl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.7 C -> actual temp = 27.0 C, colddual probe



File: /mnt/d600/home9/tllnmr/nmrdata/DATA_FROM_NMRSERVICE/Bo-Shun/2016.06/2016.06.24.u5_Ball-XYL-043-2_loc6_23.54_H1_ROESY