Supporting Information

IPy_2BF_4-Mediated Transformation of n-Pentenyl Glycosides to Glycosyl Fluorides: A New Pair of Semi-Orthogonal Glycosyl Donors

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1. Materials and Methods.

^{1}H NMR spectra were recorded at 400 and 300 MHz, ^{13}C NMR spectra were recorded at 75 MHz, and chemical shifts are reported relative to internal Me_4Si. Optical rotations were determined for solutions in chloroform. Column chromatography was performed on silica gel (230-400 mesh). TLC was conducted in precoated Kiesel gel 60 F254 (Merck). Detection was first by UV light (254 nm) then charring with a 1/20/4 solution of sulfuric acid/acetic acid/H_2O. All solvents were purified by standard techniques. Reactions requiring anhydrous conditions were performed under argon. Anhydrous magnesium sulfate was used for drying solutions. Starting *n*-pentenyl glycosides **1-7** and *n*-pentenylorthoesters **8-9** were prepared according to described procedures. [1,2]

2. General procedure for IPy_2BF_4-mediated transformation of n-pentenyl glycosides or n-pentenyl orthoesters to glycosyl fluorides.

[1] (a) Andrews, C. W.; Rodebaugh, R.; Fraser-Reid, B. *J. Org. Chem*. **1996**, *61*, 5280; (b) Roberts, C.; Madsen, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1995**, *117*, 1546.
[2] Mach, M.; Schlueter, U.; Mathew, F; Fraser-Reid B.; Hazen, K. C. *Tetrahedron* **2002**, *58*, 7345.

A solution of bis(pyridine)iodonium(I) tetrafluoroborate (IPy_2BF_4) (44.6 mg, 0.12 mmol) in dry CH_2Cl_2 (1 mL) under argon and cooled at -40ºC was treated with tetrafluoroboric acid (13μL, 0.12 mmol). After 5 min, a solution of the *n*-pentenyl glycoside or orthoester (0.10 mmol) dissolved in dry CH_2Cl_2 (2 mL) was added. When all the starting material disappeared, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and washed with 10% aqueous sodium thiosulphate containing sodium bicarbonate, saturated sodium bicarbonate and water. The organic layer was then dried and concentrated and the residue was purified by flash chromatography.

3. Experimental details of the preparation and spectroscopic characterization data of compounds.

2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl fluoride **10**.

This compound was prepared according to the general procedure from *n*-pentenyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose **1** (61 mg, 0.1 mmol). Silica gel chromatography (hexane/Ethyl acetate 9:1) provided pure **10**[3] (45 mg, 83%) $[\alpha]_D$= + 10.7º ($CHCl_3$, c 0.53), ^{1}H-NMR (300 MHz) δ 7.15-7.31 (m, 20H), 5.56 (dd, 1H, *J* = 53.2, 2.6 Hz), 4.98-4.45 (m, 8H), 3.99 (t, 1H, *J* = 9.6 Hz), 3,94 (m, 1H) 3,79 (m, 1H), 3.65 (m, 1H) 3.57 (ddd, 1H, *J* = 25.7, 9.6, 2.6 Hz) ; API-ES positive: 565.2 $(M+Na)^+$; Anal. Calcd for $C_{34}H_{35}O_5F$ (542.65): C, 75.26; H, 6.50. Found: C, 75.3; H, 6.64.

2,3,4,6-tetra-O-methyl-α-D-glucopyranosyl fluoride **11**.

This compound was prepared according to the general procedure from *n*-pentenyl 2,3,4,6-tetra-*O*-methyl- α-D-glucopyranose **2** (60.8 mg, 0.2 mmol). Silica gel chromatography (hexane/Ethyl acetate 7:3) provided pure **11**[3] (50 mg, quant). ^{1}H-NMR (300 MHz) δ 5.66 (dd, 1H, *J* = 53.3, 2.6 Hz), 3.80-3.75 (m, 1H), 3.64 (s, 3H, OMe), 3.62-3.38 (m, 3H), 3.54 (s, 3H, OMe), 3.53 (s, 3H, OMe), 3.40 (s, 3H, OMe), 3.28 (t, 1H, *J* = 9.4 Hz), 3.19 (ddd, 1H, *J* = 25.6, 9.4, 2.6 Hz); ^{13}C-NMR (75MHz) δ 104.9 (d, *J* = 224.8 Hz), 82.7, 81.2 (d, *J* = 24.6 Hz), 78.2, 72.3 (*J* = 4.0 Hz), 70.2, 60.9, 60.5, 59.1 (x 2); API-ES positive: 477.3 $(2M+H)^+$ Anal. Calcd for $C_{10}H_{19}O_5F$ (238.12): C, 50.41; H, 8.04. Found: C, 50.30; H, 8.28.

[3] Thiem, J.; Wiesner, M. *Synthesis* **1988**, 124.

2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl fluoride **12**.

This compound was prepared according to the general procedure from *n*-pentenyl 2,3,4,6-tetra-*O*-methyl- α-D-mannopyranose **3** (60.8 mg, 0.1 mmol). Silica gel chromatography (hexane/Ethyl acetate 9:1) provided pure **12**[4] (51 mg, 94%). $[\alpha]_D$= +25.9º ($CHCl_3$, c 0.56); ^{1}H-NMR (300 MHz) δ 7.35–7.18 (20H, m), 5.60 (1H, d, *J*= 50.6 Hz), 4.88 (1H, d, *J*= 10.8 Hz), 4.81 (1H, d, *J*= 12.3 Hz), 4.70–4.63 (4H, m), 4.56–4.53 (2H, m), 4.08 (t, 1H, *J*= 9.7 Hz), 3.93–3.88 (3H, m), 3.79 (dd,1H, *J*= 11.0, 4.5 Hz), 3.72 (d,1H, *J* = 10.9 Hz); API-ES positive: 565.3 $(M+Na)^+$; Anal. Calcd for $C_{34}H_{35}FO_5$: C, 75.26; H, 6.50. Found: C, 75.16; H, 6.45.

2,3,4,6-tetra-O-methyl-α-D-mannopyranosyl fluoride **13**.

This compound was prepared according to the general procedure from *n*-pentenyl 2,3,4,6-tetra-*O*-methyl- α-D-mannopyranose **4** (60.8 mg, 0.2 mmol). Silica gel chromatography (hexane/Ethyl acetate 7:3) provided **13** (45 mg, 94%). $[\alpha]_D$= +28.7º ($CHCl_3$, c 1.5.); ^{1}H-NMR (300MHz) δ 5.65 (dd, 1H, *J* = 1.6, 50.2 Hz), 3.76-3.58 (m, 6H), 3.51(s, 3H, OMe), 3.50 (s, 3H, OMe), 3.49 (s, 3H, OMe), 3.39 (s, 3H, OMe); ^{13}C-NMR (75MHz) δ 105.5 (d, *J* = 220.8 Hz), 80.4 (d, *J* = 2.0 Hz), 75.8 (d, *J* = 34.6 Hz), 75.4, 73.6 (d, *J* = 2.5Hz), 60.6, 59.5, 59.2, 58.0; API-ES positive: 477.3 $(2M+H)^+$, 261.1 $(M+Na)^+$; Anal. Calcd for $C_{10}H_{19}O_5F$ (238.12): C, 50.41; H, 8.04. Found: C, 50.17; H, 7.96.

2-O-benzoyl-3,4,6-O-tri-O-benzyl-α-D-mannopyranosyl fluoride **14**.

This compound was prepared according to the general procedure from *n*-pentenyl 2-*O*-benzoyl-3,4,6-*O*-tri-O-benzyl-α-D-mannopyranose **5** (44.6 mg, 0.12 mmol). Silica gel chromatography (hexane/Ethyl acetate 9:1) provided **14** (50 mg, 90%); ^{1}H-NMR (300MHz) δ 8.08-8.06 (m, 2 H), 8.05 (m, 1 H), 7.56-7.19 (m, 17 H), 5.75 (dd, 1H, *J* = 49.3, 1.7 Hz), 5.74 (t, 1H, *J* = 2.4 Hz), 4.89 (d, 1H, *J* = 10.5 Hz), 4.81 (d, 1H, *J* = 11.1 Hz), 4.73 (d, 1H, *J* = 12.0 Hz), 4.61 (d, 1H, *J* = 11.4 Hz), 4.57 (d, 1H, *J* = 10.8 Hz), 4.55 (d, 1H, *J* = 12.0 Hz), 4.21-3.96 (m, 3H), 3.91 (dd, 1H, *J* = 11.2, 3.6 Hz), 3.80 (dd, 1H, *J* = 11.2, 1.5 Hz); ^{13}C-

[4] Baeschlin, D. K.; Green, L. G.; Hahn, M. G.; Hinzen, B.; Ince, S. J.; Ley, S. V.; *Tetrahedron Asymmetry*, **2000**, *11*, 173.

NMR (75MHz) δ 165.3, 138.1, 138.0, 137.5, 133.4, 129.9 (x 2), 128.5 (x 2), 128.4 (x 5), 128.3 (x 3), 128.0 (x 2), 127.9 (x 2), 127.8, 127.7, 127.5 (x 2), 105.5 (d, *J* = 219.3 Hz), 77.2, 75.3, 73.9 (d, *J* = 2.5 Hz), 73.4, 73.2, 71.8, 68.3, 67.2 (d, *J* = 40.0 Hz); API-ES positive: 579 $(M+Na)^+$; Anal. Calcd for $C_{34}H_{33}O_6F$ (556.23): C, 73.36; H, 5.98. Found: C, 73.54; H, 5.86.

In a different experiment **14** was prepared from n-pentenyl orthoester **9** (44.6 mg, 0.12 mmol) according to the general procedure. Silica gel chromatography (hexane/Ethyl acetate 9:1) provided **14** (53 mg, 95%).

6-O-tertbutyldiphenylsilyl-2,3,4-O-tri-O-methyl-α-D-mannopyranosyl fluoride **15**.

This compound was prepared according to the general procedure from *n*-pentenyl 6-O-*tert*butyldimethylsilyl-2,3,4-O-tri-O-methyl-α-D-mannopyranose **6** (53 mg, 0.1 mmol). Silica gel chromatography (hexane/Ethyl acetate 8:2) provided **15** (39.3 mg, 85%). $[\alpha]_D$= +26.5º ($CHCl_3$, c 1.2); ^{1}H-NMR (300MHz) δ 7.75-7.69 (m, 5H), 7.43-7.35 (m, 5H), 5.72 (dd, 1H, *J* = 50.5, 1.9 Hz), 3.97 (dd, 1H, *J* = 11.5, 3.4 Hz), 3.85 (t, 1H, *J* = 9.5 Hz), 3.85 (dd, 1H, *J* = 11.5, 1.7 Hz), 3.74 (m, 1H), 3.67-3.63 (m, 1H), 3.57 (s, 3H), 3.56 (m, 1H), 3.55 (s, 3H), 3.54 (s, 3H), 1.07 (s, 9H) ; ^{13}C-NMR (75MHz) δ 135.9 (x 2), 135.6 (x 2), 133.8, 133.3, 129.5 (x 2), 127.6 (x 2), 127.5 (x 2), 105.6 (d, *J* = 219.4 Hz), 80.4, 75.9, 75.0, 74.8, 62.3, 60.7, 58.9, 57.9, 26.7 (x 3), 19.4; API-ES positive: 480.3 $(M+NH_4)^+$, 485.3 $(M+Na)^+$; Anal. Calcd for $C_{25}H_{35}O_5FSi$ (462.22): C, 64.9; H, 7.63. Found: C, 65.02; H, 7.58.

2,3,4,6-Tetra-O-benzoyl-α-D-mannopyranosyl fluoride **16.**

This compound was prepared according to the general procedure from *n*-pentenyl orthoester **8** (66.4 mg, 0.1 mmol). Silica gel chromatography (hexane/Ethyl acetate 8:2) provided **16**[5] (49 mg, 82%). $[\alpha]_D$= -29.7º ($CHCl_3$, c 1.6); ^{1}H-NMR (300MHz) δ 8.14-7.26 (m, 20H), 6.22 (t, 1H, *J* = 10.1 Hz), 5.96-5.86 (m, 2H), 5.86 (dd, 1H, $J_{1,2}$ = 43.1, 1.8 Hz), 4.79 (dd, 1H, *J* =12.3, 2.2 Hz), 4.61 (m, 1H), 4.49 (dd, 1H, *J* = 12.3, 3.8 Hz); API-ES

[5] Miethchen, R.; Kolp, G. *J. of Fluorine Chemistry* **1993**, *60*, 49.

positive: 622.1 $(M+Na)^+$; Anal. Calcd for $C_{34}H_{27}O_9F$ (598.57): C, 68.22; H, 4.55. Found: C, 68.14; H, 4.43.

In a different experiment, a solution of IPy_2BF_4 (55.8 mg, 0.15mmol) in dry CH_2Cl_2 (1 mL) was cooled to -78ºC and HBF_4 (16μL, 0.15mmol) was added. After 5 min. of stirring, a solution of *n*-pentenyl 2,3,4,6-tetra-O-benzoyl-α-D-mannopyranose **7** (66.4 mg, 0.1 mmol) in dry CH_2Cl_2 (3 mL) was added. The stirring was maintained at -78ºC for 30 minutes before $BF_3{\cdot}OEt_2$ (13 μL, 0.1 mmol) was added. The reaction mixture was then warmed to room temperature over 20 min and washed with 10% aqueous sodium thiosulphate containing sodium bicarbonate, saturated sodium bicarbonate and water. The organic layer was then dried and concentrated and the residue was purified by flash chromatography (hexane/Ethyl acetate 8:2) to provide pure **16** (45 mg, 75%).

n-Pentenyl 2,3,4-tri-O-methyl-6-O-(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside **18.**

To a stirred solution of fluoride **12** (54.2 mg, 0.1mmol), *n*-pentenyl glycoside **17** (29mg, 0.1mmol) and 4A molecular sieves (50 mg) in CH_2Cl_2 (5mL) was added Ytterbium (III) trifluoromethanesulfonate (62 mg, 0.1mmol). Stirring was maintained for 10 min and then the reaction mixture was diluted with CH_2Cl_2 (15 mL), washed with saturated aqueous sodium bicarbonate. The organic extract was dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (Hexane:AcOEt, 7:3) to give disaccharide **18** (55.2 mg, 68%). $[\alpha]_D$= +37.6º ($CHCl_3$, c 1.5); ^{1}H-NMR (300MHz) δ 7.32-7.06 (m, 20H), 5.71 (ddt, 1H, *J* = 17.1, 10.4, 6.6 Hz), 5.04 (s, 2H), 4.86-4.96 (m, 1H), 4.81 (d, 1H, J = 10.9Hz), 4.73 (bs, 1H), 4.65 (s, 2H), 4.61 (d, 1H, J = 12.2Hz), 4.53 (d, 1H, J = 12.2Hz), 4.51 (d, 1H, J = 12.2Hz), 4.46 (d, 1H, J = 12.1Hz), 4.43 (d, 1H, J = 10.9 Hz), 3.85-3.26 (m, 14H), 3.42 (s, 3H), 3.41 (s, 3H), 3.36 (s, 3H), 2.06-1.97 (m, 2H), 1.61-1.52 (m, 2H); ^{13}C-NMR (75MHz) δ 138.7, 138.6, 138.5, 138.4, 137.9, 128.3 (x2), 128.2 (x6), 127.8 (x2), 127.7 (x2), 127.6 (x2), 127.5 (x2), 127.4 (x2), 127.3 (x2), 114.9, 98.0, 96.6, 81.4, 79.9, 77.1, 76.1, 74.9, 74.8 (x2), 73.2, 72.3, 71.8, 71.7, 71.4, 69.2, 66.9, 65.9, 60.8, 58.8, 57.6, 30.3, 28.5; API-ES positive: 830.5 $(M+NH_4)^+$, 835.2 $(M+Na)^+$, 859.5

$(M+2Na)^+$; Anal. Calcd for $C_{48}H_{60}O_{11}$ (812.98): C, 70.91; H, 7.44. Found: C, 71.06; H, 7.37.

n-Pentenyl 2,3,4-tri-O-methyl-6-O-(2-O-benzoyl-,3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside **19.**

To a stirred solution of fluoride **14** (27.8 mg, 0.05mmol), *n*-pentenyl glycoside **17** (14.5mg, 0.05mmol) and 4A molecular sieves (25 mg) in CH_2Cl_2 (3mL) was added Ytterbium (III) trifluoromethanesulfonate (62 mg, 0.1mmol). Stirring was maintained for 10 min and then the reaction mixture was diluted with CH_2Cl_2 (15 mL), washed with saturated aqueous sodium bicarbonate. The organic extract was dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (Hexane:AcOEt, 7:3) to give disaccharide **19** (31 mg, 75%). $[\alpha]_D$= +13.2º ($CHCl_3$, c 1.3); ^{1}H-NMR (300MHz) δ 8.09-8.06 (m, 2H), 7.57-7.17 (m, 18H), 5.80 (ddt, 1H, J = 16.8, 10.2, 6.6 Hz), 5.73 (m, 1H), 5.09 (d, 1H, J = 1.8Hz), 5.05-4.95 (m, 2H), 4.88 (d, 1H, J = 1.5 Hz), 4.87 (d, 1H, J = 10.8 Hz), 4.80 (d, 1H, J = 12.3Hz), 4.76 (d, 1H, J = 12.9 Hz), 4.54 (m, 3H), 4.12-4.10 (m, 1H), 3.96 (m, 1H), 3.91 (dd, 1H, J = 10.8, 3.6 Hz), 3.81-3.57 (m, 8H), 3.51 (s, 6H), 3.51 (s, 3H), 3.46-3.37 (m, 2H); ^{13}C-NMR (75MHz) δ 165.4, 138.6, 138.5, 138.0, 137.9, 132.9, 130.0, 129.9 (x 3), 128.3 (x 2), 128.29 (x 2), 128.24 (x 2), 128.21 (x 2), 128.1 (x 2), 127.8 (x 2), 127.6, 127.5 (x 2), 127.4, 114.9, 98.1, 96.5, 81.4, 78.3, 76.3, 75.1, 74.2, 73.3, 71.5, 71.4, 71.0, 69.0, 68.7, 67.0, 66.7, 60.8, 58.8, 57.5, 30.3, 28.6; API-ES positive: 844.3 $(M+NH_4)^+$, 872 $(M+2Na)^+$; Anal. Calcd for $C_{48}H_{58}O_{12}$ (826.39): C, 69.71; H, 7.07. Found: C, 69.61; H, 6.94.

2,3,4-tri-O-methyl-6-O-(2,3,4,6-tetra-O-benzyl-D-glucopyranosyl)-α- and β--D-glucopyranosyl fluoride **21.**

To a stirred solution of pentenyl-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside **1** (122mg, 0.2mmol) and 2,3,4-tri-*O*-methyl-α-D-glucopyranosyl fluoride **20** (34.8mg, 0.15mmol) in CH_2Cl_2 (6 mL) under argon was added IDCP (234 mg, 0.5 mmol) in one portion. The solution was stirred for 2h and then the mixture was quenched by washing with a mixture of aqueous sodium bicarbonate and aqueous sodium thiosulfate solution. The separated organic extract was dried, filtered and concentrated. Purification by flash chromatography

(hexane/ethyl acetate 8:2 to 1:1) gave disaccharide **21α** (51 mg, 45%) followed by disaccharide **21β** (50 mg, 45%)

α anomer : α_D= +37.5º ($CHCl_3$, c 0.35); ^{1}H-NMR (300MHz) δ 7.30-7.05 (m, 20H), 5.48 (dd, 1H, J= 53.3, 2.7Hz), 4.98 (d, 1H, J= 17.4Hz), 4.96 (d, 1H, J=10.1Hz), 4.84 (d, 1H, J= 10.8Hz), 4.81 (d, 1H, J= 10.8Hz), 4.66 (d, 1H, J= 16.7Hz), 4.61 (d, 1H, 17.2Hz), 4.54 (d, 1H, J= 12.1Hz), 4.42 (bs, 1H), 4.40 (d, 1H, J=12.1Hz), 3.91 (t, 1H, J= 9.2Hz), 3.80-3.39 (m, 9H), 3.56 (s, 3H), 3.48 (s, 3H), 3.38 (s, 3H), 3,24 (t, 1H, J= 9.5Hz), 2.93 (ddd, 1H, J= 25.7, 9.5, 2.7Hz). ^{13}C-NMR (75MHz) δ 138.8, 138.5, 138.2, 137.9, 128.3 (x5), 127.9 (x3), 127.8 (x3), 127.7 (x3), 127.6 (x2), 127.5 (x2), 127.3 (x2), 104.9 (d, J= 226.3Hz), 94.4, 82.9, 81.8, 81.2 (d, J= 24.8Hz), 80.1, 78.4, 77.5, 75.6, 75.1, 73.4, 72.3, 72.4 (d, J= 3.5Hz), 70.3, 68.4, 66.0, 60.8, 60.6, 59.1.API-ES positive: 764.3 $(M+NH_4)^+$, 769.2 $(M+Na)^+$. Anal. Calcd for $C_{43}H_{51}FO_{10}$ (746.86): C, 69.15; H, 6.88. Found: C, 69.35; H, 6.65. **β anomer :** α_D= +17.5º ($CHCl_3$, c 0.45); ^{1}H-NMR (300MHz) δ 7.29-7.08 (m, 20H), 5.60 (dd, 1H, J= 53.3, 2.6Hz), 4.90 (d, 1H, J= 11.0Hz), 4.84 (d, 1H, J= 10.8Hz), 4.74 (d, 1H, J= 10.8Hz), 4.72 (d, 1H, J= 9.3Hz), 4.69 (d, 1H, J= 11.0Hz), 4.55 (d, 1H, J= 12.2Hz), 4.49 (d, 1H, J= 12.2Hz), 4.47 (d, 1H, J= 10.8Hz), 4.37 (d, 1H, J=7.7 Hz), 4.13 (dd, 1H, J= 11.0, 1.7 Hz), 3.83 (ddd, 1H, J= 10.0, 4.5, 1.6Hz), 3.70-3.40 (m, 8H), 3.56 (s, 3H), 3.47 (s, 3H), 3.39 (s, 3H), 3.18 (t, 1H, J= 9.6Hz), 3.11 (ddd, 1H, J= 25.7, 9.6, 2.7 Hz). ^{13}C-NMR (75MHz) δ 138.5, 138.3, 138.1, 137.9, 128.4 (x2), 128.33 (x2), 128.32 (x2), 128.31 (x2), 128.0 (x2), 127.9 (x2), 127.8 (x2), 127.7, 127.6 (x2), 127.57, 127.56, 127.55, 104.8 (d, J= 226.4Hz), 103.7, 84.8, 82.8, 81.9, 81.3 (d, J= 24.8Hz), 78.5, 77.8, 75.7, 75.0, 74.9, 74.8, 73.4, 72.2 (d, J= 3.9Hz), 68.9, 68.1, 60.9, 60.5, 59.1. API-ES positive: 769.2 $(M+Na)^+$. Anal. Calcd for $C_{43}H_{51}FO_{10}$ (746.86): C, 69.15; H, 6.88. Found: C, 69.3; H, 6.93.

2,3,4-tri-O-methyl-6-O-(2,3,4,6-tetra-O-methyl-D-mannopyranosyl)-α- and β--D-mannopyranosyl fluoride **23.**

To a stirred solution of fluoride **22** (22 mg, 0.1 mmol), *n*-pentenyl glycoside **4** (30 mg, 0.1 mmol) and 4A molecular sieves (25 mg) in CH_2Cl_2 (3mL) was added $I(coll)_2ClO_4$ (117 mg, 0.25 mmol). Stirring was maintained for 1 hour and then the reaction mixture was diluted with CH_2Cl_2 (15 mL), washed with 10% aqueous sodium thiosulphate containing sodium bicarbonate, saturated aqueous sodium bicarbonate and water. The organic extract was

dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (Hexane:AcOEt, 2:8) to give disaccharide **23α** (20 mg, 44%) followed by disaccharide **23β** (19 mg, 44%). **α–anomer** $[\alpha]_D$= +26.8º ($CHCl_3$, c 0.15); ^{1}H-NMR (300MHz) δ 5.65 (dd, 1H, J = 50.4, 2.1 Hz), 5.03 (d, 1H, J = 1.8 Hz), 3.91 (dd, 1H, J = 12.0, 4.5 Hz), 3.74-3.70 (m, 2H), 3.67-3.65 (m, 3H), 3.61 (m, 1H), 3.56 (s, 3H), 3.53 (s, 3H), 3.52 (s, 3H), 3.49 (s, 3H), 3.46 (s, 3H), 3.40 (s, 3H), 3.58-3.44 (m, 6H); ^{13}C-NMR (75MHz) δ 105.4 (d, J =221.3Hz), 97.3, 81.1, 80.6 (d, J = 1.6 Hz), 76.8, 76.3, 75.7 (d, J = 34.1 Hz), 75.1, 73.7 (d, J =2.2 Hz), 71.6, 71.3, 65.9, 60.9, 60.6, 59.4, 59.2, 58.8, 57.9, 57.7; API-ES positive: 465.2 $(M+Na)^+$; Anal. Calcd for $C_{19}H_{35}FO_{10}$ (442.47): C, 51.57; H, 7.97. Found: C, 51.64; H, 8.03. **β-anomer**.$[\alpha]_D$= -20.1º ($CHCl_3$, c 0.15); ^{1}H-NMR (300MHz) δ 5.66 (dd, 1H, J = 50.4, 1.8 Hz), 4.48 (bs, 1H), 4.22 (dd, 1H, J = 11.1, 1.5Hz), 3.87-3.82 (m,1H), 3.73-3.70 (m, 2H), 3.65 (s, 3H), 3.52 (s, 3H), 3.51 (s, 6H), 3.49 (s, 3H), 3.48 (s, 3H), 3.41 (s, 3H), 3.67-3.25 (m, H), 3.18 (dd, 1H, J = 8.7, 3.3 Hz); δ ; API-ES positive: 465.2 $(M+Na)^+$; Anal. Calcd for $C_{19}H_{35}FO_{10}$ (442.47): C, 51.57; H, 7.97. Found: C, 51.39; H, 8.15.

6-O-tertbutyldiphenylsilyl-2,3,4-tri-O-methyl-6-O-(2,3,4,6-tetra-O-methyl-D-manno-pyranosyl) -α- and β--D-mannopyranosyl fluoride **24.**

To a stirred solution of fluoride **22** (22 mg, 0.1 mmol), *n*-pentenyl glycoside **6** (52.8 mg, 0.1 mmol) and 4A molecular sieves (25 mg) in CH_2Cl_2 (3mL) was added $I(coll)_2ClO_4$ (117 mg, 0.25 mmol). Stirring was maintained for 1 hour and then the reaction mixture was diluted with CH_2Cl_2 (15 mL), washed with 10% aqueous sodium thiosulphate containing sodium bicarbonate, saturated aqueous sodium bicarbonate and water. The organic extract was dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography (Hexane:AcOEt, 1:1) to give disaccharide **24α** (32 mg, 48%) followed by disaccharide **24β** (16 mg, 24%). **α-anomer** $[\alpha]_D$= +43.5º ($CHCl_3$, c 1.0); ^{1}H-NMR (300MHz) δ 7.76-7.71 (m, 4H), 7.42-7.34 (m, 6H), 5.66 (dd, 1H, J = 50.4, 1.5 Hz), 5.05 (d, 1H, J = 1.2 Hz), 3.95-3.83 (m, 4H), 3.76-3.66 (m, 4H), 3.57-3.46 (m, H), 3.53 (s, 6H), 3.51 (s, 3H), 3.50 (s, 3H), 3.49 (s, 3H), 3.48 (s, 3H), 1.06 (s, 9H); ^{13}C-NMR (75MHz) δ 135.9 (x 2), 135.6 (x 2), 134.1, 133.6, 129.4 (x 2), 127.5 (x 2), 127.4 (x 2), 105.4 (d, *J* = 220.9 Hz), 96.8, 81.2, 80.5 (d, *J* = 1.6 Hz), 76.7, 76.1, 75.6 (d, *J* = 34.0 Hz), 75.2, 73.8 (d, *J* = 2.0 Hz),

73.0, 65.5, 63.3, 60.9, 60.6, 59.3, 58.3, 57.9, 57.6, 26.7 (x 3), 19.4.; API-ES positive: 684.3 $(M+NH_4)^+$; Anal. Calcd for $C_{34}H_{51}FO_{10}Si$ (666.85): C, 61.24; H, 7.71. Found: C, 61.09; H, 7.65. **β-anomer** $[\alpha]_D$= -9.5º ($CHCl_3$, c 0.9); ^{1}H-NMR (300MHz) δ 7.78-7.70 (m, 4H), 7.42-7.35 (m, 6H), 5.69 (dd, 1H, *J* = 50.4, 1.8 Hz, 4.48 (bs, 1H), 4.25 (dd, 1H, *J* = 11.1, 1.8 Hz), 3.95 (dd, 1H, *J* = 11.1, 5.1 Hz), 3.91-3.85 (m, 1H), 3.76 (d, 1H, *J* = 3.3 Hz), 3.72 (m, 1H), 3.65 (s, 3H), 3.62-3.55 (m, 1H), 3.53 (s, 3H), 3.50 (s, 3H), 3.49 (s, 3H), 3.48 (s, 6H), 3.44 (t, 1H, *J* = 9.3 Hz), 3.25-3.22 (m, 1H), 3.19 (dd, 1H, *J* = 9.3, 3.0 Hz), 1.05 (s, 9H);); API-ES positive: 684.3 $(M+NH_4)^+$; Anal. Calcd for $C_{34}H_{51}FO_{10}Si$ (666.85): C, 61.24; H, 7.71. Found: C, 61.15; H, 7.84.

2,3,4-tri-O-methyl-6-O-(2,3,4,6-tetra-O-benzoyl-a-D-mannopyranosyl)-α-D-glucopyranosyl fluoride ***25***.

A stirred solution of *n*-pentenyl orthoester **8** (66.4 mg, 0.1 mmol), and fluoride **22** (22.4 mg, 0.1 mmol) in CH_2Cl_2 (4 mL) and under argon was cooled to -20ºC and then NIS (44.8 mg, 0.2 mmol) and $Yb(OTf)_3$ (62mg, 0.1 mmol) were added. The solution was stirred for 1h and then was quenched by washing with a mixture of aqueous sodium bicarbonate and aqueous sodium thiosulfate solution. The separated organic extract was dried, filtered and concentrated. Purification by flash chromatography (hexane/ethyl acetate 3:2 to 1:1) gave disaccharide **25** (75 mg, 94%). $[\alpha]_D$= -2.3º ($CHCl_3$, c 0.9); ^{1}H-NMR (300MHz) δ 8.0-7.15 (m, 20H), 6.04 (t, 1H, *J* = 10.0 Hz), 5.87 (dd, 1H, *J* = 10.1, 3.3Hz), 5.70 (dd, 1H, *J* = 3.2, 1.8 Hz), 5.64 (dd, 1H, *J* = 50.3, 1.8 Hz), 5.14 (d, 1H, *J* = 1.6Hz), 4.67-4.58 (m, 1H), 4.47-4.39 (m, 2H), 3.96 (dd, 1H, *J* = 11.5, 5.3 Hz), 3.87-3.78 (m, 2H), 3.67 (m, 1H), 3.54 (s, 3H), 3.48 (s, 3H), 3.46 (s, 3H), 3.53-3.42 (m, 2H); ^{13}C-NMR (75MHz) δ 166.2, 165.4, 165.3, 165.2, 133.4 (x 2), 133.1, 133.0, 129.9, 129.8 (x 4), 129.7 (x 2), 129.6 (x 2), 129.4, 129.1, 128.9, 128.5 (x 2), 128.4 (x 2), 128.3 (x 2), 128.2 (x 2), 105.3 (d, *J* = 220.8 Hz), 98.0, 80.5, 75.5 (d, *J* = 34.0 Hz), 75.4, 73.7, 70.3, 69.9, 68.8, 67.1, 66.9, 62.8, 60.9, 59.4, 57.8; API-ES positive: 825.2 $(M+Na)^+$;Anal. Calcd for $C_{43}H_{43}FO_{14}$ (802.79): C, 64.33; H, 5.40. Found: C, 64.47; H, 5.49.

In a different experiment a solution of *n*-pentenyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranoside **7** (79.7 mg, 0.12 mmol), 2,3,4-tri-*O*-methyl-α-D-mannopyranosyl

fluoride **22** (22.4 mg, 0.1 mmol), NIS (44.8 mg ,0.2mmol) and 4A molecular sieves (25 mg) in anhyd. CH_2Cl_2 (3 mL) was stirred under argon for 10 min at room temperature. Then the reaction was cooled at -30ºC and BF_3OEt_2 (15 µl, 0.12mmol) was added. After 30min, the reaction was diluted with CH_2Cl_2 (10 mL), washed with 10% aq $Na_2S_2O_3$ and saturated aq $NaHCO_3$ (10 mL), extracted with CH_2Cl_2, dried over Na_2SO_4, filtered and concentrated. The obtained residue was a complex mixture of compounds from which disaccharide **25** could be purified by flash chromatography (Hexane:AcOEt, 7:3)(20mg, 25%).

Methyl *2,3,4-tri-O-methyl-6-O-(2,3,4,6-tetra-O-benzoyl-a-D-mannopyranosyl)-α-D-glucopyranoside* **27**.

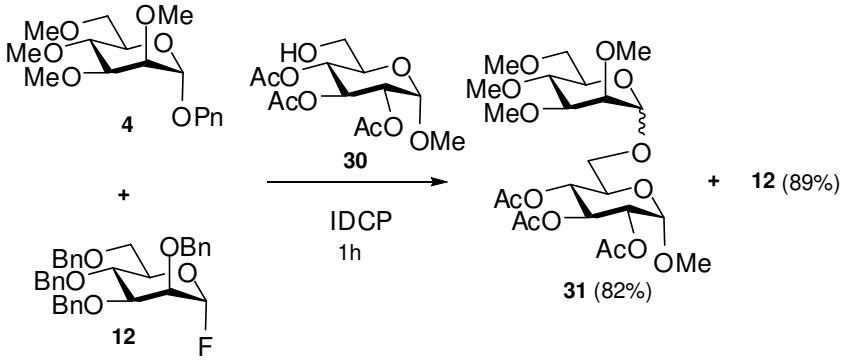
A stirred solution of **8** (57.5 mg, 0.087 mmol), **12** (47 mg, 0.087 mmol) and **26** (20 mg, 0.087 mmol) in CH_2Cl_2 (4 mL) under argon was cooled to -30ºC and then NIS (38.7 mg, 0.173 mmol) and BF_3OEt_2 (1.1µl, 0.0087mmol) were added. The solution was stirred for 20 minutes and then was quenched by washing with a mixture of aqueous sodium bicarbonate and aqueous sodium thiosulfate solution. The separated organic extract was dried, filtered and concentrated. Purification by flash chromatography (hexane/ethyl acetate 3:2 to 1:1) gave recovered **12** (40 mg, 85%) and disaccharide **27** (68 mg, 96%). $[\alpha]_D$= +4.3 º ($CHCl_3$, c 3.2); ^{1}H-NMR (300MHz) δ 8.05-7.17 (m, 20H), 6.02 (t, 1H, *J* = 10.0 Hz), 5.85 (dd, 1H, *J* = 10.0, 3.2 Hz), 5.67 (dd, 1H, *J*= 3.1, 1.8 Hz), 5.14 (d, 1H, *J* = 1.4Hz), 4.74 (d, 1H, *J* = 3.5 Hz), 4.68 (dd, 1H, *J* = 11.9, 2.0 Hz), 4.48 (ddd, 1H, *J* = 9.9, 4.3, 2.0Hz), 4.39 (dd, 1H, *J* = 11.9, 4.6Hz), 3.91 (dd, 1H, *J* = 11.0Hz, 5.4Hz), 3.79 (dd, 1H, *J* = 10.9, 1.4Hz), 3.69-3.63 (m, 1H), 3.57 (s, 3H), 3.53 (s, 3H), 3.49 (m, 1H) 3.46 (s, 3H), 3.42 (s, 3H), 3.11 (dd, 1H, *J* = 9.7, 3.7 Hz), 3.05 (m, 1H); ^{13}C-NMR (75MHz) δ 166.4, 165.7, 165.6, 165.5, 133.7 (x 2), 133.4, 133.3, 130.2, 130.1 (x 2), 129.9 (x 6), 129.6 (x 2), 129.3 (x 4), 129.2 (x 2), 128.8, 128.7, 128.6, 97.7, 97.5, 83.8, 82.0, 79.8, 70.6, 70.2, 70.0, 69.2, 67.2, 66.8, 63.1, 61.1, 60.8, 59.3, 55.4; API-ES positive:837.2 $(M+Na)^+$; Anal. Calcd for $C_{44}H_{46}O_{15}$ (814.83): C, 64.86; H, 5.69. Found: C, 65.02; H, 5.73.

One pot assembly of trisaccharide **29**.

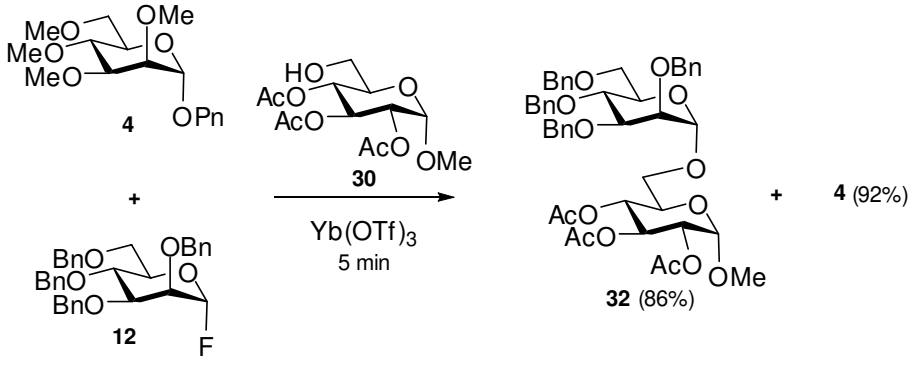
A mixture of n-pentenyl orthoester **8** (73mg, 0.11mmol), 2,3,4 -tri-O-methyl-α-D-mannopyranosyl fluoride **22** (22.4mg, 0.1mmol) and 4A molecular sieves in CH_2Cl_2 (4mL)

was stirred under argon at -20ºC for 10min. Then NIS (24.6mg, 0.11mmol) and $Yb(OTf)_3$ (68.2mg, 0.11mmol) was added. The reaction mixture was stirred at -20ºC for 1h, after which n-pentenyl-2,3,4-tri-O-methyl-α-D-mannopyranoside **17** (26.1mg, 0.09mmol) in CH_2Cl_2 (2mL) was added. The reaction was allowed to warm to room temperature and then $Yb(OTf)_3$ (68.2mg, 0.11mmol) was added. Upon stirring for 10 minutes, the reaction was was quenched by washing with a mixture of aqueous sodium bicarbonate and aqueous sodium thiosulfate solution. The separated organic extract was dried, filtered and concentrated. Purification by flash chromatography (hexane/ethyl acetate 1:1) trisaccharide **29** (69mg , 72%); $[\alpha]_D$= -2.3º ($CHCl_3$, c 0.9); ^{1}H-NMR (300MHz) δ 8.31-7.79 (m, 8H), 7.61-7.22 (m, 12H), 6.10 (t, 1H, *J* = 9.9 Hz), 5.96 (dd, 1H, *J* = 10.2, 3.3 Hz), 5.77 (ddt, 1H, *J* = 17.1, 10.5, 6.6 Hz), 5.76 (m, 1H), 5.26 (d, 1H, *J* = 1.8Hz), 5.12 (d, 1H, *J* = 1.0 Hz), 5.03-4.92 (m, 2H), 4.88 (bs, 1H), 4.71-4.68 (m, 1H), 4.57-4.47 (m, 2H), 4.05-3.97 (m, 2H), 3.91-3.87 (m, 1H), 3.81-3.35(m, 11H), 3.58 (s, 3H), 3.56 (s, 3H), 3.49 (s, 3H), 3.48 (s, 3H), 3.47 (s, 3H), 3.45 (s, 3H), 2.11-2.04 (m, 2H), 1.69-1.60 (m, 2H);^{13}C-NMR (75MHz) δ 166.2, 165.4, 165.2, 165.1, 137.9, 133.3, 133.2, 132.9, 129.9, 129.8 (x 2), 129.77 (x 2), 129.73 (x 2) 129.6 (x 2), 129.5, 129.2, 129.0, 128.5 (x 2), 128.4 (x 2), 128.3 (x 2), 128.2 (x 2), 114.9, 97.6, 96.9, 96.6, 81.39, 81.38, 77.1, 76.6, 76.3, 75.8, 71.4, 71.1, 70.4, 69.9, 68.7, 67.1, 67.0 (x 2), 66.0, 62.9, 60.8, 60.7, 58.7, 58.6, 57.5, 57.4, 30.3, 28.6; API-ES positive: 1090.3 $(M+NH_4)^+$, 1095.4 $(M+Na)^+$; Anal. Calcd for $C_{57}H_{68}O_{20}$ (1073,14): C, 63.80; H, 6.39. Found: C, 63.93; H, 6.51.

*Competition experiments between n-pentenyl glycoside **4** and glycosyl fluoride **12**.*



Experiment A. To a stirred solution of **4** (15.2 mg, 0.05 mmol), **12** (27.1 mg, 0.05 mmol) and **30** (16 mg, 0.05 mmol) in CH_2Cl_2 (4 mL) under argon was added IDCP (46.8 mg, 0.05 mmol) in one portion. The solution was stirred for 30 minutes and then the mixture was quenched by washing with a mixture of aqueous sodium bicarbonate and aqueous sodium thiosulfate solution. The separated organic extract was dried, filtered and concentrated. Purification by flash chromatography (hexane/ethyl acetate 9:1 to 1:1) gave recovered **12** (24 mg, 89%) and Methyl 2,3,4-tri-O-acetyl-6-O-(2,3,4,6-tetra-O-methyl-α-D-mannopyranosyl)–D-glucopyranoside **31** (22 mg, 82%) as a 1.4:1 mixture of anomers. **α–anomer** $[\alpha]_D$= +2.2 º ($CHCl_3$, c 0.12); ^{1}H-NMR (300MHz) δ 5.48 (t, 1H, *J* = 9.8 Hz), 4.96 (t, 1H, *J* = 9.8 Hz), 4.93 (d, 1H, *J* = 3.3 Hz), 4.86 (dd, 1H, *J* = 10.1, 3.7 Hz), 4.36 (bs, 1H), 4.07-3.97 (m, 3H), 3.73 (m, 1H), 3.68-3.32 (m, 4H), 3.64 (s, 3H), 3.52 (s, 3H), 3.49 (s, 3H), 3.40 (s, 3H), 3.38 (s, 3H), 3.28-3.22 (m, 1H), 3.17 (dd, 1H, *J* = 9.0, 3.2 Hz), 2.08 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H); API-ES positive 561.3 $(M+Na)^+$; Anal. Calcd for $C_{23}H_{38}O_{14}$ (538.54): C, 51.30; H, 7.11. Found: C, 51.07; H, 7.34; **β–anomer** ^{1}H-NMR (300MHz) δ 5.46 (t, 1H, *J* = 9.6 Hz), 5.11 (t, 1H, *J* = 9.6 Hz), 4.95-4.88 (m, 4H), 4.00 (ddd, 1H, *J* = 10.1, 4.1, 2.3 Hz), 3.81 (dd, 1H, *J* = 11.3, 4.2 Hz), 3.64-3.54 (m, 7H), 3.52 (s, 3H), 3.50 (s, 3H), 3.49 (m, 1H), 3.47 (s, 3H), 3.40 (s, 3H), 3.38 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H); API-ES positive: 561.2 $(M+Na)^+$; Anal. Calcd for $C_{23}H_{38}O_{14}$ (538.54): C, 51.30; H, 7.11. Found: C, 51.45; H, 7.27.



Experiment B. To a stirred solution of **4** (15.2 mg, 0.05 mmol), **12** (27.1 mg, 0.05 mmol) and **30** (16 mg, 0.05 mmol) in CH_2Cl_2 (4 mL) under argon was added $Yb(OTf)_3$ (31 mg, 0.05 mmol) in one portion. The solution was stirred for 5 minutes and then the mixture was

quenched by washing with aqueous sodium bicarbonate solution. The separated organic extract was dried, filtered and concentrated. Purification by flash chromatography (hexane/ethyl acetate 9:1 to 1:1) gave recovered **4** (14mg, 92%) and *Methyl 2,3,4-tri-O-acetyl-6-O-(2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside* **32**[6] (36 mg, 86%); ^{1}H-NMR (300MHz) δ 7.37-7.16 (m, 20H), 5.43 (t, 1H, *J*= 9.8 Hz), 5.01 (t, 1H, *J*= 9.8 Hz), 4.90-4.49 (m, 11H), 3.96-3.83 (m, 3H), 3.76-3.66 (m, 5H), 3.51 (m, 1H), 3.30 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H), 1.94 (s, 3H).

[6] (a) Wuiff, G.; Wichelhaus, J. *Chem. Ber.* 1979, *112,* 2847-2853; (b) Crich, D.; Sun, S.; *Tetrahedron* **1998**, *54*, 8321.

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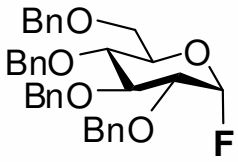

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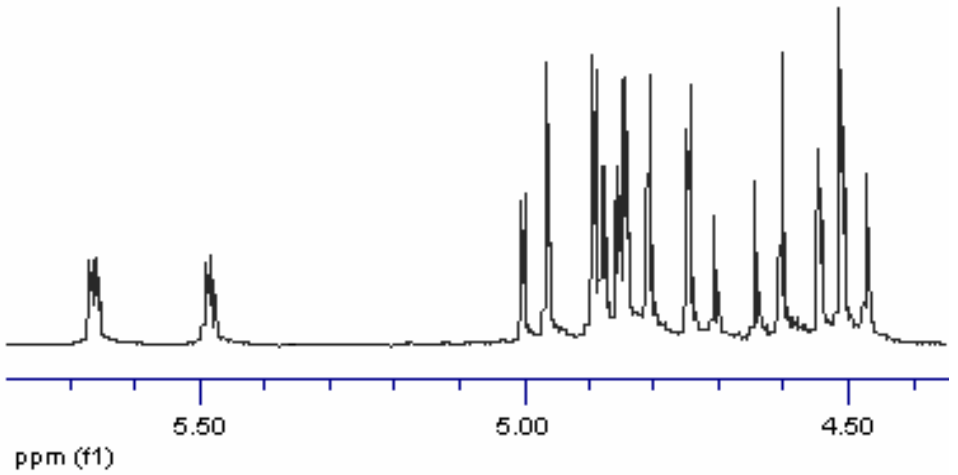

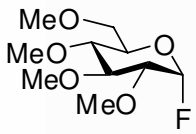

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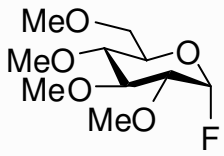

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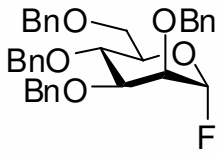

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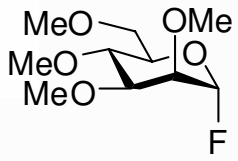

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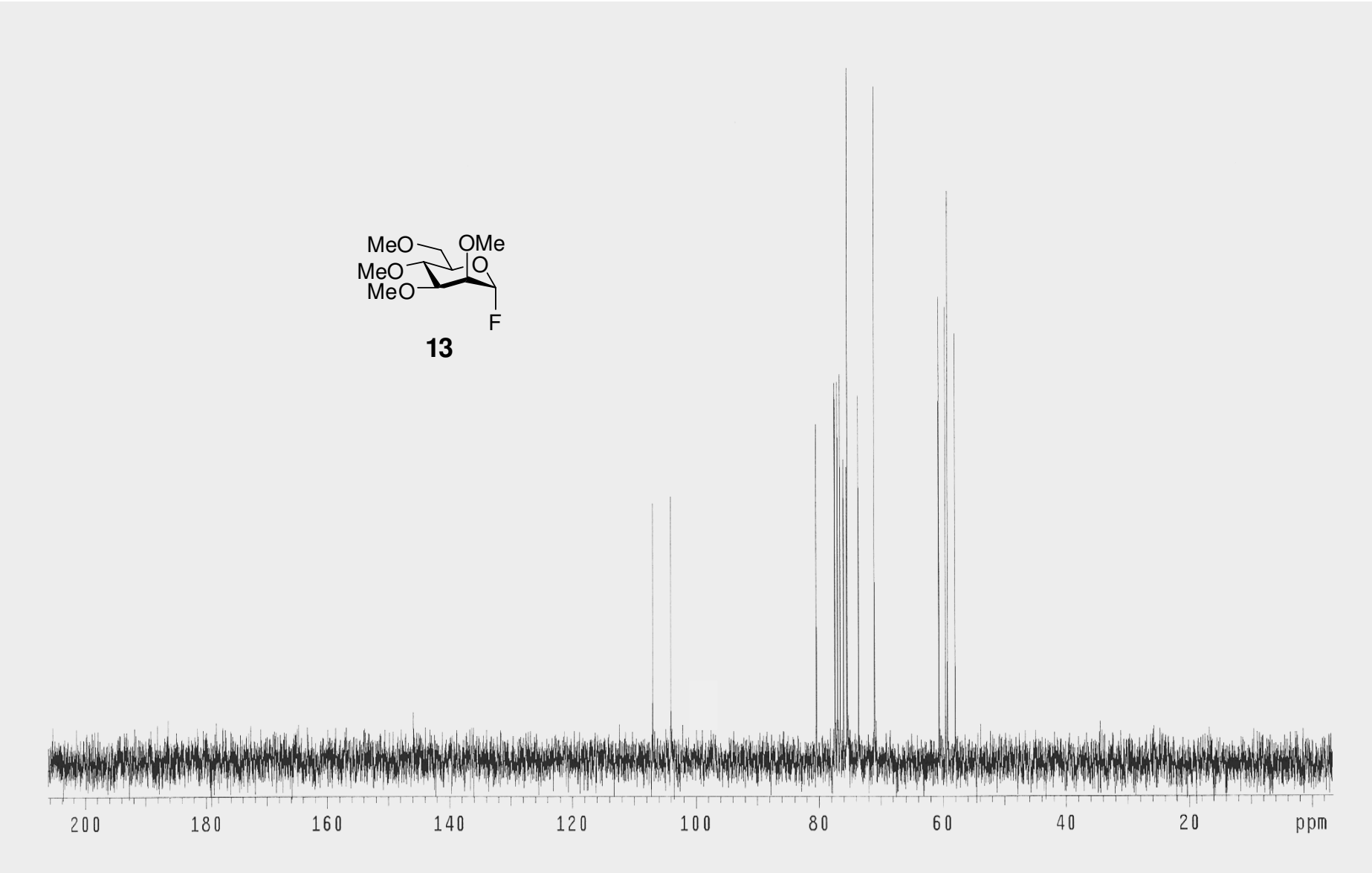
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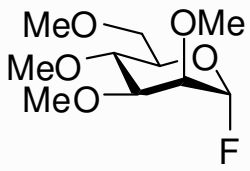

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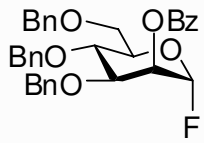

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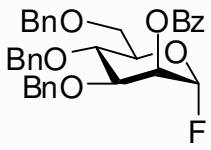
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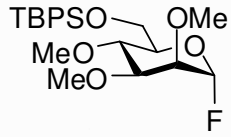

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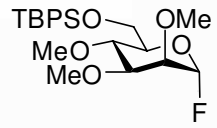
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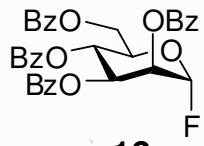
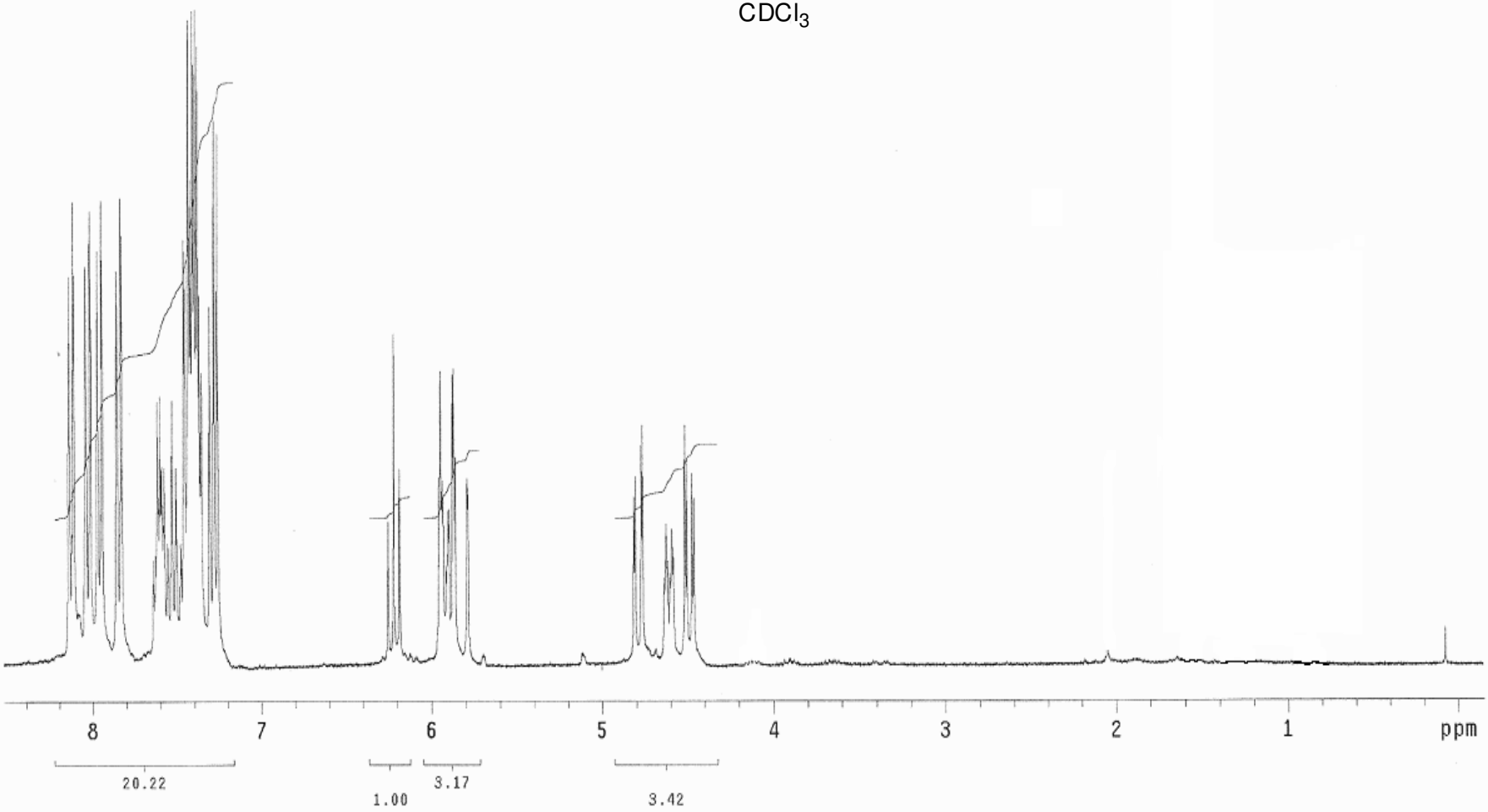
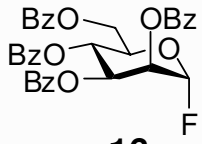


16

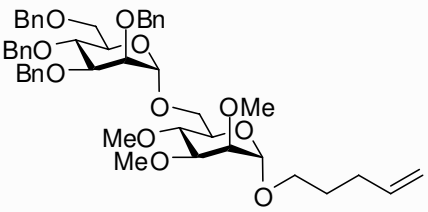
$CDCl_3$





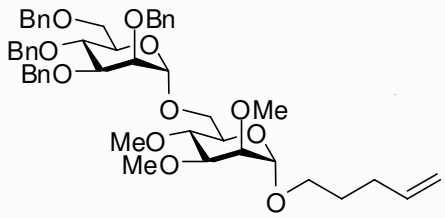
16

C_6D_6


BnO
OBn
BnO
O
BnO
O
OMe
MeO
O
MeO
O

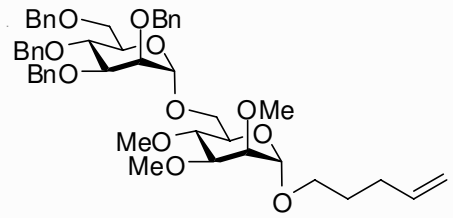
18

7
6
5
4
3
2
1
20.12
1.00
11.64
21.25
1.97
2.98


BnO
OBn
BnO
O
BnO
O
OMe
MeO
O
MeO
O

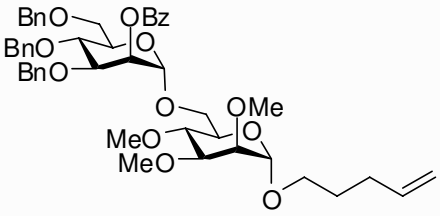
18

140
130
120
110
100
90
80
70
60
50
40
30
ppm

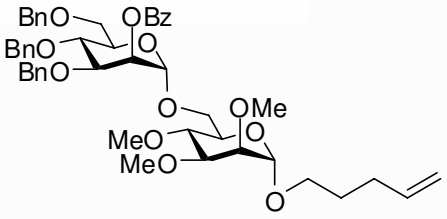

BnO
OBn
BnO
O
BnO
O
OMe
MeO
O
MeO
O

18

140
130
120
110
100
90
80
70
60
50
40
30
ppm

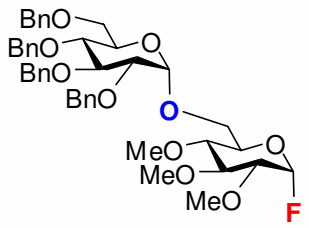


19

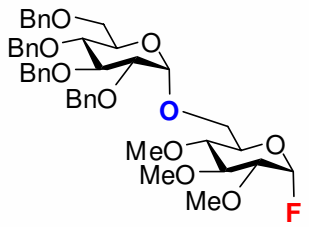

BnO
OBz
BnO
O
BnO
O
OMe
MeO
O
MeO
O

19

160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

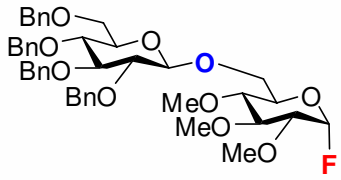


21α

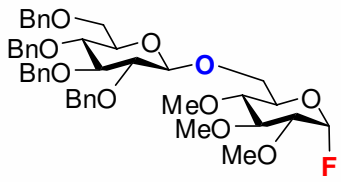

BnO
BnO
BnO
BnO
O
O
MeO
MeO
MeO
F

21α

140
130
120
110
100
90
80
70
60
opm (f1)

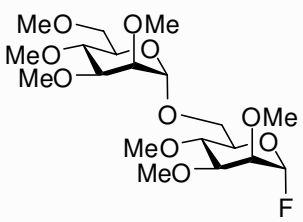


21β

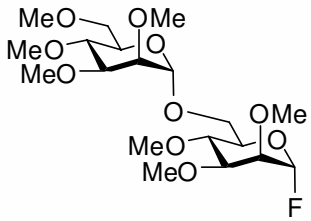

BnO
BnO
BnO
BnO
O
O
MeO
MeO
MeO
F

21β

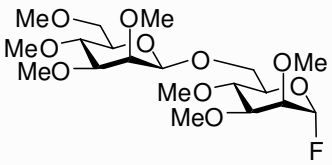
140
130
120
110
100
90
80
70
60
ppm (f1)



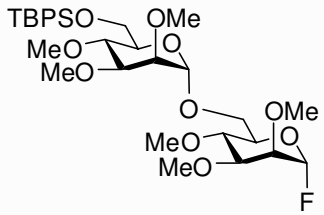
23α



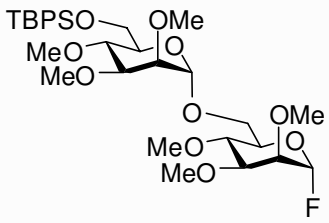
23α



23β

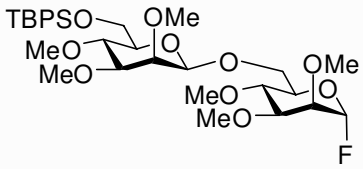


24α

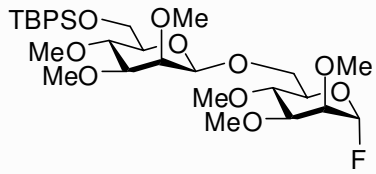

TBPSO
OMe
MeO
O
MeO
O
OMe
MeO
O
MeO
F

24α

130
120
110
100
90
80
70
60
50
40
30
20
ppm (f1)

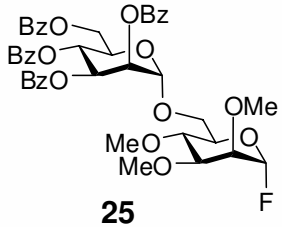


24β

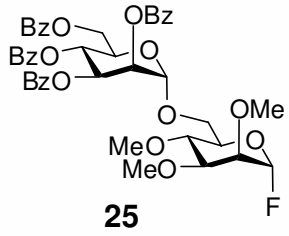

TBPSO
OMe
MeO
MeO
O
O
OMe
MeO
MeO
O
F

24β

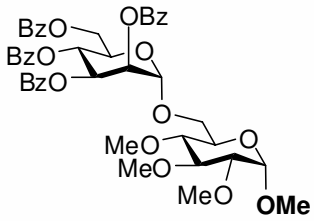
130
120
110
100
90
80
70
60
50
40
30
ppm



25

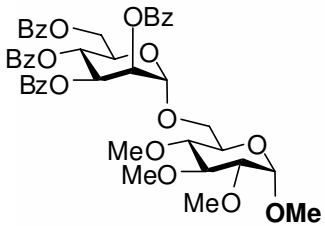


25

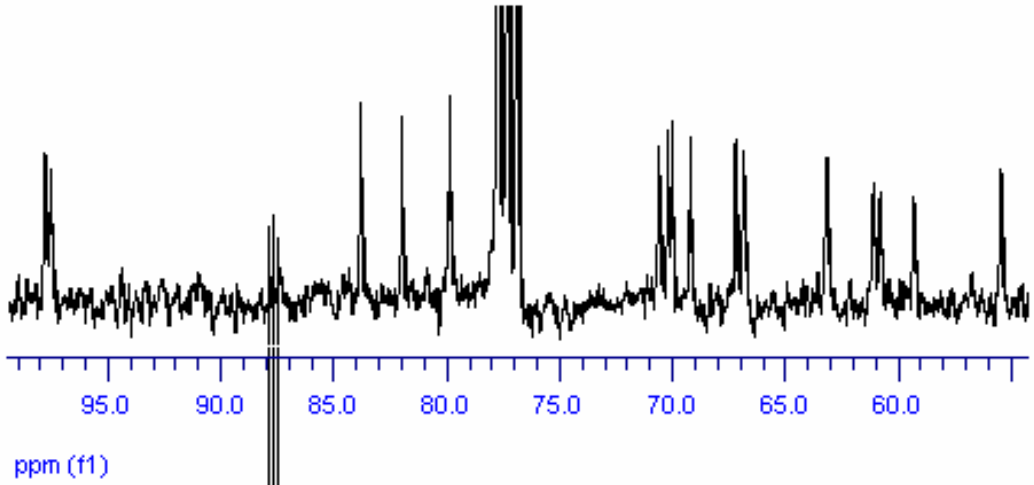

BzO
BzO
BzO
OBz
O
O
MeO
MeO
MeO
O
OMe

27

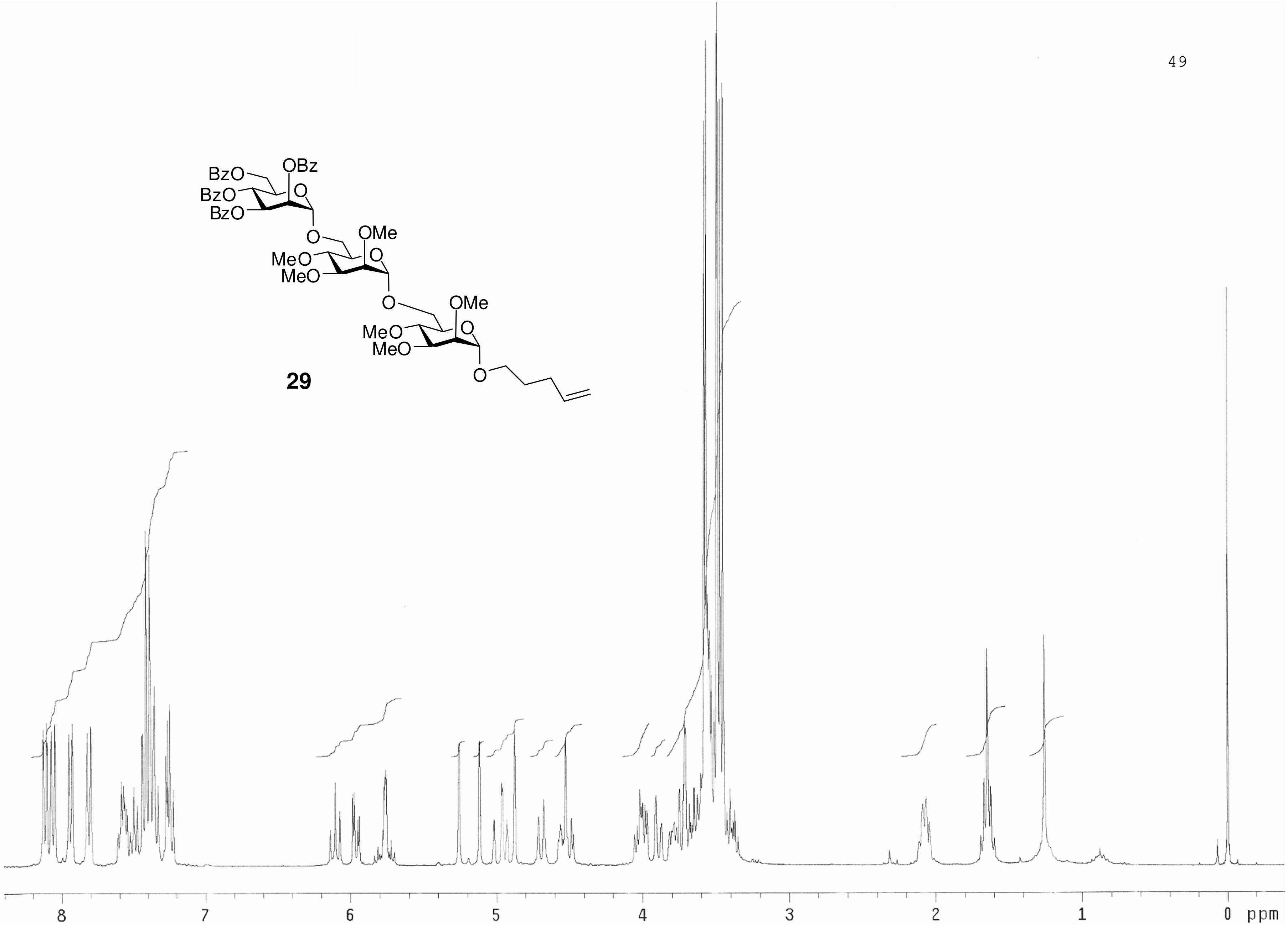
6.00
5.50
5.00
4.50
ppm (f1)
8.0
7.0
6.0
5.0
4.0
3.0
ppm (f1)

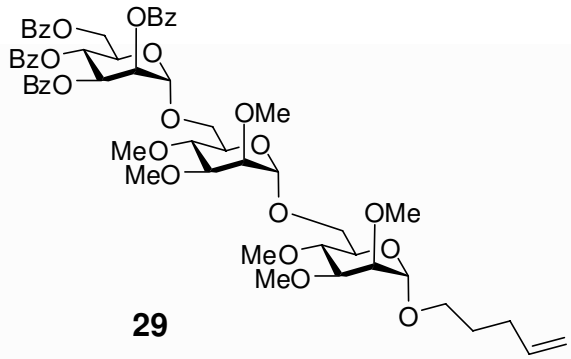

BzO
OBz
BzO
O
BzO
O
MeO
O
MeO
MeO
OMe

27


95.0
90.0
85.0
80.0
75.0
70.0
65.0
60.0
ppm (f1)

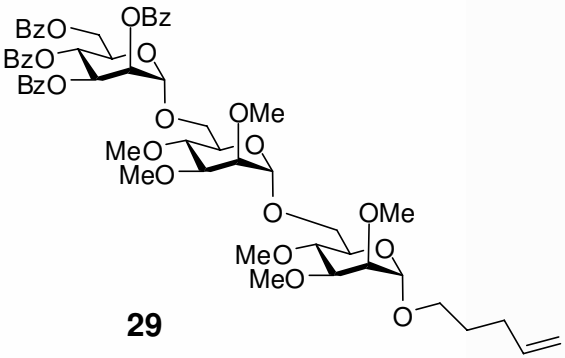
150
100
50
0
ppm (f1)


BzO
OBz
BzO
BzO
OMe
MeO
MeO
OMe
MeO
MeO
29
8
7
6
5
4
3
2
1
0 ppm


BzO
OBz
BzO
O
BzO
O
OMe
MeO
O
MeO
O
OMe
MeO
O
MeO
O

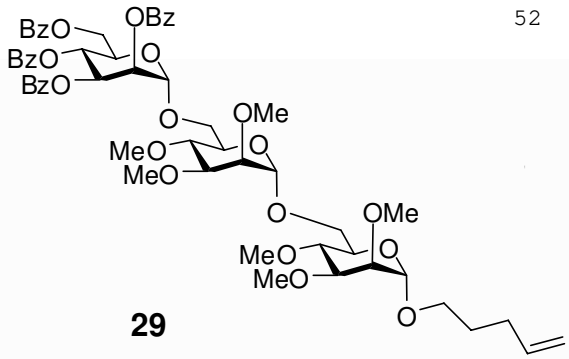
29

6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
ppm


BzO
OBz
BzO
O
BzO
O
OMe
MeO
O
MeO
O
OMe
MeO
O
MeO
O

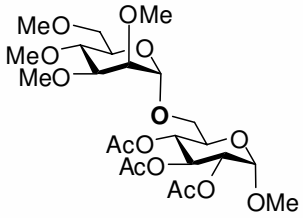
29

160
140
120
100
80
60
40
20
ppm

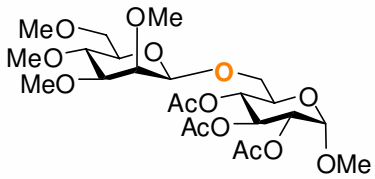

BzO
OBz
BzO
O
BzO
O
OMe
MeO
O
MeO
O
OMe
MeO
O
MeO
O

29

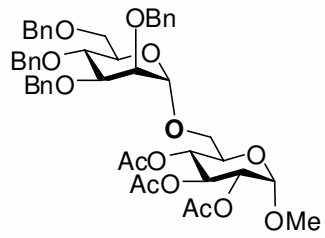
180
160
140
120
100
80
60
40
20
ppm



31α



31β



32