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Supporting Information

Intramolecular 1,8-Hydrogen Atom Transfer Reactions in (1? 4)-*O*-Disaccharide Systems. Conformational and Stereochemical Requirements.

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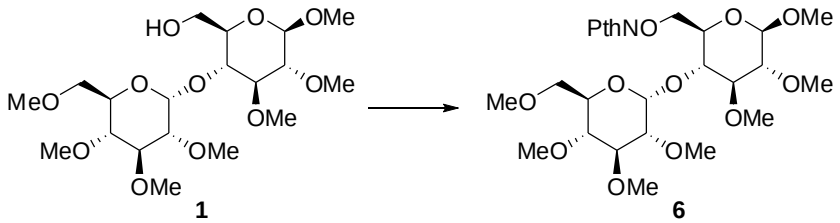
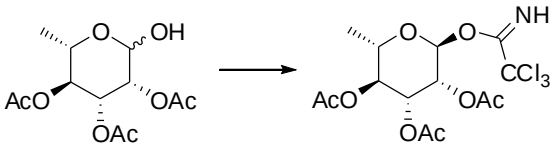
General Methods: Melting points were determined with a hot-stage apparatus. Optical rotations were measured at the sodium line at ambient temperature in $CHCl_3$ solutions. IR spectra were recorded in film unless otherwise stated. NMR spectra were determined at 500 MHz for ^1H and 125.7 MHz for ^{13}C in $CDCl_3$ unless otherwise stated, in the presence of TMS as internal standard. Mass spectra were determined at 70 eV unless otherwise stated. Merck silica gel 60 PF (0.063–0.2 mm) was used for column chromatography. Circular layers of 1 mm of Merck silica gel 60 PF_{254} were used on a Chromatotron for centrifugally assisted chromatography. Commercially available reagents and solvents were analytical grade or were purified by standard procedures prior to use. All reactions involving air- or moisture-sensitive materials were carried out under a nitrogen atmosphere. The spray reagents for TLC analysis were conducted with 0.5% vanillin in H_2SO_4 – EtOH (4:1) and further heating until development of colour.

General procedure for the synthesis of phthalimide derivatives: DEAD (2.5 mmol) was added dropwise to a stirred solution of the corresponding alcohol (1 mmol), *N*-hydroxyphthalimide (2.5 mmol) and PPh_3 (2.5 mmol) in dry THF (10.8 mL) under nitrogen at 0 ^oC and the resulting solution was stirred at this temperature for 0.5–4 h. Then the solvent was removed and the reaction was quenched with water and extracted with $CHCl_3$. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The obtained residue was purified by column chromatography to give the corresponding phthalimide derivatives**.**



Methyl 2,3,4,6-Tetra-*O*-methyl-*a*-D-glucopyranosyl-(1? 4)-2,3-di-*O*-methyl-6-*O*-phthalimido-*b*-D-glucopyranoside (6): Following the general procedure, using in this case DEAD (4 mmol), *N*-hydroxyphthalimide (4 mmol) and PPh_3 (4 mmol) in dry THF (2.7 mL) precursor **1** gave after column

chromatography (benzene–EtOAc, 6:4) the phthalimide **6** (82 %) as a syrup: $[\alpha]_D$ = +88.0 (*c* = 2.60 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): *d* = 2.98 (dd, *J* = 8.7, 8.7 Hz, 1H), 3.15 (dd, *J* = 9.8, 3.7 Hz, 1H), 3.19 (dd, *J* = 9.7, 9.7 Hz, 1H), 3.31 (s, 3H), 3.34 (s, 3H), 3.37 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.37 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.50 (s, 3H), 3.51 (s, 3H), 3.51 (s, 3H), 3.54 (m, 3H), 3.55 (s, 3H), 3.59 (s, 3H), 3.71 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.76 (dd, *J* = 10.0, 6.5 Hz, 1H), 4.14 (d, *J* = 7.7 Hz, 1H), 4.30 (dd, *J* = 12.5, 6.3 Hz, 1H), 4.51 (d, *J* = 12.5 Hz, 1H), 5.49 (d, *J* = 3.9 Hz, 1H), 7.71 (m, 2H), 7.79 (m, 2H); ^{13}C NMR (125.7 MHz, $CDCl_3$): *d* = 56.7 (CH_3), 59.1 (CH_3), 59.4 (CH_3), 59.7 (CH_3), 60.1 (CH_3), 60.3 (CH_3), 60.7 (CH_3), 70.7 (CH_2), 71.0 (CH), 73.5 (CH), 73.6 (CH), 76.8 (CH_2), 79.1 (CH), 81.5 (CH), 83.0 (CH), 83.5 (CH), 85.7 (CH), 97.1 (CH), 103.8 (CH), 123.3 (2 × CH), 128.9 (2 × C), 134.3 (2 × C), 163.3 (2 × C); IR (film): $\tilde{n}$ = 1734 cm^{-1}; MS (70 eV, EI): *m/z* (%): 586 (<1) $[M+H]^+$, 554 (<1), 522 (<1), 490 (<1), 410 (6); HRMS (EI): *m/z* (%): calcd for $C_{27}H_{40}NO_{13}$ $[M+H]^+$: 586.2499, found: 586.2490; elemental analysis calcd (%) for $C_{27}H_{39}NO_{13}$ (585.60): C 55.38, H 6.71, N 2.39; found: C 55.46, H 6.67, N 2.30.

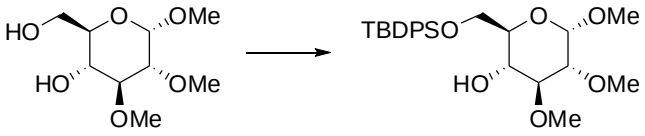


47S **48S**

2,3,4-Tri-*O*-acetyl-1-*O*-(2,2,2-trichloroethanimidoyl)-*a*-L-rhamnopyranose (48S):[1,2] To a solution of **47S**[3] (532 mg, 1.834 mmol) in dry CH_2Cl_2 (10.2 mL) were added trichloroacetonitrile (919 µL, 9.172 mmol) and NaH (17.5 mg, 2.384 mmol) under nitrogen and the mixture stirred at room temperature for 1 h. The reaction mixture was concentrated under reduced pressure and the residue purified by column chromatography (hexanes–EtOAc, 25:75) to give trichloroacetimidate **48S** (580 mg, 1.339 mmol, 73 %) as a colourless oil: $[a]_D$ = –43.8 (*c* = 0.420 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): *d* = 1.26 (d, *J* = 6.2 Hz, 3H), 1.99 (s, 3H), 2.06 (s, 3H), 2.18 (s, 3H), 4.08 (dddd, *J* = 9.9, 6.2, 6.2, 6.2 Hz, 1H), 5.16 (dd, *J* = 10.0, 10.0 Hz, 1H), 5.35 (dd, *J* = 10.2, 3.5 Hz, 1H), 5.44 (dd, *J* = 3.4, 2.0 Hz, 1H), 6.19 (d, *J* = 1.9 Hz, 1H), 8.72 ppm (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *d* = 17.4 (CH_3), 20.6 (CH_3), 20.7 (2 × CH_3), 68.1

[1] Numbers ending in S refer to products only cited in the Supporting Information.
[2] J. Wang, J. Li, D. Tuttle, J. Y. Takemoto, C.-W. T. Chang, *Org. Lett*. **2002**, *4*, 3997- 4000.
[3] M. K. Gurjar, A. S. Mainkar, *Tetrahedron* **1992**, *48*, 6729–6738.

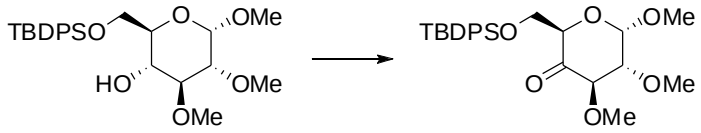
(CH), 68.8 (CH), 69.3 (CH), 70.3 (CH), 90.6 (C), 94.7 (CH), 159.9 (C), 169.7 (C), 169.8 (2 × C); IR (film): $\tilde{n}$ = 3324, 2988, 1748, 1681, 1372, 1222, 1049 cm^{-1}; MS (70 eV, EI): *m/z* (%): 273 (34) [*M*–$OCNHCCl_3$]$^+$, 230 (22), 157 (48), 111 (100); HRMS (EI): *m/z* calcd for $C_{12}H_{17}O_7$ [*M*–$OCNHCCl_3$]$^+$: 273.0974, found: 273.0974; elemental analysis calcd (%) for $C_{14}H_{18}Cl_3NO_8$ (434.65): C 38.69; H 4.17; N 3.22; found: C 38.56; H 4.07; N 3.55.



49S **50S**

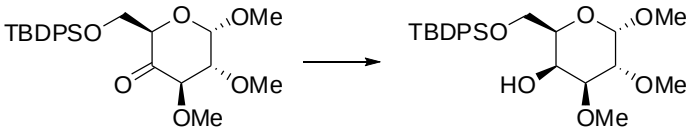
Methyl 6-*O*-*tert*-Butyldiphenylsilyl-2,3-di-*O*-methyl-*a*-D-glucopyranoside (50S): To a solution of diol **49S**[4] (715 mg, 3.22 mmol) in dry DMF (12.5 mL) were added imidazole (657 mg, 9.66 mmol) and TBDPSCl (0.9 mL, 3.54 mmol) under nitrogen at 0 °C and the mixture stirred at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure and the residue poured into ice-water and extracted with Et_2O. The extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc, 70:30) to give the alcohol **50S** (1.46 g, 3.17 mmol, 98 %) as a colourless oil: $[a]_D$ = +143.0 (*c* = 0.348 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): *d* = 1.06 (s, 9H), 2.69 (s, 1H), 3.22 (dd, *J* = 9.4, 3.6 Hz, 1H), 3.39 (s, 3H), 3.47 (dd, *J* = 9.3, 9.3 Hz, 1H), 3.51 (s, 3H), 3.56 (dd, *J* = 9.3, 9.3 Hz, 1H), 3.648 (s, 3H), 3.652 (ddd, *J* = 9.2, 4.5, 4.5 Hz, 1H), 3.86 (dd, *J* = 10.8, 4.6 Hz, 1H), 3.88 (dd, *J* = 10.8, 4.4 Hz, 1H), 4.82 (d, *J* = 3.5 Hz, 1H), 7.37–7.45 (m, 6H), 7.68–7.72 ppm (m, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$): *d* = 19.2 (C), 26.7 (3 × CH_3), 55.0 (CH_3), 58.5 (CH_3), 61.2 (CH_3), 64.4 (CH_2), 70.6 (CH), 71.7 (CH), 81.7 (CH), 82.8 (CH), 97.3 (CH), 127.7 (4 × CH), 129.7 (2 × CH), 133.1 (2 × C), 133.6 ppm (4 × CH); IR (film): $\tilde{n}$ = 3449, 3048, 2932, 1428, 1059 cm^{-1}; MS (70 eV, EI): *m/z* (%): 371 (5) [*M*–C_4H_9–CH_3OH]$^+$, 339 (6), 293 (2), 241 (18), 199 (100); HRMS (EI): *m/z* calcd for $C_{20}H_{23}O_5Si$ [*M*–C_4H_9–CH_3OH]$^+$: 371.1318, found: 371.1315; elemental analysis calcd (%) for $C_{25}H_{36}O_6Si$ (460.64): C 65.19, H 7.88; found: C 65.19, H 7.99.

[4] a) L. Weiler, D. Nicoll-Griffith, *Tetrahedron* **1991**, *47*, 2733–2750; b) D. Trimnell, W. M. Doane, C. R. Russell, C. E. Rist, *Carbohydr. Res.* **1969**, *11*, 497–507.



50S **51S**

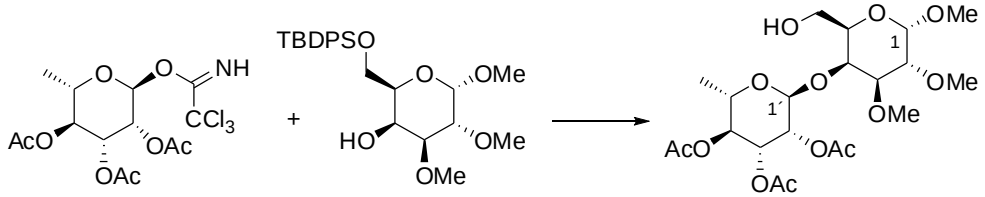
Methyl 6-*O*-*tert*-Butyldiphenylsilyl-2,3-di-*O*-methyl-*a*-D-*xylo*-hexopyranosid-4-ulose (51S): To a solution of alcohol **50S** (1 g, 2.17 mmol) in dry Et_2O (24 mL) containing DMSO (1.1 mL, 15.2 mmol), pyridine (175 µL, 2.17 mmol), and DCC (2.23 g, 10.8 mmol) was added TFA (167 µL, 2.17 mmol) under nitrogen at 0 °C. The reaction mixture was stirred at room temperature for 2 h. After this time oxalic acid (390 mg, 4.34 mmol) was added at 0 °C and the stirring continued at room temperature for 0.5 h. The reaction mixture was filtered over Celite, poured into brine and extracted with Et_2O. The organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc, 70:30) to give ketone **51S** (784 mg, 1.69 mmol, 79 %) as a colourless oil: $[a]_D$ = +52.8 (*c* = 0.718 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): *d* = 1.04 (s, 9H), 3.52 (dd, *J* = 9.9, 3.4 Hz, 1H), 3.54 (s, 3H), 3.56 (s, 3H), 3.58 (s, 3H), 3.89 (dd, *J* = 11.3, 6.5 Hz, 1H), 4.08 (d, *J* = 9.9 Hz, 1H), 4.08 (dd, *J* = 13.0, 3.1 Hz, 1H), 4.19 (dd, *J* = 6.5, 3.2 Hz, 1H), 5.03 (d, *J* = 3.4 Hz, 1H), 7.36–7.45 (m, 6H), 7.68–7.69 ppm (m, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$): *d* = 19.2 (C), 26.7 (3 × CH_3), 55.8 (CH_3), 59.6 (CH_3), 60.2 (CH_3), 61.9 (CH_2), 74.1 (CH), 82.5 (CH), 84.4 (CH), 97.5 (CH), 127.6 (4 × CH), 129.7 (2 × CH), 133.2 (C), 133.3 (C), 135.6 (2 × CH), 135.6 (2 × CH), 202.1 ppm (C); IR (film): $\tilde{n}$ = 3049, 2931, 2857, 1735 (C=O), 1428, 1112, 1053 cm^{-1}; MS (70 eV, EI): *m/z* (%): 427 (<1) $[M–CH_3O]^+$, 369 (54), 255 (55), 199 (54), 101 (100); HRMS (EI): *m/z* calcd for $C_{24}H_{31}O_5$ $[M–CH_3O]^+$: 427.1941, found: 427.1941; elemental analysis calcd (%) for $C_{25}H_{34}O_6Si$ (458.62): C 65.47, H 7.47; found: C 65.48, H 7.20.



51S **52S**

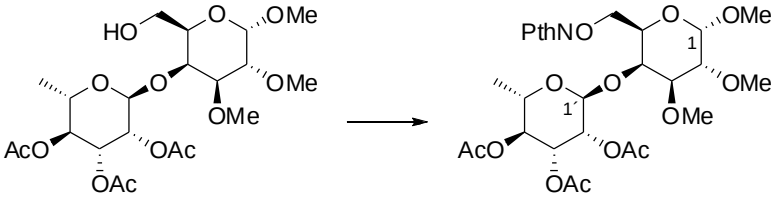
Methyl 6-*O*-*tert*-Butyldiphenylsilyl-2,3-di-*O*-methyl-*a*-D-galactopyranoside (52S): To a solution of ketone **51S** (837 mg, 1.827 mmol) in EtOH/H_2O (6.8 mL, 9/1) was added $NaBH_4$ (125 mg, 3.289 mmol)

and the mixture stirred at room temperature for 1 h. After this time the mixture was cooled to 0 °C, solid NH_4Cl was added and stirring was continued for 1 h. The mixture was then filtered over Celite and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc, 85:15) to give the alcohol **52S** (575 mg, 1.25 mmol, 68 %) and the alcohol **50S** (267 mg, 0.580 mmol, 32 %), described previously. Compound **52S**: $[a]_D$ = +80.6 (*c* = 0.320 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): *d* = 1.07 (s, 9H), 2.54 (br s, 1H), 3.38 (s, 3H), 3.50 (s, 3H), 3.51 (s, 3H), 3.51 (dd, *J* = 9.5, 3.2 Hz, 1H), 3.59 (dd, *J* = 9.8, 3.7 Hz, 1H), 3.76 (ddd, *J* = 5.8, 5.8, 0.8 Hz, 1H), 3.86 (dd, *J* = 10.3, 5.6 Hz, 1H), 3.94 (dd, *J* = 10.6, 6.1 Hz, 1H), 4.17 (dd, *J* = 3.2, 1.1 Hz, 1H), 4.87 (d, *J* = 3.4 Hz, 1H), 7.36–7.45 (m, 6H), 7.68–7.71 ppm (m, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$): *d* = 19.2 (C), 26.8 (3 × CH_3), 55.1 (CH_3), 57.7 (CH_3), 58.9 (CH_3), 63.4 (CH_2), 66.6 (CH), 69.7 (CH), 77.5 (CH), 79.3 (CH), 97.7 (CH), 127.7 (6 × CH), 129.7 (2 × CH), 133.2 (C), 133.3 (C), 135.6 ppm (2 × CH); IR (film): $\tilde{n}$ = 3478, 3071, 2932, 1428, 1104, 1050 cm^{-1}; MS (70 eV, EI): *m/z* (%): 371 (4) $[M–C_4H_9–CH_3OH]^+$, 339 (14), 311 (12), 255 (13), 237 (100); HRMS (EI): *m/z* calcd for $C_{20}H_{23}O_5Si$ $[M–C_4H_9–CH_3OH]^+$: 371.1315, found: 371.1318; elemental analysis calcd (%) for $C_{25}H_{36}O_6Si$ (460.64): C 65.19, H 7.88; found: C 65.12, H 7.86.



Methyl 2,3,4-Tri-*O*-acetyl-*a*-L-rhamnopyranosyl-(1? 4)-2,3-di-*O*-methyl-*a*-D-galactopyranoside (10): To a solution of trichloroacetimidate **48S** (450 mg, 1.083 mmol) and alcohol **52S** (217 mg, 0.472 mmol) in dry CH_2Cl_2 (9 mL) containing molecular sieves 3Å (217 mg) was added a 0.1 M solution of TMSOTf/CH_2Cl_2 (240 µL, 0.024 mmol) under nitrogen at 0 °C and the mixture stirred at this temperature for 1.5 h. The reaction mixture was poured into a saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. To the residue in dry THF (12.2 mL) was added a 1 M solution of Bu_4NF/THF (1.2 mL, 1.18 mmol) under nitrogen and the mixture stirred at room temperature for 19 h. After this time the solvent

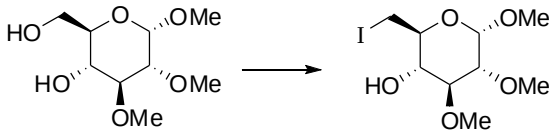
was evaporated under reduced pressure and the residue purified by column chromatography (hexanes–EtOAc, 30:70) to give the disaccharide **10** (209 mg, 0.423 mmol, 90 %) as a white crystalline solid: m.p. 154.5–156.2 °C (from acetone–*n*-hexane); $[a]_D$ = +27.0 (*c* = 0.315 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): *d* = 1.23 (d, *J* = 6.3 Hz, 3H), 1.99 (s, 3H), 2.05 (s, 3H), 2.14 (s, 3H), 3.42 (s, 3H), 3.47 (s, 3H), 3.53 (s, 3H), 3.56 (dd, *J* = 10.1, 2.9 Hz, 1H), 3.64 (dd, *J* = 10.1, 3.5 Hz, 1H), 3.66 (m, 1H), 3.80–3.86 (m, 2H), 3.98 (dddd, *J* = 9.7, 6.2, 6.2, 6.2 Hz, 1H), 4.11 (dd, *J* = 2.6, 0 Hz, 1H), 4.87 (d, *J* = 3.5 Hz, 1H), 5.05 (d, *J* = 1.9 Hz, 1H), 5.07 (dd, *J* = 9.9, 9.9 Hz, 1H), 5.31 (dd, *J* = 10.0, 3.3 Hz, 1H), 5.47 ppm (dd, *J* = 3.3, 2.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *d* = 17.5 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 55.4 (CH_3), 58.7 (CH_3), 59.2 (CH_3), 62.0 (CH_2), 67.5 (CH), 69.0 (CH), 69.8 (CH), 69.9 (CH), 70.9 (CH), 75.1 (CH), 78.0 (CH), 79.8 (CH), 98.1 (CH), 99.7 (CH), 169.8 (C), 169.9 (C), 170.0 ppm (C); IR (film): $\tilde{n}$ = 3486, 2937, 2840, 1748, 1372, 1224, 1046 cm^{-1}; MS (FAB): *m/z* (%): 517 (4) $[M+Na]^+$, 495 (3) $[M+H]^+$, 273 (100); HRMS (FAB): *m/z* calcd for $C_{21}H_{34}O_{13}Na$ $[M+Na]^+$: 517.1897, found: 517.1905; elemental analysis calcd (%) for $C_{21}H_{34}O_{13}$ (494.49): C 51.01, H 6.93; found: C 51.19, H 6.95.



10 **15**

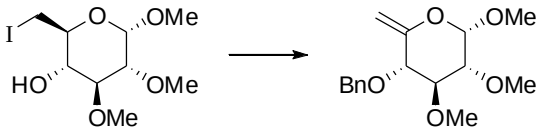
Methyl 2,3,4-Tri-*O*-acetyl-*a*-L-rhamnopyranosyl-(1? 4)-2,3-di-*O*-methyl-6-*O*-phthalimido-*a*-D-galactopyranoside (15): Following the general procedure, the alcohol **10** gave after column chromatography (hexanes–EtOAc, 80:20) the phthalimide **15** (84 %) as an amorphous solid: $[a]_D$ = +17.5 (*c* = 0.245 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): *d* = 1.15 (d, *J* = 6.3 Hz, 3H), 1.97 (s, 3H), 2.04 (s, 3H), 2.12 (s, 3H), 3.44 (s, 3H), 3.48 (s, 3H), 3.52 (s, 3H), 3.59 (dd, *J* = 10.1, 2.7 Hz, 1H), 3.66 (dd, *J* = 10.1, 3.5 Hz, 1H), 3.95 (dddd, *J* = 9.9, 6.3, 6.3, 6.3 Hz, 1H), 4.13 (ddd, *J* = 6.1, 6.1, 0 Hz, 1H), 4.33 (dd, *J* = 11.1, 5.9 Hz, 1H), 4.36 (dd, *J* = 11.1, 6.2 Hz, 1H), 4.40 (dd, *J* = 1.1, 0 Hz, 1H), 4.87 (d, *J* = 3.5 Hz, 1H), 5.05 (dd, *J* = 9.9, 9.9 Hz, 1H), 5.07 (d, *J* = 1.5 Hz, 1H), 5.29 (d, *J* = 10.1, 3.3 Hz, 1H), 5.50 (dd, *J* = 3.0, 2.1 Hz, 1H), 7.76 (m, 2H), 7.84 ppm (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *d* = 17.3 (CH_3), 20.7 (CH_3),

20.8 (CH_3), 20.9 (CH_3), 55.8 (CH_3), 58.6 (CH_3), 59.3 (CH_3), 67.3 (CH), 67.6 (CH), 69.1 (CH), 69.9 (CH), 70.8 (CH), 75.0 (CH), 77.4 (CH_2), 77.6 (CH), 79.6 (CH), 98.4 (CH), 99.3 (CH), 123.6 (2 × CH), 128.8 (2 × C), 134.6 (2 × CH), 163.5 (2 × C), 169.8 (C), 169.9 (C), 170.0 ppm (C); IR (film): $\tilde{n}$ = 2939, 2835, 1791, 1735, 1372, 1225, 1044 cm^{-1}; MS (FAB): *m/z* (%): 663 (3) $[M+Na+H]^+$, 662 (9) $[M+Na]^+$, 273 (28), 55 (100); HRMS (FAB): *m/z* calcd for $C_{29}H_{38}NO_{15}Na$ $[M+Na+H]^+$: 663.2139, found: 663.2166; elemental analysis calcd (%) for $C_{29}H_{37}NO_{15}$ (639.60): C 54.46, H 5.83, N, 2.19; found: C 54.10, H 5.78, N 2.68.



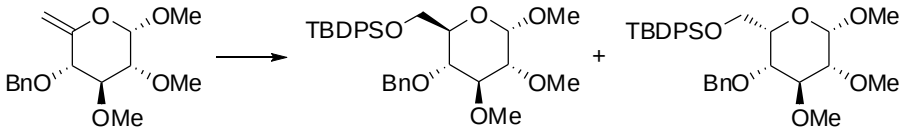
49S **53S**

Methyl 6-Deoxy-6-iodo-2,3-di-*O*-methyl-*a*-D-glucopyranoside (53S): To a solution of diol **49S** (3.04 g, 13.7 mmol) in dry toluene (150 mL) were added PPh_3 (4.3 g, 16.44 mmol), imidazole (1.39 g, 20.55 mmol) and iodine (5.21 g, 20.55 mmol), and the mixture heated to 100 ºC for 1 h. The reaction mixture was poured into a saturated solution of $NaHCO_3$ and extracted with EtOAc. The organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Column chromatography of the residue (hexanes–EtOAc, 70:30 ? 60:40) gave the iodo-derivative **53S** (3.95 g, 11.9 mmol, 92 %) as a dark oil: $[a]_D$ = +87.6 (*c* = 0.324 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): *d* = 2.64 (d, *J* = 2.8 Hz, 1H), 3.24 (dd, *J* = 9.5, 3.6 Hz, 1H), 3.27 (ddd, *J* = 9.1, 9.1, 2.7 Hz, 1H), 3.32 (dd, *J* = 10.6, 6.8 Hz, 1H), 3.42 (ddd, *J* = 9.3, 6.8, 2.4 Hz, 1H), 3.46 (dd, *J* = 9.1, 9.1 Hz, 1H), 3.48 (s, 3H), 3.49 (s, 3H), 3.57 (dd, *J* = 10.6, 2.4 Hz, 1H), 3.62 (s, 3H), 4.86 ppm (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): *d* = 7.1 (CH_2), 55.5 (CH_3), 58.4 (CH_3), 61.2 (CH_3), 69.7 (CH), 73.7 (CH), 81.9 (CH), 82.3 (CH), 97.4 ppm (CH); IR (film): $\tilde{n}$ = 3436, 2925, 2849, 1454, 1071 cm^{-1}; MS (70 eV, EI): *m/z* (%): 300 (2) $[M–CH_3OH]^+$, 205 (<1), 89 (100); HRMS (EI): *m/z* calcd for $C_8H_{13}IO_4$ $[M–CH_3OH]^+$: 299.9859, found: 299.9850; elemental analysis calcd (%) for $C_9H_{17}IO_5$ (332.13): C 32.55, H 5.16; found: C 32.42, H 5.14.



53S **54S**

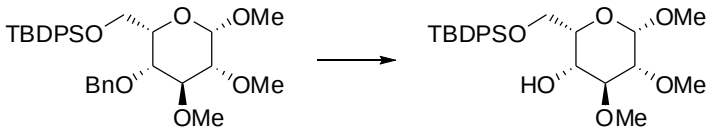
Methyl 4-*O*-Benzyl-6-deoxy-2,3-di-*O*-methyl-*a*-D-*xylo*-hex-5-enopyranoside (54S): To a solution of **53S** (500 mg, 1.5 mmol) in dry DMF (20 mL) were added BnBr (358 µL, 3.01 mmol) and NaH (452 mg, 15.0 mmol) under nitrogen and the mixture stirred at room temperature for 72 h. The reaction mixture was poured into ice-water and extracted with Et_2O. The extracts were dried over anhydrous Na_2SO_4 and concentrated and the residue purified by column chromatography (hexanes–EtOAc, 60:40) to give the olefin **54S** (416 mg, 1.4 mmol, 88 %) as a colourless oil: $[a]_D$ = +62.3 (*c* = 0.154 in $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6): *d* = 3.19 (s, 6H), 3.20 (dd, *J* = 9.5, 3.2 Hz, 1H), 3.50 (s, 3H), 3.87- 3.90 (m, 2H), 4.66 (d, *J* = 11.7 Hz, 1H), 4.67 (d, *J* = 3.2 Hz, 1H), 4.72 (d, *J* = 11.6 Hz, 1H), 4.82 (br d, *J* = 1.1 Hz, 1H), 5.05 (br d, *J* = 1.3 Hz, 1H), 7.09 (m, 1H), 7.15–7.19 (m, 2H), 7.28- 7.35 ppm (m, 2H); ^{13}C NMR (100.6 MHz, C_6D_6): *d* = 55.1 (CH_3), 58.3 (CH_3), 60.8 (CH_3), 74.2 (CH_2), 79.9 (CH), 82.1 (CH), 83.2 (CH), 96.6 (CH_2), 98.9 (CH), 127.7- 128.5 (5 × CH), 139.0 (C), 154.8 ppm (CH); IR (film): $\tilde{n}$ = 2930, 2837, 1662, 1454, 1161, 1087, 1011 cm^{-1}; MS (70 eV, EI): *m/z* (%): 249 (7) [*M*- CH_2OCH_3]$^+$, 232 (4), 177 (9), 121 (8), 91 (100); HRMS (EI): *m/z* calcd for $C_{14}H_{17}O_4$ [*M*- CH_2OCH_3]$^+$: 249.1127, found: 249.1123; elemental analysis calcd (%) for $C_{16}H_{22}O_5$ (294.34): C 65.29, H 7.53; found: C 65.23, H 7.57.



54S **55S** **56S**

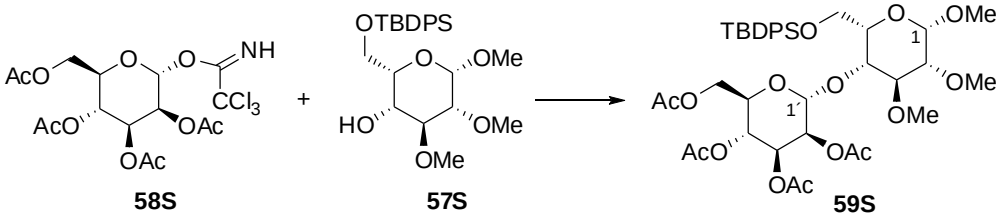
Methyl 4-*O*-Benzyl-6-*O*-*tert*-butyldiphenylsilyl-2,3-di-*O*-methyl-*ß*-L-idopyranoside (4e): To a solution of olefin **54S** (1.35 g, 4.6 mmol) in dry THF (25 mL) under nitrogen was added dropwise a solution of BH_3·THF complex (23 mL, 23 mmol, 1 M in THF). After 2 h of stirring, the excess borane was quenched carefully by adding a drop of water. Dropwise addition of a mixture of 1 M NaOH (7.5 mL) and 30% hydrogen peroxide (7.5 mL), removal of the cooling bath, and continued stirring for 30 min resulted in a heterogeneous white mixture. The reaction mixture was then poured into ice-water, washed

with brine, extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated in vacuum. To the residue in dry DMF (33 mL) were added imidazole (959 mg, 14.1 mmol) and TBDPSCl (1.1 mL, 4.23 mmol) under nitrogen and the mixture stirred at room temperatura for 1 h. The reaction mixture was concentrated under reduced pressure and the residue purified by column chromatography (hexanes–EtOAc, 80:20) to yield methyl 4-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2,3-di-*O*-methyl-*a*-D-glucopyranoside (**55S**) (187 mg, 0.34 mmol, 7 %) and compound **54S** (942 mg, 1.71 mmol, 37 %), both as colourless oils. Compound **55S**: $[a]_D$ = +61.5 (*c* = 0.574 in $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6): *d* = 1.20 (s, 9H), 3.16 (s, 3H), 3.20 (s, 3H), 3.26 (dd, *J* = 9.5, 3.4 Hz, 1H), 3.56 (s, 3H), 3.70 (dd, *J* = 10.1, 9.0 Hz, 1H), 3.83 (ddd, *J* = 9.8, 3.2, 3.2 Hz, 1H), 3.90 (dd, *J* = 9.1, 9.1 Hz, 1H), 3.98- 3.99 (m, 2H), 4.68 (d, *J* = 11.7 Hz, 1H), 4.74 (d, *J* = 3.4 Hz, 1H), 5.00 (d, *J* = 11.4 Hz, 1H), 7.10- 7.29 (m, 11H), 7.82- 7.89 ppm (m, 4H); ^{13}C NMR (100.6 MHz, C_6D_6): *d* = 19.6 (C), 27.0 (3 × CH_3), 54.7 (CH_3), 57.9 (CH_3), 60.8 (CH_3), 63.6 (CH_2), 72.0 (CH), 74.9 (CH_2), 78.3 (CH), 82.8 (CH), 84.3 (CH), 97.8 (CH), 127.5- 128.4 (10 × CH), 129.9 (2 × CH), 133.9 (C), 134.1 (C), 136.0 (2 × CH), 136.2 (2 × CH), 139.5 ppm (C); IR (film): $\tilde{n}$ = 3069, 2930, 2856, 1472, 1159, 1112, 1034 cm^{-1}; MS (FAB): *m/z* (%): 573 (15) [*M*+Na]$^+$, 459 (<1), 281 (3), 91 (100); HRMS (FAB): *m/z* calcd for $C_{32}H_{42}O_6NaSi$ [*M*+Na]$^+$: 573.2648, found: 573.2659; elemental analysis calcd (%) for $C_{32}H_{42}O_6Si$ (550.76): C 69.78, H 7.69; found: C 69.82, H 7.81. Compound **56S**: $[a]_D$ = +12.4 (*c* = 0.290 in $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6): *d* = 1.19 (s, 9H), 3.21 (dd, *J* = 7.3, 3.1 Hz, 1H), 3.29 (s, 3H), 3.32 (s, 3H), 3.41 (s, 3H), 3.59 (dd, *J* = 7.0, 4.8 Hz, 1H), 3.69 (dd, *J* = 7.3, 7.3 Hz, 1H), 4.24- 4.28 (m, 2H), 4.34 (d, *J* = 11.8 Hz, 1H), 4.36 (m, 1H), 4.44 (d, *J* = 11.8 Hz, 1H), 4.73 (d, *J* = 3.1 Hz, 1H), 7.07- 7.22 (m, 11H), 7.78- 7.82 ppm (m, 4H); ^{13}C NMR (125.7 MHz, C_6D_6): *d* = 19.5 (C), 27.1 (3 × CH_3), 56.4 (CH_3), 58.8 (CH_3), 59.6 (CH_3), 64.1 (CH_2), 72.4 (CH_2), 76.1 (CH), 77.2 (CH), 78.6 (CH), 80.5 (CH), 100.5 (CH), 127.5- 128.4 (9 × CH), 129.9 (2 × CH), 134.0 (C), 134.2 (C), 136.01 (2 × CH), 136.04 (2 × CH), 139.0 ppm (C); IR (film): $\tilde{n}$ = 3051, 2930, 1480, 1095 cm^{-1}; MS (FAB): *m/z* (%): 573 (17) [*M*+Na]$^+$, 537 (5), 91 (100); HRMS (FAB): *m/z* calcd for $C_{32}H_{42}O_6NaSi$ [*M*+Na]$^+$: 573.2648, found: 573.2659; elemental analysis calcd (%) for $C_{32}H_{42}O_6Si$ (550.76): C 69.78, H 7.69; found: C 69.71, H 7.78.



56S **57S**

Methyl 6-*O*-*tert*-Butyldiphenylsilyl-2,3-di-*O*-methyl-ß-L-idopyranoside (57S): To a solution of compound **56S** (50 mg, 0.091 mmol) in EtOAc (1 mL) was added 10% Pd/C (30 mg) and the mixture stirred at room temperature for 24 h under a hydrogen atmosphere. After the catalyst was filtered off, the solvent was removed under reduced pressure to afford the alcohol **57S** (39 mg, 0.084 mmol, 93 %) as a colourless oil: $[a]_D$ = +49.8 (*c* = 0.913 in $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6): *d* = 1.20 (s, 9H), 2.95 (s, 3H), 3.25 (s, 3H), 3.27 (ddd, *J* = 3.4, 1.1, 1.1 Hz, 1H), 3.28 (s, 3H), 3.55 (dd, *J* = 3.2, 3.2 Hz, 1H), 3.70 (d, *J* = 11.6 Hz, 1H), 3.89 (d, *J* = 11.7, 2.9, 1.3, 1.3 Hz, 1H), 4.10 (dd, *J* = 6.6, 6.6, 1.3 Hz, 1H), 4.20 (dd, *J* = 10.0, 6.1 Hz, 1H), 4.32 (dd, *J* = 9.8, 6.6 Hz, 1H), 4.62 (d, *J* = 1.1 Hz, 1H), 7.19- 7.26 (m, 6H), 7.83- 7.89 ppm (m, 4H); ^{13}C NMR (100.6 MHz, C_6D_6): *d* = 19.5 (C), 27.1 (3 × CH_3), 56.4 (CH_3), 57.2 (CH_3), 60.3 (CH_3), 63.6 (CH_2), 65.8 (CH), 76.2 (CH), 77.9 (CH), 78.7 (CH), 101.6 (CH), 128.0 (4 × CH), 129.88 (CH), 129.93 (CH), 134.0 (C), 134.1 (C), 136.0 (2 × CH), 136.1 ppm (2 × CH); IR (film): $\tilde{n}$ = 3506, 2931, 2856, 1105, 1046 cm^{-1}; MS (FAB): *m/z* (%): 483 (28) $[M+Na]^+$, 237 (24), 221 (44), 135 (81), 73 (100); HRMS (FAB): *m/z* calcd for $C_{25}H_{36}O_6NaSi$ $[M+Na]^+$: 483.2179, found: 483.2181; elemental analysis calcd (%) for $C_{32}H_{42}O_6Si$ (460.64): C 65.19, H 7.88; found: C 65.22, H 7.84.

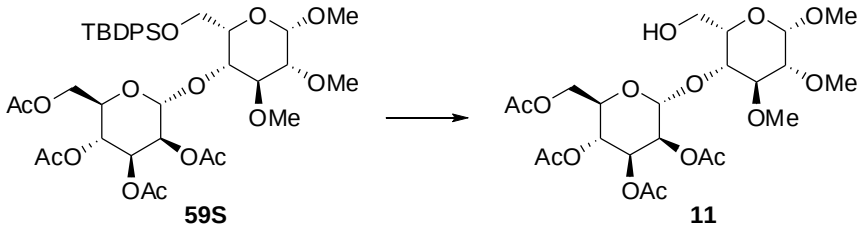


58S **57S** **59S**

Methyl 2,3,4,6-Tetra-*O*-acetyl-*a*-D-mannopyranosyl-(1? 4)-6-*O*-*tert*-butyldiphenylsilyl-2,3-di-*O*-methyl-ß-L-idopyranoside (59S): To a solution of trichloroacetimidate **58S**[5] (125 mg, 0.255 mmol) and alcohol **57S** (47 mg, 0.101 mmol) in dry CH_2Cl_2 (2.5 mL) containing molecular sieves 3Å (100 mg) was added over a period of 20 minutes a 0.1 M solution of $BF_3{\cdot}Et_2O/CH_2Cl_2$ (0.5 mL, 0.05 mmol) under

[5] (a) M. Upreti, D. Ruhela, R. A. Vishwakarma, *Tetrahedron* **2000**, *56*, 6577–6584; (b) R. R. Schmidt, *Angew. Chem.* **1986**, *98*, 213–236. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 212–235.

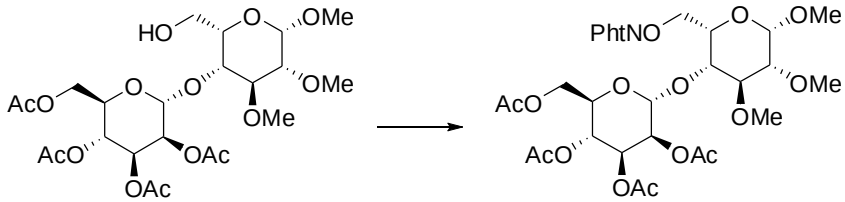
nitrogen and the mixture was stirred at this temperature for 0.5 h. The reaction mixture was poured into a saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by chromatotron chromatography (hexanes–EtOAc, 70:30) to give the disaccharide **59S** (48.7 mg, 0.061 mmol, 61 %) as a foam: $[a]_D$ = +39.8 (*c* = 0.264 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 1.06 (s, 9H), 1.95 (s, 3H), 1.98 (s, 3H), 2.04 (s, 3H), 2.14 (s, 3H), 3.26 (dd, *J* = 5.8, 2.3 Hz, 1H), 3.42 (s, 3H), 3.50 (s, 6H), 3.65 (dd, *J* = 5.9, 5.9 Hz, 1H), 3.81 (dd, *J* = 5.6, 3.2 Hz, 1H), 3.89 (dd, *J* = 12.2, 2.1 Hz, 1H), 3.93–4.04 (m, 4H), 4.14 (dd, *J* = 12.2, 5.0 Hz, 1H), 4.64 (d, *J* = 2.7 Hz, 1H), 5.09 (s, 1H), 5.23–5.28 (m, 3H), 7.37–7.44 (m, 6H), 7.66–7.70 ppm (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *d* = 19.2 (C), 20.6 (2 × CH_3), 20.7 (CH_3), 20.8 (CH_3), 26.9 (3 × CH_3), 56.7 (CH_3), 59.4 (CH_3), 59.6 (CH_3), 62.3 (CH_2), 63.0 (CH_2), 68.9 (3 × CH), 69.7 (CH), 72.3 (CH), 75.3 (CH), 76.3 (CH), 79.0 (CH), 96.9 (CH), 99.9 (CH), 127.8 (14 × CH), 129.7 (CH), 129.8 (CH), 133.3 (C), 133.5 (C), 135.5 (CH), 135.6 (CH), 169.4 (C), 169.6 (C), 169.9 (C), 170.5 ppm (C); IR (film): $\tilde{n}$ = 3059, 2933, 2858, 1751, 1225 cm^{-1}; MS (70 eV, EI): *m/z* (%): 733 (1) $[M–C_4H_9]^+$, 701 (1), 492 (1), 331 (97), 169 (100); HRMS (EI): *m/z* calcd for $C_{35}H_{45}O_{15}Si$ $[M–C_4H_9]^+$: 733.2528, found: 733.2548; elemental analysis calcd (%) for $C_{39}H_{54}O_{15}Si$ (790.92): C 59.22, H 6.88; found: C 59.19, H 7.07.



59S **11**

Methyl 2,3,4,6-Tetra-*O*-acetyl-*a*-D-mannopyranosyl-(1? 4)-2,3-di-*O*-methyl-*ß*-L-idopyranoside (11): To a solution of compound **59S** (150 mg, 0.189 mmol) in dry THF (5 mL) was added a 1 M solution of Bu_4NF/THF (378 µL, 0.378 mmol), and the mixture was stirred at room temperature for 12 h. The reaction mixture was poured into a saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Column chromatography of the reaction residue (hexanes–EtOAc, 20:80) gave the alcohol **11** (77 mg, 0.139 mmol,

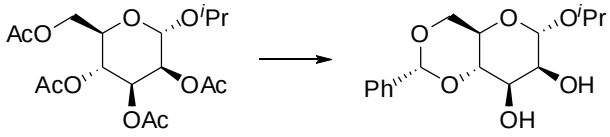
73 %) as a foam: $[a]_D$ = +58.3 (*c* = 0.314 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 1.98 (s, 3H), 2.04 (s, 3H), 2.09 (s, 3H), 2.14 (s, 3H), 3.25 (dd, *J* = 7.1, 3.2 Hz, 1H), 3.52 (s, 3H), 3.53 (s, 3H), 3.55 (s, 3H), 3.73 (dd, *J* = 7.1, 7.1 Hz, 1H), 3.79 (dd, *J* = 7.1, 5.0 Hz, 1H), 3.84 (dd, *J* = 11.7, 4.5 Hz, 1H), 3.95 (dd, *J* = 11.7, 6.4 Hz, 1H), 4.01 (ddd, *J* = 6.6, 4.8, 4.8 Hz, 1H), 4.04 (ddd, *J* = 9.3, 5.8, 2.4 Hz, 1H), 4.09 (dd, *J* = 12.2, 2.4 Hz, 1H), 4.24 (dd, *J* = 12.2, 5.8 Hz, 1H), 4.73 (d, *J* = 2.9 Hz, 1H), 5.09 (d, *J* = 1.3 Hz, 1H), 5.24 (dd, *J* = 9.5, 9.5 Hz, 1H), 5.27 (dd, *J* = 3.2, 1.8 Hz, 1H), 5.29 ppm (dd, *J* = 9.5, 3.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *d* = 20.6 (CH_3), 20.7 (2 × CH_3), 20.9 (CH_3), 57.2 (CH_3), 59.5 (CH_3), 60.1 (CH_3), 62.3 (CH_2), 62.7 (CH_2), 66.4 (CH), 68.7 (CH), 69.3 (CH), 69.7 (CH), 75.0 (CH), 75.3 (CH), 77.6 (CH), 79.9 (CH), 98.2 (CH), 99.7 (CH), 169.6 (C), 169.8 (C), 169.9 (C), 170.6 ppm (C); IR (film): $\tilde{n}$ = 3499, 2932, 1748, 1227 cm^{-1}; MS (70 eV, EI): *m/z* (%): 492 (1) $[M–CH_3CO_2H]^+$, 331 (56), 169 (30), 88 (100); HRMS (EI): *m/z* calcd for $C_{21}H_{32}O_{13}$ $[M–CH_3CO_2H]^+$: 492.1843, found: 492.1842; elemental analysis calcd (%) for $C_{23}H_{36}O_{15}$ (552.52): C 50.00, H 6.57; found: C 50.03, H 6.60.



11 **16**

Methyl 2,3,4,6-Tetra-*O*-acetyl-*a*-D-mannopyranosyl-(1? 4)-2,3-di-*O*-methyl-6-*O*-phthalimido-*ß*-L-idopyranoside (16): Following the general procedure, the alcohol **11** gave after column chromatography (hexanes–EtOAc, 20:80) the phthalimide **16** (61 %) as a foam: $[a]_D$ = +32.9 (*c* = 0.480 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 1.97 (s, 3H), 2.02 (s, 3H), 2.10 (s, 3H), 2.15 (s, 3H), 3.27 (dd, *J* = 6.4, 2.6 Hz, 1H), 3.51 (s, 3H), 3.538 (s, 3H), 3.539 (s, 3H), 3.64 (dd, *J* = 6.4, 6.4 Hz, 1H), 3.94 (dd, *J* = 6.1, 4.8 Hz, 1H), 4.12 (dd, *J* = 12.2, 2.1 Hz, 1H), 4.18 (ddd, *J* = 9.5, 5.0, 2.1 Hz, 1H), 4.31 (dd, *J* = 12.2, 5.0 Hz, 1H), 4.42 (ddd, *J* = 6.9, 4.8, 4.8 Hz, 1H), 4.53 (dd, *J* = 11.1, 4.8 Hz, 1H), 4.59 (dd, *J* = 11.1, 6.6 Hz, 1H), 4.72 (d, *J* = 2.6 Hz, 1H), 5.11 (d, *J* = 1.9 Hz, 1H), 5.27 (dd, *J* = 9.8, 9.8 Hz, 1H), 5.30 (dd, *J* = 2.9, 2.1 Hz, 1H), 5.33 (dd, *J* = 9.8, 3.2 Hz, 1H), 7.75 (m, 2H), 7.82 ppm (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *d* = 20.6 (CH_3,), 20.69 (CH_3), 20.71 (CH_3), 20.9 (CH_3), 57.1 (CH_3), 59.6 (CH_3), 59.8 (CH_3), 62.5 (CH_2), 66.1

(CH), 68.9 (CH), 69.8 (CH), 69.7 (CH), 72.6 (CH), 73.5 (CH), 76.5 (CH), 77.2 (CH_2), 79.0 (CH), 97.8 (CH), 100.3 (CH), 123.5 (2 × CH), 129.0 (2 × C), 134.5 (2 × CH), 163.3 (2 × C), 169.5 (C), 169.8 (C), 170.0 (C), 170.7 ppm (C); IR (film): $\tilde{n}$ = 2939, 1739, 1372, 1227 cm^{-1}; MS (70 eV, EI): *m/z* (%): 697 (<1) $[M]^+$, 638 (<1), 535 (1), 492 (<1), 331 (97), 88 (100); HRMS (EI): *m/z* calcd for $C_{31}H_{39}NO_{17}$ $[M]^+$: 697.2218, found: 697.2204; elemental analysis calcd (%) for $C_{31}H_{39}NO_{17}$ (697.64): C 53.37, H 5.63, N 2.01; found: C 53.30, H 5.96, N 2.15.

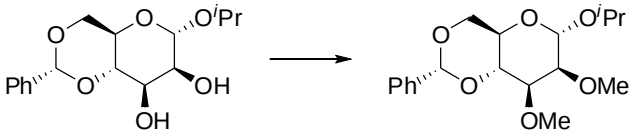


60S **61S**

Isopropyl 4,6-*O*-Benzylidene-*a*-D-mannopyranoside (61S): A mixture of isopropyl 2,3,4,6-tetra-*O*-acetyl-*a*-D-mannopyranoside (**60S**)[6] (1 g, 2.56 mmol), Amberjet 4400–OH ion-exchange resin (1.7 g) and MeOH (12.5 mL) was stirred at room temperature for 24 h. The resin was then filtered off and the filtrate concentrated under reduced pressure. To the residue in dry DMF (12.2 mL) containing molecular sieves 3Å (1.54 g) were added $PhCH(OMe)_2$ (339 µL, 2.26 mmol) and CSA (6 mg, 0.022 mmol) under nitrogen and the mixture was heated to 60 ºC for 2 h under 32 mbar of pressure. The reaction mixture was poured into a saturated solution of $NaHCO_3$ and extracted with EtOAc. The organic extracts were dried over anhydrous Na_2SO_4, concentrated under reduced pressure and the residue purified by column chromatography (hexanes–EtOAc, 1:1) to give compound **61S** (495 mg, 1.56 mmol, 62 %) as a white crystalline solid: m.p. 134–135 ^oC (from EtOAc–*n*-hexane); $[a]_D$ = +67.5 (*c* = 0.668 in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): *d* = 1.16 (d, *J* = 6.1 Hz, 3H), 1.22 (d, *J* = 6.4 Hz, 3H), 2.82 (d, *J* = 2.4 Hz, 1H), 2.85 (d, *J* = 2.4 Hz, 1H), 3.78–3.96 (m, 5H), 4.08 (ddd, *J* = 8.7, 3.2, 3.2 Hz, 1H), 4.24 (dd, *J* = 9.8, 4.0 Hz, 1H), 4.95 (d, *J* = 1.3 Hz, 1H), 5.56 (s, 1H), 7.35–7.40 (m, 3H), 7.48–7.51 ppm (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *d* = 21.3 (CH_3), 23.2 (CH_3), 63.0 (CH), 68.6 (CH), 68.8 (CH_2), 69.5 (CH), 71.5 (CH), 79.1 (CH), 98.2 (CH), 102.2 (CH), 126.2 (2 × CH), 128.3 (2 × CH), 129.2 (CH), 137.2 ppm (C); IR (film): $\tilde{n}$ = 3357,

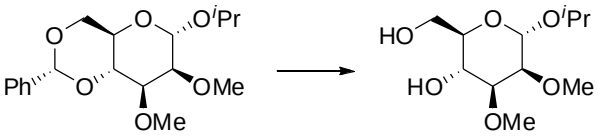
[6] a) P. Tiwari, A. K. Misra, *J. Org. Chem.* **2006**, *71*, 2911–2913; b) C. Nóbrega, J. T. Vázquez, *Tetrahedron: Asymmetry* **2003**, *14*, 2793–2802.

2922, 1378, 1099, 1059 cm^{-1}; MS (70 eV, EI): *m/z* (%): 310 (7) $[M]^+$, 251 (13), 179 (23), 107 (100); HRMS (EI): *m/z* calcd for $C_{16}H_{22}O_6$ $[M]^+$: 310.1416, found: 310.1404; elemental analysis calcd (%) for $C_{16}H_{22}O_6$ (310.34): C 61.92, H 7.15; found: C 61.69, H 7.31.



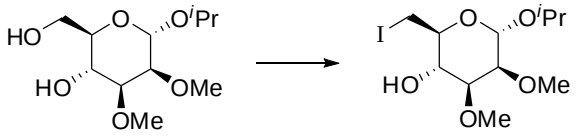
61S **62S**

Isopropyl 4,6-*O*-Benzylidene-2,3-di-*O*-methyl-*a*-D-mannopyranoside (62S): To a solution of the diol **61S** (1 g, 3.22 mmol) in dry DMF (10 mL) was added NaH (562 mg, 12.88 mmol) and the mixture was stirred at 0 ºC under nitrogen until all hydrogen evolution ceased. Then an excess of methyl iodide (1 mL, 16.1 mmol) was added dropwise and stirring continued at room temperature for 12 h. Excess reagent was destroyed by slow addition of MeOH and the solvent was removed in high vacuo. The residue obtained was poured into ice-water and extracted with Et_2O. The organic extracts were dried over anhydrous Na_2SO_4, concentrated under reduced pressure and the residue was purified by column chromatography (hexanes–EtOAc, 9:1) to yield compound **62S** (1.2 g, 3.55 mmol, 80 %) as a colourless oil: $[a]_D$ = +64.1 (*c* = 0.960 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 1.17 (d, *J* = 6.1 Hz, 3H), 1.23 (d, *J* = 6.1 Hz, 3H), 3.55 (s, 3H), 3.57 (s, 3H), 3.59 (dd, *J* = 3.2, 1.9 Hz, 1H), 3.74 (dd, *J* = 9.8, 3.2 Hz, 1H), 3.82–3.85 (m, 2H), 3.93 (sep, *J* = 6.1 Hz, 1H), 4.06 (m, 1H), 4.22 (m, 1H), 4.98 (d, *J* = 1.3 Hz, 1H), 5.59 (s, 1H), 7.32–7.38 (m, 3H), 7.48–7.51 ppm (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *d* = 21.3 (CH_3), 23.2 (CH_3), 59.0 (CH_3), 59.7 (CH_3), 63.9 (CH), 68.8 (CH_2), 69.4 (CH), 77.6 (CH), 79.3 (CH), 79.4 (CH), 96.3 (CH), 101.5 (CH), 126.0 (2 × CH), 128.1 (2 × CH), 128.7 (CH), 137.6 ppm (C); IR (film): $\tilde{n}$ = 2927, 1459, 1380, 1122, 1044 cm^{-1}; MS (70 eV, EI): *m/z* (%): 339 (95) $[M+H]^+$, 279 (52), 233 (41), 173 (99), 88 (100); HRMS (EI): *m/z* calcd for $C_{18}H_{27}O_6$ $[M+H]^+$: 339.1808, found: 339.1815; elemental analysis calcd (%) for $C_{18}H_{26}O_6$ (338.40): C 63.89, H 7.74; found: C 63.71, H 7.74.



62S **63S**

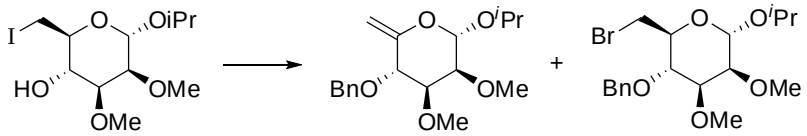
Isopropyl 2,3-Di-*O*-methyl-*a*-D-mannopyranoside (63S): To a solution of compound **62S** (76 mg, 0.225 mmol) in MeOH (2 mL) was added *p*-TsOH·H_2O (3 mg, 0.013 mmol) and the mixture stirred at room temperature for 4 h. After removing the solvent in vacuum, the reaction mixture was poured into a saturated solution of $NaHCO_3$ and extracted with EtOAc. The organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Column chromatography (hexanes–EtOAc, 1:9) of the residue gave the diol **63S** (44.4 mg, 0.177 mmol, 73 %) as a colourless oil: $[a]_D$ = +56.7 (*c* = 0.150 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): *d* = 1.16 (d, *J* = 6.2 Hz, 3H), 1.21 (d, *J* = 6.4 Hz, 3H), 2.08 (br s, 2H), 3.48 (s, 3H), 3.49 (dd, *J* = 9.5, 3.1 Hz, 1H), 3.50 (s, 3H), 3.56 (dd, *J* = 3.1, 1.7 Hz, 1H), 3.68 (ddd, *J* = 9.3, 5.0, 3.9 Hz, 1H), 3.79 (dd, *J* = 11.8, 5.3 Hz, 1H), 3.85 (dd, *J* = 9.8, 9.8 Hz, 1H), 3.86 (dd, *J* = 11.5, 3.6 Hz, 1H), 3.93 (sep, *J* = 6.2 Hz, 1H), 5.02 ppm (d, *J* = 1.7 Hz, 1H); ^{13}C NMR (125.7 MHz, $CDCl_3$): *d* = 21.2 (CH_3), 23.2 (CH_3), 57.1 (CH_3), 59.1 (CH_3), 63.0 (CH_2), 67.6 (CH), 69.1 (CH), 71.9 (CH), 76.4 (CH), 81.1 (CH), 95.3 (CH); IR (film): $\tilde{n}$ = 3434, 2928, 1379, 1119, 1042 cm^{-1}; MS (70 eV, EI): *m/z* (%): 219 (<1) [*M*–CH_3O]$^+$, 191 (4), 159 (7), 103 (17), 88 (100); HRMS (EI): *m/z* calcd for $C_{10}H_{19}O_5$ [*M*–CH_3O]$^+$: 219.1232, found: 219.1237; elemental analysis calcd (%) for $C_{11}H_{22}O_6$ (250.29): C 52.79, H 8.86; found: C 52.62, H 8.98.



63S **64S**

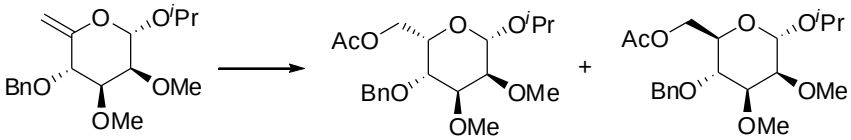
Isopropyl 6-Deoxy-6-iodo-2,3-di-*O*-methyl-*a*-D-mannopyranoside (64S): A solution of diol **63S** (5.71 g, 22.8 mmol) in dry toluene (150 mL) containing PPh_3 (7.2 g, 27.4 mmol), imidazole (2.32 g, 34.2 mmol) and iodine (7.6 g, 30.1 mmol) was heated to 100 ºC under nitrogen for 1 h. The reaction mixture was poured into a saturated solution of $NaHCO_3$ and extracted with EtOAc. The organic extracts were dried over

Na_2SO_4 anhydrous and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc, 70:30 ? 60:40) to give the iodo-derivative **64S** (5.41 g, 15.03 mmol, 66 %) as a yellow oil: $[a]_D$ = +40.9 (*c* = 0.374 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 1.16 (d, *J* = 6.1 Hz, 3H), 1.22 (d, *J* = 6.4 Hz, 3H), 3.25 (dd, *J* = 10.3, 8.2 Hz, 1H), 3.459 (s, 3H), 3.460 (dd, *J* = 9.3, 3.2 Hz, 1H), 3.48 (s, 3H), 3.55 (dd, *J* = 3.2, 1.8 Hz, 1H), 3.59 (m, 1H), 3.62 (dd, *J* = 10.3, 2.9 Hz, 1H), 3.65 (dd, *J* = 9.1, 9.1 Hz, 1H), 4.07 (sep, *J* = 6.1 Hz, 1H), 5.04 ppm (d, *J* = 1.6 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *d* = 6.5 (CH_2), 20.9 (CH_3), 23.2 (CH_3), 57.0 (CH_3), 58.9 (CH_3), 68.7 (CH), 70.6 (CH), 71.9 (CH), 76.3 (CH), 80.7 (CH), 94.8 ppm (CH); IR (film): $\tilde{n}$ = 3458, 2927, 1381, 1118, 1048 cm^{-1}; MS (70 eV, EI): *m/z* (%): 343 (<1) $[M–OH]^+$, 328 (1), 268 (3), 240 (2), 88 (100); HRMS (EI): *m/z* calcd for $C_{11}H_{20}IO_4$ $[M–OH]^+$: 343.0406, found: 343.0417; elemental analysis calcd (%) for $C_{11}H_{21}IO_5$ (360.19): C 36.68, H 5.88; found: C 36.73, H 5.70.



Isopropyl 4-*O*-Benzyl-6-deoxy-2,3-di-*O*-methyl-*a*-D-*lyxo*-hex-5-enopyranoside (65S) and Isopropyl 4-*O*-Benzyl-6-bromo-6-deoxy-2,3-di-*O*-methyl-*a*-D-mannopyranoside (66S): To a solution of compound **64S** (500 mg, 1.33 mmol) in dry DMF (17 mL) were added BnBr (316 µL, 2.66 mmol) and NaH (319 mg, 13.3 mmol) under nitrogen and the mixture stirred at room temperature for 24 h. After removing the solvent under high vacuum, the residue was poured into ice-water and extracted with EtOAc. The organic extracts were dried over anhydrous Na_2SO_4, concentrated under reduced pressure and the residue was purified by column chromatography (hexanes–EtOAc, 9:1) to afford the olefin **65S** (234 mg, 0.651 mmol, 55 %) and compound **66S** (82 mg, 0.203 mmol, 15 %), both as colourless oils. Compound **65S**: $[a]_D$ = +18.6 (*c* = 0.866 in $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6): *d* = 0.99 (d, *J* = 6.2 Hz, 3H), 1.19 (d, *J* = 6.4 Hz, 3H), 3.25 (s, 3H), 3.33 (s, 3H), 3.66 (dd, *J* = 3.2, 3.2 Hz, 1H), 3.84 (dd, *J* = 8.3, 3.1 Hz, 1H), 3.97 (sep, *J* = 6.2 Hz, 1H), 4.43 (ddd, *J* = 8.1, 1.3, 1.3 Hz, 1H), 4.62 (s, 2H), 4.86 (d, *J* = 1.4 Hz, 1H), 4.89 (d, *J* = 1.4 Hz, 1H), 5.13 (d, *J* = 3.4 Hz, 1H), 7.07 (m, 1H), 7.13–7.15 (m, 2H), 7.30–7.32

ppm (m, 2H); ^{13}C NMR (125.7 MHz, C_6D_6): *d* = 21.3 (CH_3), 23.4 (CH_3), 58.5 (CH_3), 59.3 (CH_3), 69.6 (CH), 73.3 (CH_2), 77.2 (CH), 78.9 (CH), 80.9 (CH), 96.4 (CH_2), 98.2 (CH), 127.5–128.6 (5 × CH), 139.1 (C), 156.2 ppm (C); IR (film): $\tilde{n}$ = 2925, 1662, 1452, 1157, 1086 cm^{-1}; MS (70 eV, EI): *m/z* (%): 322 (<1) $[M]^+$, 249 (15), 159 (39), 91 (100); HRMS (EI): *m/z* calcd for $C_{18}H_{26}O_5$ $[M]^+$: 322.1780, found: 322.1767; elemental analysis calcd (%) for $C_{18}H_{26}O_5$ (322.40): C 67.06, H 8.13; found: C 67.06, H 8.07. Compound **66S**: $[a]_D$ = +63.0 (*c* = 0.398 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 1.15 (d, *J* = 6.1 Hz, 3H), 1.19 (d, *J* = 6.1 Hz, 3H), 3.519 (s, 3H), 3.521 (s, 3H), 3.54 (dd, *J* = 10.6, 6.6 Hz, 1H), 3.55 (dd, *J* = 2.9, 1.8 Hz, 1H), 3.65 (dd, *J* = 9.0, 2.9 Hz, 1H), 3.66 (dd, *J* = 10.9, 2.4 Hz, 1H), 3.69 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.80 (ddd, *J* = 8.7, 6.6, 2.1 Hz, 1H), 3.98 (sep, *J* = 6.2 Hz, 1H), 4.62 (d, *J* = 10.8 Hz, 1H), 4.93 (d, *J* = 10.8 Hz, 1H), 5.04 (d, *J* = 1.6 Hz, 1H), 7.28–7.36 ppm (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *d* = 21.1 (CH_3), 23.2 (CH_3), 33.5 (CH_2), 57.6 (CH_3), 59.0 (CH_3), 69.0 (CH), 71.1 (CH), 75.4 (CH_2), 77.1 (CH), 77.6 (CH), 81.6 (CH), 94.7 (CH), 127.8 (CH), 128.1 (2 × CH), 128.5 (2 × CH), 138.4 ppm (C); IR (film): $\tilde{n}$ = 2928, 1458, 1380, 1120, 1042 cm^{-1}; MS (70 eV, EI): *m/z* (%): 404/402 (<1) $[M]^+$, 345/343 (2), 177 (96), 91 (100); HRMS (EI): *m/z* calcd for $C_{18}H_{27}{}^{81}BrO_5$ $[M]^+$: 404.1021, found: 404.1030; elemental analysis calcd (%) for $C_{18}H_{27}BrO_5$ (403.31): C 53.60, H 6.75; found: C 53.62, H 6.91.

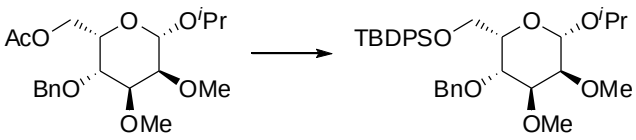


66S **67S** **68S**

Isopropyl 6-*O*-Acetyl-4-*O*-benzyl-2,3-di-*O*-methyl-ß-L-gulopyranoside (67S) and Isopropyl 6-*O*-Acetyl-4-*O*-benzyl-2,3-di-*O*-methyl-*a*-D-mannopyranoside (68S): To a solution of olefin **66S** (60 mg, 0.187 mmol) in dry THF (1 mL) under nitrogen was added dropwise a solution of BH_3·THF complex (0.93 mL, 0.935 mmol, 1 M in THF). After 12 h of stirring, the excess borane was quenched carefully by adding a drop of water. Dropwise addition of a mixture of 1 M NaOH (0.3 mL) and 30% hydrogen peroxide (0.3 mL), removal of the cooling bath, and continued stirring for 30 min resulted in a heterogeneous white mixture. The reaction mixture was then poured into ice-water, washed with brine,

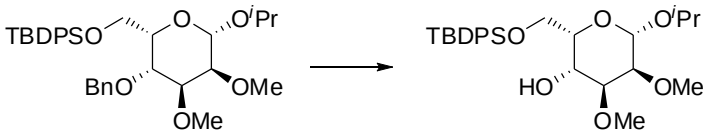
extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated in vacuum. To the residue in dry pyridine (3 mL) was added Ac_2O (1 mL,) under nitrogen and the mixture stirred at room temperatura for 12 h. The reaction mixture was then poured into 10% aqueous HCl and extracted with CH_2Cl_2, washed with a saturated solution of $NaHCO_3$, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatotron chromatography (hexanes–EtOAc, 80:20) to give compound **67S** (43.6 mg, 0.114 mmol, 61 %) and compound **68S** (8.6 mg, 0.022 mmol, 12 %), both as colourless oils. Compound **67S**: $[a]_D$ = +57.7 (*c* = 0.350 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): *d* = 1.19 (s, *J* = 6.3 Hz, 3H), 1.24 (s, *J* = 6.0 Hz, 3H), 1.99 (s, 3H), 3.32 (*J* = 8.2, 3.2 Hz, 1H), 3.38 (s, 3H), 3.508 (s, 3H), 3.510 (*J* = 3.8, 1.3 Hz, 1H), 3.64 (dd, *J* = 3.5, 3.5 Hz, 1H), 3.95 (sep, *J* = 6.0 Hz, 1H), 3.96 (m, 1H), 4.13 (dd, *J* = 11.0, 5.7 Hz, 1H), 4.26 (dd, *J* = 11.0, 6.9 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.71 (d, *J* = 8.2 Hz, 1H), 7.29–7.37 ppm (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *d* = 20.6 (CH_3), 22.0 (CH_3), 23.4 (CH_3), 59.0 (CH_3), 59.4 (CH_3), 63.0 (CH_2), 70.4 (CH), 72.0 (CH), 72.5 (CH_2), 73.1 (CH), 77.1 (CH), 77.9 (CH), 99.3 (CH), 127.9 (CH), 128.1 (2 × CH), 128.3 (2 × CH), 137.5 (C), 170.4 ppm (C); IR (film): $\tilde{n}$ = 2906, 1743, 1371, 1239, 1125, 1089 cm^{-1}; MS (70 eV, EI): *m/z* (%): 382 (<1) $[M]^+$, 323 (2), 280 (1), 177 (65), 103 (79), 91 (100); HRMS (EI): *m/z* calcd for $C_{20}H_{30}O_7$ $[M]^+$: 382.1992, found: 382.1997; elemental analysis calcd (%) for $C_{20}H_{30}O_7$ (382.45): C 62.81, H 7.91; found: C 62.99, H 7.88. Compound **68S**: $[a]_D$ = +68.3 (*c* = 0.224 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 1.16 (d, *J* = 6.1 Hz, 3H), 1.19 (d, *J* = 6.1 Hz, 3H), 2.04 (s, 3H), 3.51 (s, 3H), 3.52 (s, 3H), 3.55 (dd, *J* = 3.2, 1.8 Hz, 1H), 3.66 (dd, *J* = 9.0, 2.9 Hz, 1H), 3.72 (dd, *J* = 9.4, 9.4 Hz, 1H), 3.83 (ddd, *J* = 9.5, 4.5, 2.9 Hz, 1H), 3.91 (sep, *J* = 6.1 Hz, 1H), 4.28 (dd, *J* = 11.6, 2.9 Hz, 1H), 4.31 (dd, *J* = 11.9, 4.7 Hz, 1H), 4.54 (d, *J* = 10.6 Hz, 1H), 4.90 (d, *J* = 10.6 Hz, 1H), 5.03 (d, *J* = 1.6 Hz, 1H), 7.26–7.35 ppm (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *d* = 20.7 (CH_3), 21.3 (CH_3), 23.0 (CH_3), 57.5 (CH_3), 58.8 (CH_3), 63.5 (CH_2), 69.5 (CH), 69.6 (CH), 74.6 (CH), 75.0 (CH_2), 77.4 (CH), 81.5 (CH), 94.9 (CH), 127.6 (CH), 128.0 (2 × CH), 128.3 (2 × CH), 138.2 (C), 170.7 ppm (C); IR (film): $\tilde{n}$ = 2929, 1742, 1374, 1241, 1120, 1048 cm^{-1}; MS (70 eV, EI): *m/z* (%): 382 (<1) $[M]^+$, 323

(<1), 262 (4), 177 (56), 91 (100); HRMS (EI): *m/z* calcd for $C_{20}H_{30}O_7$ $[M]^+$: 382.1992, found: 382.2000; elemental analysis calcd (%) for $C_{20}H_{30}O_7$ (382.45): C 62.81, H 7.91; found: C 62.62, H 7.96.



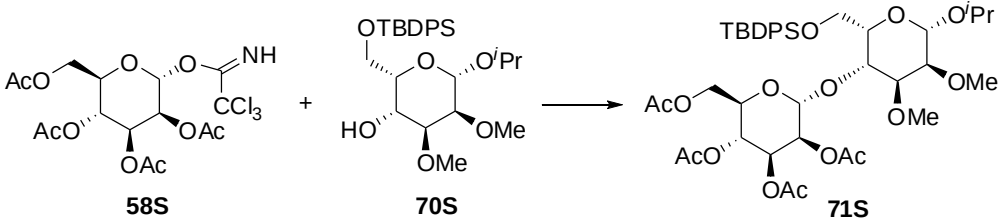
67S **69S**

Isopropyl 4-*O*-Benzyl-6-*O*-*tert*-butyldiphenylsilyl-2,3-di-*O*-methyl-ß-L-gulopyranoside (69S): To a solution of compound **67S** (66 mg, 0.173 mmol) in MeOH (3 mL) was added K_2CO_3 (22 mg, 0.173 mmol) and the mixture was stirred at room temperature for 24 h. The reaction mixture was then neutralised with Dowex (50 × 8) ion-exchange resin, filtered and concentrated under vacuum. To the residue in dry DMF (3 mL) were added imidazole (42 mg, 0.617 mmol) and TBDPSCl (53 µL, 0.207 mmol) under nitrogen at 0 °C and the mixture was stirred at room temperature for 12 h. The reaction mixture was poured into ice-water and extracted with CH_2Cl_2. The organic phase was washed with 10% aqueous HCl, dried over Na_2SO_4, and concentrated under reduced pressure. Chromatotron chromatography (hexanes–EtOAc, 9:1) of the residue afforded compound **69S** (90 mg, 0.155 mmol, 90 %) as a colourless oil: $[a]_D$ = +30.9 (*c* = 0.194 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): *d* = 1.06 (s, 9H), 1.15 (d, *J* = 6.2 Hz, 3H), 1.18 (d, *J* = 6.2 Hz, 3H), 3.29 (dd, *J* = 8.1, 3.4 Hz, 1H), 3.36 (s, 3H), 3.48 (s, 3H), 3.58 (dd, *J* = 3.4, 3.4 Hz, 1H), 3.72 (br d, *J* = 3.6 Hz, 1H), 3.78–3.88 (m, 3H), 3.91 (sep, *J* = 6.2 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.66 (d, *J* = 8.4 Hz, 1H), 7.27–7.44 (m, 11H), 7.65–7.67 ppm (m, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$): *d* = 19.2 (C), 22.0 (CH_3), 23.6 (CH_3), 26.8 (3 × CH_3), 58.7 (CH_3), 59.5 (CH_3), 62.2 (CH_2), 71.6 (CH), 72.9 (CH), 73.0 (CH), 73.1 (CH_2), 77.6 (CH), 78.1 (CH), 99.2 (CH), 127.7 (4 × CH), 127.8 (CH), 128.0 (2 × CH), 128.3 (2 × CH), 129.7 (2 × CH), 133.4 (C), 133.5 (C), 135.5 (2 × CH), 135.6 (2 × CH), 138.2 ppm (C); IR (film): $\tilde{n}$ = 2928, 1459, 1378, 1110, 1054 cm^{-1}; MS (70 eV, EI): *m/z* (%): 521 (<1) $[M–C_4H_9]^+$, 489 (7), 241 (37), 103 (71), 91 (100); HRMS (EI): *m/z* calcd for $C_{30}H_{37}O_6Si$ $[M–C_4H_9]^+$: 521.2359, found: 521.2368; elemental analysis calcd (%) for $C_{34}H_{46}O_6Si$ (578.81): C 70.55, H 8.01; found: C 70.61, H 8.12.



69S **70S**

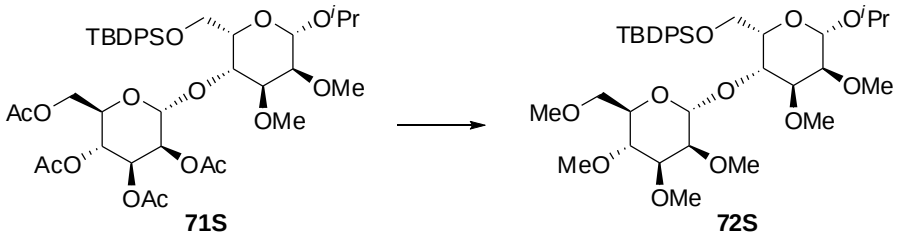
Isopropyl 6-*O*-*tert*-Butyldiphenylsilyl-2,3-di-*O*-methyl-ß-L-gulopyranoside (70S): To a solution of compound **69S** (215 mg, 0.372 mmol) in EtOAc (5 mL) was added 10% Pd/C (50 mg) and the mixture was stirred at room temperature for 12 h under a hydrogen atmosphere. After the catalyst was filtered off, the solvent was removed under reduced pressure to afford the alcohol **70S** (167 mg, 0.342 mmol, 92 %) as a colourless oil: $[a]_D$ = +53.7 (*c* = 0.756 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 1.06 (s, 9H), 1.20 (d, *J* = 6.1 Hz, 3H), 1.27 (d, *J* = 6.4 Hz, 3H), 3.36 (dd, *J* = 8.2, 3.4 Hz, 1H), 3.47 (s, 3H), 3.54 (s, 3H), 3.70 (dd, *J* = 3.7, 3.7 Hz, 1H), 3.82 (ddd, *J* = 5.3, 4.2, 1.1 Hz, 1H), 3.87 (dd, *J* = 10.6, 4.2 Hz, 1H), 3.91 (dd, *J* = 10.9, 5.3 Hz, 1H), 3.97 (sep, *J* = 6.2 Hz, 1H), 4.03 (d, *J* = 3.7, 0.8 Hz, 1H), 4.71 (d, *J* = 8.2 Hz, 1H), 7.36–7.44 (m, 6H), 7.68–7.73 ppm (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *d* = 19.1 (C), 22.1 (CH_3), 23.7 (CH_3), 26.7 (3 × CH_3), 59.0 (CH_3), 59.4 (CH_3), 64.4 (CH_2), 68.2 (CH), 71.8 (CH), 71.9 (CH), 77.6 (CH), 79.6 (CH), 100.0 (CH), 127.7 (2 × CH), 127.8 (2 × CH), 129.85 (CH), 129.87 (CH), 132.7 (C), 132.9 (C), 135.5 (2 × CH), 135.7 ppm (2 × CH); IR (film): $\tilde{n}$ = 3476, 2932, 1428, 1378, 1113, 1032 cm^{-1}; MS (70 eV, EI): *m/z* (%): 371 (5), 339 (18), 241 (100), 163 (54), 88 (93); HRMS (EI): *m/z* calcd for $C_{20}H_{23}O_5Si$ [*M*–C_4H_9–$(CH_3)_2CHOH$]$^+$, 371.1315, found: 371.1306; elemental analysis calcd (%) for $C_{27}H_{40}O_6Si$ (488.69): C 66.36, H 8.25; found: C 66.43, H 8.19.



58S **70S** **71S**

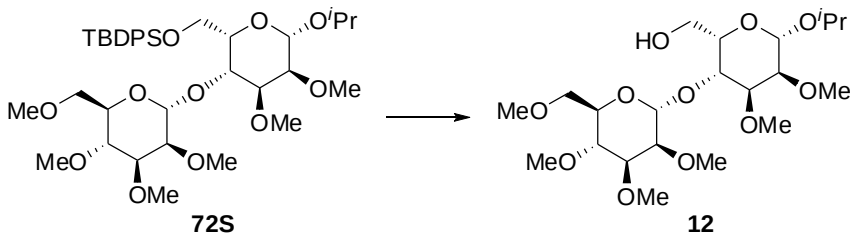
Isopropyl 2,3,4,6-Tetra-*O*-acetyl-*a*-D-mannopyranosyl-(1? 4)-6-*O*-*tert*-butyldiphenylsilyl-2,3-di-*O*-methyl-ß-L-gulopyranoside (71S): To a solution of trichloroacetimidate **58S** (50 mg, 0.101 mmol) and alcohol **70S** (25 mg, 0.050 mmol) in dry CH_2Cl_2 (1.7 mL) containing molecular sieves 3Å (25 mg) was added a 0.1 M solution of TMSOTf/CH_2Cl_2 (10.1 µL, 0.50 µmol) under nitrogen at room temperature and

the mixture was stirred for 2 h. The reaction mixture was poured into a saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc, 8:2) to give the disaccharide **71S** (30.6 mg, 0.037 mmol, 75 %) as a foam: $[a]_D$ = +49.3 (*c* = 0.570 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 1.05 (s, 9H), 1.17 (d, *J* = 6.1 Hz, 3H), 1.19 (d, *J* = 6.1 Hz, 3H), 1.96 (s, 3H), 1.97 (s, 3H), 2.00 (s, 3H), 2.15 (s, 3H), 3.25 (dd, *J* = 8.2, 3.4 Hz, 1H), 3.47 (s, 3H), 3.54 (s, 3H), 3.76 (dd, *J* = 3.4, 3.4 Hz, 1H), 3.79 (dd, *J* = 12.4, 1.9 Hz, 1H), 3.85–3.94 (m, 5H), 3.96 (ddd, *J* = 9.5, 4.8, 2.4 Hz, 1H), 4.08 (dd, *J* = 12.4, 4.5 Hz, 1H), 4.66 (d, *J* = 8.0 Hz, 1H), 4.99 (d, *J* = 1.6 Hz, 1H), 5.18 (dd, *J* = 3.2, 1.8 Hz, 1H), 5.25 (dd, *J* = 9.5, 9.5 Hz, 1H), 5.31 (dd, *J* = 10.0, 3.2 Hz, 1H), 7.36–7.42 (m, 6H), 7.65–7.68 ppm (m, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *d* = 19.1 (C), 20.55 (CH_3), 20.58 (CH_3), 20.62 (CH_3), 20.8 (CH_3), 22.1 (CH_3), 23.5 (CH_3), 26.8 (3 × CH_3), 59.2 (CH_3), 59.7 (CH_3), 62.0 (CH_2), 62.7 (CH_2), 65.7 (CH), 68.8 (CH), 69.1 (CH), 70.1 (CH), 71.5 (CH), 72.1 (CH), 72.7 (CH), 76.6 (CH), 77.8 (CH), 95.9 (CH), 99.4 (CH), 127.8 (4 × CH), 129.78 (CH), 129.80 (CH), 133.1 (C), 133.4 (C), 135.4 (2 × CH), 135.6 (2 × CH), 169.5 (C), 169.6 (C), 170.1 (C), 170.4 ppm (C); IR (film): $\tilde{n}$ = 2927, 1751, 1372, 1226, 1113, 1064 cm^{-1}; MS (70 eV, EI): *m/z* (%): 761 (2) $[M–C_4H_9]^+$, 729 (1), 701 (2), 585 (1), 413 (2), 331 (100); HRMS (EI): *m/z* calcd for $C_{37}H_{49}O_{15}Si$ $[M–C_4H_9]^+$: 761.2841, found: 761.2819; elemental analysis calcd (%) for $C_{41}H_{58}O_{15}Si$ (818.98): C 60.13, H 7.14; found: C 60.23, H 7.07.



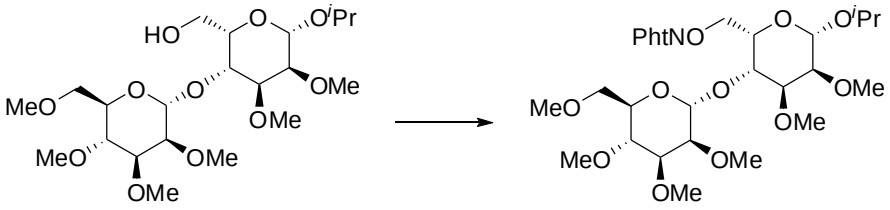
Isopropyl 2,3,4,6-Tetra-*O*-methyl-*a*-D-mamnopyranosyl-(1? 4)-6-*O*-*tert*-butyldiphenylsilyl-2,3-di-*O*-methyl-*ß*-L-gulopyranoside (72S): To a solution of compound **71S** (100 mg, 0.122 mmol) in MeOH (6 mL) was added K_2CO_3 (23 mg, 0.183 mmol) and the mixture was stirred at room temperature for 2 h. The reaction mixture was then neutralised with Dowex (50 × 8) ion-exchange resin, filtered and concentrated under vacuum. To the residue in dry DMF (5 mL) was added NaH (39 mg, 0.976 mmol) and the mixture

was stirred at 0 ºC under nitrogen until all hydrogen evolution ceased. Then an excess of methyl iodide (76 µL, 1.22 mmol) was added dropwise and stirring continued at room temperature for 12 h. Excess reagent was destroyed by slow addition of MeOH and the solvent was removed in high vacuo. The residue obtained was poured into ice-water and extracted with Et_2O. The organic extracts were dried over Na_2SO_4 anhydrous, concentrated under reduced pressure and the residue was purified by column chromatography (hexanes–EtOAc, 1:1) to give compound **72S** (52 mg, 0.073 mmol, 60 %) as a colourless oil: $[a]_D$ = +49.7 (*c* = 0.316 in $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6): *d* = 1.08 (d, *J* = 6.1 Hz, 3H), 1.220 (d, *J* = 6.1 Hz, 3H), 1.222 (s, 9H), 3.14 (s, 3H), 3.16 (s, 3H), 3.24 (s, 3H), 3.32 (s, 3H), 3.41 (s, 3H), 3.44–3.47 (m, 2H), 3.47 (s, 3H), 3.48–3.56 (m, 3H), 3.74–3.82 (m, 2H), 3.85 (dd, *J* = 3.3, 3.3 Hz, 1H), 3.98 (sep, *J* = 6.1 Hz, 1H), 4.12 (ddd, *J* = 3.4, 1.6 Hz, 1H), 4.19 (dd, *J* = 10.3, 5.3 Hz, 1H), 4.25 (dd, *J* = 10.3, 6.9 Hz, 1H), 4.39 (ddd, *J* = 6.9, 5.3, 1.6 Hz, 1H), 5.09 (d, *J* = 7.9 Hz, 1H), 5.14 (d, *J* = 2.1 Hz, 1H), 7.18–7.29 (m, 6H), 7.84–7.89 ppm (m, 4H); ^{13}C NMR (100.6 MHz, C_6D_6): *d* = 19.5 (C), 22.0 (CH_3), 24.0 (CH_3), 27.1 (3 × CH_3), 57.6 (CH_3), 59.0 (CH_3), 59.2 (CH_3), 59.4 (CH_3), 59.7 (CH_3), 60.0 (CH_3), 64.6 (CH_2), 71.1 (CH), 71.2 (CH), 72.2 (CH_2), 73.3 (CH), 74.2 (CH), 76.6 (CH), 76.9 (CH), 78.4 (CH), 79.5 (CH), 82.1 (CH), 95.8 (CH), 99.8 (CH), 127.7 (4 × CH), 129.9 (2 × CH), 133.9 (C), 134.2 (C), 136.08 (2 × CH), 136.14 ppm (2 × CH); IR (film): $\tilde{n}$ = 2928, 1457, 1380, 1120, 1042 cm^{-1}; MS (70 eV, EI): *m/z* (%): 706 (<1) $[M]^+$, 649 (<1), 629 (2), 473 (2), 219 (100); HRMS (EI): *m/z* calcd for $C_{37}H_{58}O_{11}Si$ $[M]^+$: 706.3748, found: 706.3738; elemental analysis calcd (%) for $C_{37}H_{58}O_{11}Si$ (706.94): C 62.86, H 8.27; found: C 62.83, H 8.32.



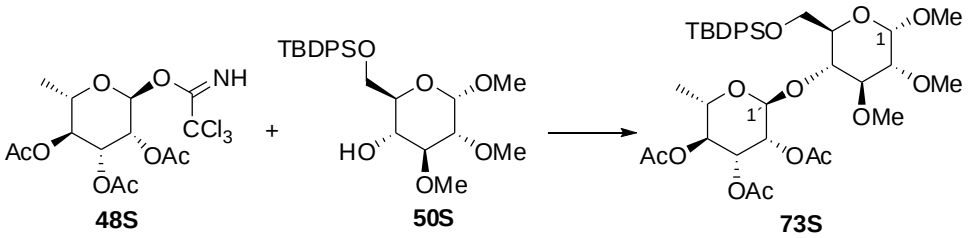
Isopropyl 2,3,4,6-Tetra-*O*-methyl-*a*-D-mannopyranosyl-(1? 4)-2,3-di-*O*-methyl-*ß*-L-gulopyranoside (12): To a solution of compound **72S** (319 mg, 0.452 mmol) in dry THF (14 mL) was added a 1 M solution of Bu_4NF/THF (0.9 mL, 0.903 mmol) under nitrogen, and the mixture stirred at room

temperature for 12 h. The reaction mixture was poured into a saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Column chromatography (hexanes–EtOAc, 2:8) of the reaction residue gave the alcohol **12** (210 mg, 0.448 mmol, 99 %) as a foam: $[a]_D$ = +108.3 (*c* = 0.108 in $CHCl_3$); ^{1}H NMR (400 MHz, C_6D_6): *d* = 1.07 (d, *J* = 6.0 Hz, 3H), 1.16 (d, *J* = 6.3 Hz, 3H), 3.06 (s, 3H), 3.17 (s, 3H), 3.23 (s, 3H), 3.26 (s, 3H), 3.29 (s, 3H), 3.38 (br dd, *J* = 6.9, 6.9 Hz, 1H), 3.41–3.44 (dd, *J* = 9.9, 7.5 Hz, 2H), 3.50 (s, 3H), 3.50–3.54 (m, 2H), 3.55 (dd, *J* = 8.0, 3.2 Hz, 1H), 3.60 (dd, *J* = 7.4, 3.2 Hz, 1H), 3.74 (dd, *J* = 3.4, 3.4 Hz, 1H), 3.87 (sep, *J* = 6.2 Hz, 1H), 3.97 (ddd, *J* = 10.8, 5.4, 5.4 Hz, 1H), 4.04 (ddd, *J* = 9.3, 7.8, 1.5 Hz, 1H), 4.12 (ddd, *J* = 10.8, 8.4, 6.9 Hz, 1H), 4.24 (ddd, *J* = 8.7, 5.7, 1.6 Hz, 1H), 4.26 (dd, *J* = 3.6, 1.5 Hz, 1H), 5.03 (d, *J* = 7.8 Hz, 1H), 5.12 ppm (d, *J* = 3.0 Hz, 1H); ^{13}C NMR (100.6 MHz, C_6D_6): *d* = 22.1 (CH_3), 24.0 (CH_3), 57.7 (CH_3), 58.8 (CH_3), 59.1 (CH_3), 59.3 (CH_3), 59.4 (CH_3), 59.5 (CH_3), 60.4 (CH_2), 71.2 (CH), 72.2 (CH), 73.0 (CH_2), 73.29 (CH), 73.32 (CH), 77.6 (CH), 77.9 (CH), 79.0 (CH), 79.7 (CH), 81.3 (CH), 97.9 (CH), 100.0 ppm (CH); IR (film): $\tilde{n}$ = 3479, 2929, 1460, 1376, 1117, 1057 cm^{-1}; MS (70 eV, EI): *m/z* (%): 408 (3) $[M–(CH_3)_2CHOH]^+$, 305 (19), 187 (100); HRMS (EI): *m/z* calcd for $C_{18}H_{32}O_{10}$ $[M–(CH_3)_2CHOH]^+$: 408.1995, found: 408.2008; elemental analysis calcd (%) for $C_{21}H_{40}O_{11}$ (468.54): C 53.83, H 8.61; found: C 53.82, H 8.61.



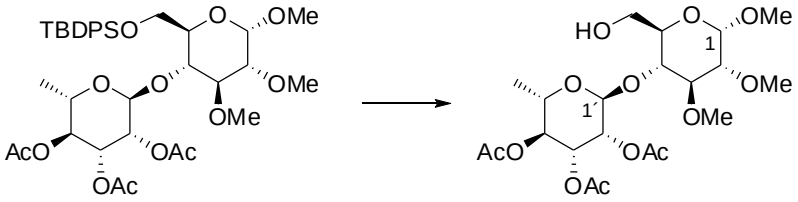
Isopropyl 2,3,4,6-Tetra-*O*-methyl-*a*-D-mannopyranosyl-(1? 4)-2,3-di-*O*-methyl-6-*O*-phthalimido-*ß*-L-gulopyranoside (17): Following the general procedure, using in this case DEAD (5 mmol), *N*-hydroxyphthalimide (4 mmol) and PPh_3 (4 mmol) and stirring the mixture at room temperature, precursor **12** gave after column chromatography (Et_2O–EtOAc, 90:10 ? 70:30) the phthalimide **17** (49 %) as a foam: $[a]_D$ = +62.9 (*c* = 0.124 in $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6): *d* = 1.09 (d, *J* = 6.0 Hz, 3H), 1.11 (d, *J* = 6.0 Hz, 3H), 3.20 (s, 3H), 3.22 (s, 3H), 3.26 (s, 3H), 3.29 (s, 3H), 3.37 (s, 3H), 3.45 (s, 3H), 3.49

(dd, *J* = 2.8, 2.8 Hz, 1H), 3.51 (dd, *J* = 8.5, 3.1 Hz, 1H), 3.60 (dd, *J* = 10.5, 2.0 Hz, 1H), 3.62 (dd, *J* = 8.0, 3.1 Hz, 1H), 3.64 (dd, *J* = 10.5, 5.4 Hz, 1H), 3.69 (dd, *J* = 9.4, 8.0 Hz, 1H), 3.82 (dd, *J* = 3.4, 3.4 Hz, 1H), 3.96 (ddd, *J* = 9.7, 5.4, 2.0 Hz, 1H), 4.01 (sep, *J* = 6.2 Hz, 1H), 4.20 (dd, *J* = 4.0, 1.7 Hz, 1H), 4.73 (ddd, *J* = 7.1, 4.0, 1.7 Hz, 1H), 4.77 (dd, *J* = 11.7, 3.7 Hz, 1H), 4.85 (dd, *J* = 11.7, 7.1 Hz, 1H), 5.15 (d, *J* = 2.6 Hz, 1H), 5.17 (d, *J* = 7.7 Hz, 1H), 6.75 (m, 2H), 7.22 ppm (m, 2H); ^{13}C NMR (125.7 MHz, C_6D_6): *d* = 22.0 (CH_3), 23.9 (CH_3), 57.7 (CH_3), 59.0 (CH_3), 59.1 (CH_3), 59.3 (CH_3), 59.6 (CH_3), 59.7 (CH_3), 71.1 (CH), 71.7 (CH), 72.46 (CH), 72.52 (CH_2), 73.4 (CH), 76.8 (CH), 77.2 (CH), 78.2 (CH_2), 78.6 (CH), 79.1 (CH), 81.7 (CH), 96.8 (CH), 99.6 (CH), 123.0 (2 × CH), 129.4 (2 × C), 133.6 (2 × CH), 163.4 ppm (2 × C); IR (film): $\tilde{n}$ = 2931, 1790, 1734, 1372, 1105, 1054 cm^{-1}; MS (70 eV, EI): *m/z* (%): 614 (<1) [*M*+H]$^+$, 554 (<1), 219 (84), 187 (56), 88 (100); HRMS (EI): *m/z* calcd for $C_{29}H_{44}NO_{13}$ [*M*+H]$^+$: 614.2813, found: 614.2820; elemental analysis calcd (%) for $C_{29}H_{43}NO_{13}$ (613.65): C 56.76, H 7.06, N 2.28; found: C 56.82, H 7.05, N 2.48.



Methyl 2,3,4-Tri-*O*-acetyl-*a*-L-rhamnopyranosyl-(1? 4)-6-*O*-*tert*-butyldiphenylsilyl-2,3-di-*O*-methyl-*a*-D-glucopyranoside (73S): To a solution of trichloroacetimidate **48S** (425 mg, 0.981 mmol) and alcohol **50S** (205 mg, 0.446 mmol) in dry CH_2Cl_2 (8.5 mL) containing molecular sieves 3Å (205 mg) was added a 1 M solution of TMSOTf/CH_2Cl_2 (45 µL, 0.045 mmol) under nitrogen at 0 ^{o}C and the mixture was stirred at this temperature for 2 h. After this time a further 1 M solution of TMSOTf/CH_2Cl_2 (45 µL, 0.045 mmol) was added, and stirring continued for an additional 1 h. The reaction mixture was poured into a saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc, 85:15) to give the disaccharide **73S** (324 mg, 0.443 mmol, 99 %) as a colourless oil: [a]$_D$ = +23.5 (*c* = 0.310 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 1.03 (s, 9H), 1.23 (d,

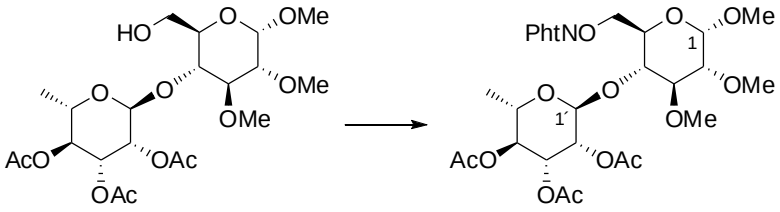
J = 6.1 Hz, 3H), 1.98 (s, 3H), 2.05 (s, 3H), 2.06 (s, 3H), 3.24 (dd, *J* = 9.5, 3.7 Hz, 1H), 3.32 (s, 3H), 3.520 (dd, *J* = 9.3, 9.3 Hz, 1H), 3.525 (s, 3H), 3.57 (m, 1H), 3.61 (s, 3H), 3.82 (dd, *J* = 11.9, 1.6 Hz, 1H), 3.86 (dd, *J* = 9.5, 9.5 Hz, 1H), 3.88 (dd, *J* = 11.9, 2.9 Hz, 1H), 4.20 (dddd, *J* = 9.8, 6.1, 6.1, 6.1 Hz, 1H), 4.77 (d, *J* = 3.7 Hz, 1H), 5.06 (d, *J* = 1.6 Hz, 1H), 5.08 (dd, *J* = 9.9, 9.9 Hz, 1H), 5.22 (dd, *J* = 3.4, 1.9 Hz, 1H), 5.26 (dd, *J* = 9.8, 3.4 Hz, 1H), 7.32–7.42 (m, 6H), 7.62–7.65 (m, 2H), 7.69–7.72 ppm (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *d* = 17.1 (CH_3), 19.3 (C), 20.6 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 26.7 (3 × CH_3), 54.9 (CH_3), 58.5 (CH_3), 60.6 (CH_3), 62.7 (CH_2), 66.5 (CH), 69.3 (CH), 70.0 (CH), 70.9 (CH), 71.0 (CH), 74.9 (CH), 81.1 (CH), 82.6 (CH), 96.9 (CH), 97.6 (CH), 127.3 (2 × CH), 127.5 (2 × CH), 129.4 (CH), 129.5 (CH), 133.3 (C), 133.5 (C), 135.5 (2 × CH), 135.9 (2 × CH), 169.8 (C), 169.9 (C), 170.0 ppm (C); IR (film): $\tilde{n}$ = 2936, 2858, 1748, 1372, 1224, 1047 cm^{-1}; MS (70 eV, EI): *m/z* (%): 675 (7) [*M*–C_4H_9]$^+$, 555 (1), 273 (100), 153 (82); HRMS (EI): *m/z* calcd for $C_{33}H_{43}O_{13}Si$ [*M*–C_4H_9]$^+$: 675.2473, found: 675.2469; elemental analysis calcd (%) for $C_{37}H_{52}O_{13}Si$ (732.89): C 60.64, H 7.15; found: C 60.81, H 7.01.



73S **13**

Methyl 2,3,4-Tri-*O*-acetyl-*a*-L-rhamnopyranosyl-(1? 4)-2,3-di-*O*-methyl-*a*-D-glucopyranoside (13): To a solution of compound **73S** (470 mg, 0.642 mmol) in dry THF (16.4 mL) was added a 1 M solution of Bu_4NF/THF (1.6 mL, 1.6 mmol), and the mixture was stirred at room temperature for 19 h. The reaction mixture was concentrated under reduced pressure and the residue purified by column chromatography (hexanes–EtOAc, 50:50 ? 25:75) to give the alcohol **13** (217 mg, 0.439 mmol, 68 %) as an amorphous solid: $[a]_D$ = +44.7 (*c* = 0.235 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): *d* = 1.21 (d, *J* = 6.3 Hz, 3H), 1.88 (br s, 1H), 1.99 (s, 3H), 2.04 (s, 3H), 2.13 (s, 3H), 3.23 (dd, *J* = 9.5, 3.7 Hz, 1H), 3.41 (s, 3H), 3.50 (s, 3H), 3.51 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.59 (s, 3H), 3.63 (ddd, *J* = 9.8, 2.4, 2.4 Hz, 1H), 3.67 (dd, *J* = 10.0, 8.7 Hz, 1H), 3.79 (dd, *J* = 12.2, 2.6 Hz, 1H), 3.84 (dd, *J* = 12.2, 1.9 Hz, 1H), 4.13 (dddd, *J* = 9.8, 6.3, 6.3, 6.3 Hz, 1H), 4.82 (d, *J* = 3.7 Hz, 1H), 4.96 (d, *J* = 1.6 Hz, 1H), 5.08 (dd, *J* = 10.0, 10.0 Hz,

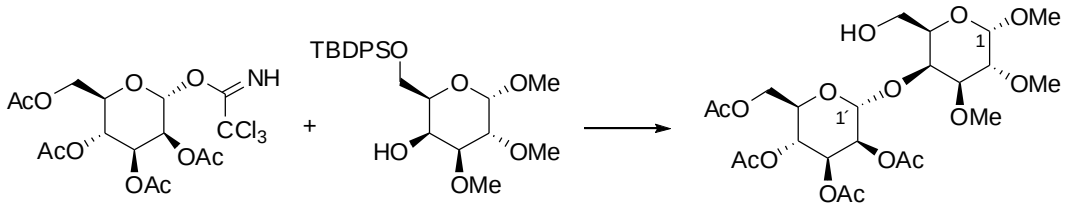
1H), 5.16 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.24 ppm (dd, *J* = 10.0, 3.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *d* = 17.1 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 55.2 (CH_3), 58.7 (CH_3), 60.7 (CH_3), 61.0 (CH_2), 66.8 (CH), 69.2 (CH), 70.2 (CH), 70.5 (CH), 70.9 (CH), 75.4 (CH), 81.2 (CH), 82.6 (CH), 97.4 (CH), 98.0 (CH), 170.0 (C), 170.2 (C), 170.5 ppm (C); IR (film): $\tilde{n}$ = 3502, 2917, 2848, 1748, 1372, 1225, 1046 cm^{-1}; MS (70 eV, EI): *m/z* (%): 434 (3) $[M-CH_3CO_2H]^+$, 374 (1), 359 (1), 273 (50), 88 (100); HRMS (EI): *m/z* calcd for $C_{19}H_{30}O_{11}$ $[M-CH_3CO_2H]^+$: 434.1788, found: 434.1794; elemental analysis calcd (%) for $C_{21}H_{34}O_{13}$ (494.49): C 51.01, H 6.93; found: C 51.16, H 6.84.



13 **18**

Methyl 2,3,4-Tri-*O*-acetyl-*a*-L-rhamnopyranosyl-(1? 4)-2,3-di-*O*-methyl-6-*O*-phthalimido-*a*-D-glucopyranoside (18): Following the general procedure, the alcohol **13** gave after column chromatography (hexanes–EtOAc, 70:30) the phthalimide **18** (94 %) as a colourless oil: $[a]_D$ = +48.1 (*c* = 0.210 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): *d* = 1.24 (d, *J* = 6.3 Hz, 3H), 1.96 (s, 3H), 2.05 (s, 3H), 2.17 (s, 3H), 3.34 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.44 (s, 3H), 3.50 (s, 3H), 3.54 (dd, *J* = 9.4, 9.4 Hz, 1H), 3.60 (s, 3H), 3.82 (ddd, *J* = 10.1, 2.0, 2.0 Hz, 1H), 4.01 (dd, *J* = 9.8, 9.8 Hz, 1H), 4.17 (dddd, *J* = 10.0, 6.3, 6.3, 6.3 Hz, 1H), 4.34 (dd, *J* = 10.3, 2.4 Hz, 1H), 4.46 (dd, *J* = 10.3, 2.1 Hz, 1H), 4.87 (d, *J* = 3.5 Hz, 1H), 5.12 (dd, *J* = 9.7, 9.7 Hz, 1H), 5.24 (d, *J* = 3.5 Hz, 1H), 5.25 (dd, *J* = 9.1, 3.5 Hz, 1H), 5.40 (s, 1H), 7.73 (m, 2H), 7.77 ppm (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *d* = 17.1 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 55.5 (CH_3), 58.6 (CH_3), 60.3 (CH_3), 66.7 (CH), 68.9 (CH), 69.3 (CH), 69.9 (CH), 71.0 (CH), 75.1 (CH), 75.3 (CH_2), 80.8 (CH), 81.9 (CH), 97.3 (CH), 98.1 (CH), 123.4 (2 × CH), 128.8 (2 × C), 134.4 (2 × CH), 163.0 (2 × C), 170.0 (C), 170.1 (C), 170.5 ppm (C); IR (film): $\tilde{n}$ = 2938, 1791, 1738, 1372, 1226, 1084, 1046 cm^{-1}; MS (FAB): *m/z* (%): 662 (4) $[M+Na]^+$, 661 (16) $[M+Na-H]^+$, 286 (16), 273 (100);

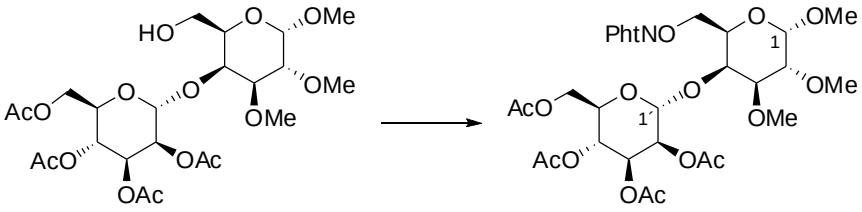
HRMS (FAB): *m/z* calcd for $C_{29}H_{36}NO_{15}Na$ [*M*+Na–H]$^+$: 661.1983, found: 661.1957; elemental analysis calcd (%) for $C_{29}H_{37}NO_{15}$ (639.60): C 54.46, H 5.83, N 2.19; found: C 54.58, H 5.52, N 2.03.



58S **52S** **14**

Methyl 2,3,4,6-Tetra-*O*-acetyl-*a*-D-mannopyranosyl-(1? 4)-2,3-di-*O*-methyl-*a*-D-galactopyranoside (14): To a solution of trichloroacetimidate **58S** (378 mg, 0.770 mmol) and alcohol **52S** (161 mg, 0.350 mmol) in dry CH_2Cl_2 (6.7 mL) containing molecular sieves 3Å (161 mg) was added a 0.1 M solution of TMSOTf/CH_2Cl_2 (35 µL, 3.5 µmol) under nitrogen at 0 ^oC and the mixture was stirred at room temperature for 1 h. The reaction mixture was poured into a saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. To the residue in dry THF (9.4 mL) was added a 1 M solution of Bu_4NF/THF (875 µL, 0.875 mmol) under nitrogen and the mixture was stirred at room temperature for 16 h. After this time the solvent was evaporated under reduced pressure and the residue purified by column chromatography (hexanes–EtOAc, 30:70) to give the disaccharide **14** (192 mg, 0.348 mmol, 99 %) as a foam: $[a]_D$ = +134.1 (*c* = 0.185 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 2.00 (s, 3H), 2.02 (s, 3H), 2.08 (s, 3H), 2.15 (s, 3H), 3.40 (s, 3H), 3.45 (s, 3H), 3.50 (s, 3H), 3.53 (dd, *J* = 10.3, 3.2 Hz, 1H), 3.61 (dd, *J* = 10.3, 3.4 Hz, 1H), 3.68–3.82 (m, 3H), 4.04 (dd, *J* = 12.4, 2.4 Hz, 1H), 4.20 (dd, *J* = 3.2, 0 Hz, 1H), 4.33 (dd, *J* = 12.4, 3.7 Hz, 1H), 4.49 (ddd, *J* = 10.1, 2.9, 2.9 Hz, 1H), 4.89 (d, *J* = 3.7 Hz, 1H), 5.01 (d, *J* = 1.6 Hz, 1H), 5.19 (dd, *J* = 3.2, 1.6 Hz, 1H), 5.32–5.38 ppm (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *d* = 20.67 (CH_3), 20.69 (2 × CH_3), 20.9 (CH_3), 55.3 (CH_3), 58.1 (CH_3), 58.2 (CH_3), 60.6 (CH_2), 62.1 (CH_2), 65.8 (CH), 68.5 (CH), 68.9 (CH), 69.5 (CH), 70.2 (CH), 74.4 (CH), 77.0 (CH), 78.5 (CH), 97.6 (CH), 98.5 (CH), 169.7 (C), 170.0 (C), 170.7 ppm (2 × C); IR (film): $\tilde{n}$ = 3486, 2924, 2853, 1748, 1371, 1227 cm^{-1}; MS (70 eV, EI): *m/z* (%): 535 (3) [*M*–OH]$^+$, 331 (45), 169 (100), 109 (73); HRMS (EI): *m/z* calcd for

$C_{23}H_{35}O_{14}$ [*M*–OH]$^+$: 535.2027, found: 535.2034; elemental analysis calcd (%) for $C_{23}H_{36}O_{15}$ (552.52): C 50.00, H 6.57; found: C 50.09, H 6.89.



Methyl 2,3,4,6-Tetra-*O*-acetyl-*a*-D-mannopyranosyl-(1? 4)-2,3-di-*O*-methyl-6-*O*-phthalimido-*a*-D-galactopyranoside (19): Following the general procedure, the alcohol **14** afforded after purification by column chromatography (Et_2O–EtOAc, 90:10) the phthalimide **19** (96 %) as a foam: $[a]_D$ = +75.6 (*c* = 0.226 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): *d* = 1.98 (s, 3H), 2.04 (s, 3H), 2.11 (s, 3H), 2.20 (s, 3H), 3.45 (s, 3H), 3.51 (s, 3H), 3.53 (s, 3H), 3.58 (dd, *J* = 10.3, 2.9 Hz, 1H), 3.66 (dd, *J* = 10.3, 3.7 Hz, 1H), 4.09 (dd, *J* = 12.2, 2.4 Hz, 1H), 4.10 (m, 1H), 4.25 (dd, *J* = 9.0, 9.0 Hz, 1H), 4.29 (dd, *J* = 9.0, 5.6 Hz, 1H), 4.38 (dd, *J* = 12.5, 3.4 Hz, 1H), 4.47 (d, *J* = 2.9 Hz, 1H), 4.55 (m, 1H), 4.92 (d, *J* = 3.4 Hz, 1H), 5.36 (dd, *J* = 3.2, 1.3 Hz, 1H), 5.37–5.42 (m, 3H), 7.75 (m, 2H), 7.80 ppm (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): *d* = 20.71 (CH_3), 20.73 (CH_3), 20.8 (CH_3), 21.0 (CH_3), 55.9 (CH_3), 58.1 (CH_3), 58.4 (CH_3), 62.3 (CH_2), 66.0 (CH), 66.5 (CH), 68.6 (CH), 69.3 (CH), 69.5 (CH), 73.8 (CH), 74.7 (CH_2), 76.9 (CH), 78.5 (CH), 98.0 (CH), 99.2 (CH), 123.6 (2 × CH), 128.8 (2 × C), 134.6 (2 × CH), 163.1 (2 × C), 169.7 (C), 170.0 (C), 170.2 (C), 170.8 ppm (C); IR (film): $\tilde{n}$ = 2932, 2835, 1741, 1370, 1228 cm^{-1}; MS (70 eV, EI): *m/z* (%): 697 (<1) [*M*]$^+$, 577 (<1), 492 (2), 417 (1), 331 (100); HRMS (EI): *m/z* calcd for $C_{31}H_{39}NO_{17}$ [*M*]$^+$: 697.2218, found: 697.2220; elemental analysis calcd (%) for $C_{31}H_{39}NO_{17}$ (697.64): C 53.37, H 5.63, N 2.01; found: C 53.42, H 5.69, N 1.94.