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Highly Regio- and Stereoselective Synthesis of Mannose-Containing Oligosaccharides using Acetobromosugars as the Donors and Partially Protected Mannose Derivatives as the Acceptors *via* Sugar Orthoester Intermediates

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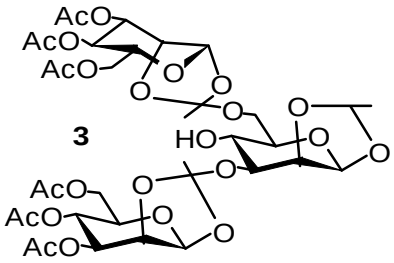
Supporting Information

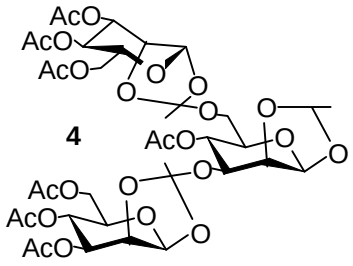
Typical conditions for orthoester preparation: To a stirred solution of 2,3,4,6-tetra-*O*-acetyl-α-D-glycopyranosyl bromide (450 mg, 1 mmol), and 2,4-lutidine (138 μL, 1 mmol), and methyl 6-*O*-benzoyl-α-D-mannopyranoside (308 mg, 1 mmol) in dichloromethane (20 mL) under nitrogen atmosphere was added silver triflate (254 mg, 1 mmol) in a dark room, and the reaction was carried out at room temperature and monitored by TLC (1:1 petroleum ether/ethyl acetate). After completion of the reaction the mixture was partitioned between dichloromethane and water, the organic phase was concentrated, dried, and subjected to column chromatography with 1.5:1 petroleum ether/ethyl acetate as the eluent, giving the product **12** (490 mg, 78%) as a syrup capable of being used for further rearrangement.

Typical rearrangement conditions: To a stirred solution of sugar-sugar orthoester **12** (400 mg, 0.64 mmol) in dichloromethane (10 mL) was added TMSOTf (12 μL, 0.1 equiv.) under nitrogen atmosphere, and the reaction was monitored by TLC (1:1 petroleum ether/ethyl acetate). After completion of the reaction to the mixture was added triethyl amine (20 μL). The mixture was filtered and the filtrate was washed with CH_2Cl_2. The combined solution was washed with N HCl (10 mL), sat. aq. $NaHCO_3$ (10 mL), and aq. NaCl (2×10 mL), then dried over anhydrous Na_2SO_4, concentrated. The residule was subjected to column chromatography with 1.5:1 petroleum ether/ethyl acetate as the eluent, giving the product **14** (330 mg, 82%) as amorphous.

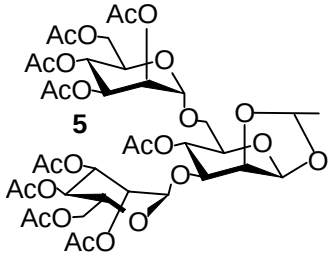
All new products gave satisfactory elemental analysis results. Optical rotation and ^{1}H NMR ($CDCl_3$, 400MHz) data of some new compounds are as follows.



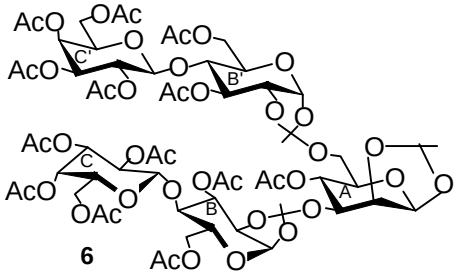
3: $[\alpha]_D$ +5.2° (c 1.5, $CHCl_3$); m.p. 110-112°C; ^1H NMR δ_H (R) 5.54, 5.50 (2 d, J 2.7 Hz, H-1', 1''), 5.30-5.15 (m, 6 H, H-1, 3', 3'', 4', 4'', CH_3CH), 4.75, 4.63 (2 dd, $J_{2',3'}$ 3.8 Hz, $J_{2'',3''}$ 3.9 Hz, H-2', 2''), 4.23-4.13 (m, 4 H, H-6', 6''), 4.06 (dd, 1 H, $J_{1,2}$ 2.4 Hz, $J_{2,3}$ 3.6 Hz, H-2), 3.84-3.68 (m, 6 H, H-3, 4, 5', 5'', 6), 3.40-3.35 (m, 1 H, H-5), 2.11, 2.10, 2.07, 2.07, 2.06, 2.05 (6 s, 18 H, 6 CH_3CO), 1.85, 1.74 (2 s, 6 H, 2 CH_3CO), 1.47 (d, 3 H, J 5.0 Hz, CH_3CH). Anal. Calcd. for $C_{36}H_{50}O_{24}$: C, 49.89; H, 5.81. Found: C, 49.96; H, 5.89.



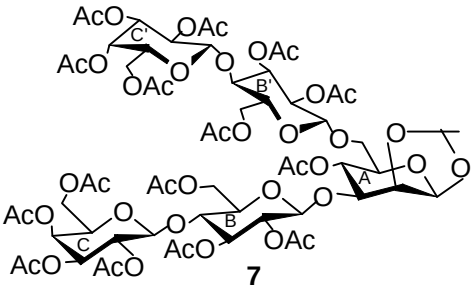
4: $[\alpha]_D$ +0.4° (c 0.1, $CHCl_3$); m.p. 135-138°C; ^1H NMR δ_H (R) 5.49, 5.43 (2 d, $J_{1',2'}$, $J_{1'',2''}$ 2.8 Hz, 2.6 Hz, H-1', 1''), 5.30-5.16 (m, 6 H, H-1, 3', 3'', 4', 4'', CH_3CH), 5.12 (t, 1 H, J 9.6 Hz, H-4), 4.66 (dd, 1 H, $J_{1'',2''}$ 2.9 Hz, $J_{2'',3''}$ 3.9 Hz, H-2''), 4.58 (dd, 1 H, $J_{1',2'}$ 2.8 Hz, $J_{2',3'}$ 4.0 Hz, H-2'),4.24-4.08 (m, 5 H, H-2, 6', 6''), 4.01 (dd, 1 H, $J_{2,3}$ 4.6 Hz, $J_{3,4}$ 9.6 Hz, H-3), 3.75-3.65 (m, 2 H, H-5', 5''), 3.60 (d, 2 H, $J_{6a,6b}$ 4.5 Hz, H-6), 3.55-3.50 (m, 1 H, H-5), 2.12, 2.10, 2.07, 2.06, 2.06, 2.05, 2.04 (7 s, 21 H, 7 CH_3CO), 1.77, 1.71 (2 s, 6 H, 2 CH_3CO_3), 1.49 (d, 3 H, J 4.9 Hz, CH_3CH). Anal. Calcd. for $C_{38}H_{52}O_{25}$: C, 50.22; H, 5.77. Found: C, 50.01; H, 5.94.



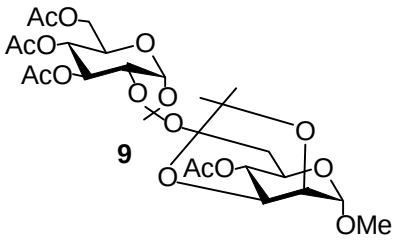
5: $[\alpha]_D$ +16.9° (c 0.15, $CHCl_3$); m.p. 177-178°C; ^{1}H NMR δ_H (R) 5.36-5.21 (m, 8 H, H-1, 2', 3', 3'', 4, 4', 4'', CH_3CH), 5.14 (dd, 1 H, $J_{1'',2''}$ 1.9 Hz, $J_{2'',3''}$ 3.1 Hz, H-2''), 4.98 (d, 1 H, $J_{1'',2''}$ 1.9 Hz, H-1''), 4.78 (d, 1 H, $J_{1',2'}$ 1.7 Hz, H-1'), 4.34-4.27 (m, 4 H, H-2, 5', 6''), 4.10-4.01 (m, 3 H, H-5'', 6'), 3.91 (dd, 1 H, $J_{2,3}$ 3.8 Hz, $J_{3,4}$ 9.7 Hz, H-3), 3.80 (dd, 1 H, $J_{5,6a}$ 6.3 Hz, $J_{6a,6b}$ 10.4 Hz, H-6_a), 3.62-3.56 (m, 2 H, H-5, 6_b), 2.16, 2.15, 2.15, 2.11, 2.09, 2.06, 2.06, 2.00, 1.98 (9 s, 27 H, 9 CH_3CO), 1.53 (d, 3 H, J 5.0 Hz, CH_3CH). Anal. Calcd. for $C_{38}H_{52}O_{25}$: C, 50.22; H, 5.77. Found: C, 50.07; H, 5.81.



6: $[\alpha]_D$ +2.4° (c 0.15, $CHCl_3$); ^{1}H NMR δ_H (R) 5.69 (d, 1 H, $J_{1B,2B}$ 5.1 Hz, H-1B), 5.65 (d, 1 H, $J_{1B',2B'}$ 5.2 Hz, H-1B'), 5.50 (dd, 1 H, $J_{2B,3B}$ 2.4 Hz, $J_{3B,4B}$ 1.2 Hz, H-3B), 5.42 (t, 1 H, J 1.9 Hz, H-3B'), 5.38 (2 d, 2 H, J 3.3 Hz, H-4C, 4C'), 5.26 (d, 1 H, $J_{1A,2A}$ 1.6 Hz, H-1A), 5.26 (q, 1 H, J 5.0 Hz, CH_3CH), 5.16 (2 dd, 2 H, $J_{1C(C'),2C(C')}$ 8.0 Hz, $J_{2C(C'),3C(C')}$ 9.6 Hz, H-2C, 2C'), 5.10 (t, 1 H, J 9.5 Hz, H-4A), 5.00 (2 dd, 2 H, $J_{2C(C'),3C(C')}$ 9.6 Hz, $J_{3C(C'),4C(C')}$ 3.4 Hz, H-3C, 3C'), 4.60, 4.55 (2 d, 2 H, $J_{1C(C'),2C(C')}$ 8.0 Hz, H-1C, 1C'), 4.41 (dd, 1 H, H-2B), 4.35 (dd, 1 H, H-2B'), 4.30-4.20 (m, 3 H, H-2A, $6B_a$, $6B'_a$), 4.13-4.05 (m, 6 H, H-$6B_b$, $6B'_b$, 6C, 6C'), 3.98-3.88 (m, 3 H, H-3A, 5C, 5C'), 3.85-3.78 (m, 2 H, H-5B, 5B'), 3.64 (2 t, 2 H, J 9.5 Hz, H-4B, 4B'), 3.60-3.58 (m, 3 H, H-5A, 6A), 2.17-1.98 (13 s, 39 H, 13 CH_3CO), 1.74, 1.68 (2 s, 6 H, 2 CH_3CO_3), 1.47 (d, 3 H, J 5.0 Hz, CH_3CH). Anal. Calcd. for $C_{62}H_{84}O_{41}$: C, 50.14; H, 5.70. Found: C, 49.76; H, 5.51.

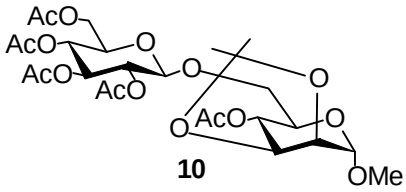


7: $[\alpha]_D$ –3.6° (c 0.1, $CHCl_3$); ^1H NMR δ_H (R) 5.34 (2 d, 2 H, J 3.0 Hz, H-4C, 4C'), 4.90, 4.85, 4.81, 4.69 (4 d, J 7.9 Hz, H-1B, 1B', 1C, 1C'), 2.17-1.97 (m, 45 H, 15 C*H*$_3$CO), 1.47 (d, 3 H, J 4.9 Hz, C*H*$_3$CH). Anal. Calcd. for $C_{62}H_{84}O_{41}$: C, 50.14; H, 5.70. Found: C, 50.44; H, 6.11.



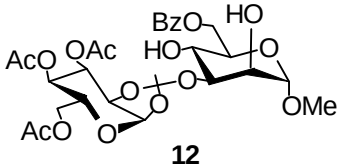
9

9: $[\alpha]_D$ +29.6° (c 3.3, $CHCl_3$); ^1H NMR (200Hz) δ_H 5.71 (d, 1 H, $J_{1',2'}$ 5.4 Hz, H-1'), 5.17 (t, 1 H, $J_{2',3'}$, $J_{3',4'}$ 2.7 Hz, H-3'), 5.01-4.86 (m, 3 H, H-1, 4, 4'), 4.35 (dd, 1 H, $J_{1',2'}$ 5.4 Hz, $J_{2',3'}$ 2.7 Hz, H-2'), 4.28-3.36 (m, 8 H, H-2, 3, 5, 5', 6, 6'), 3.38 (s, 3 H, OC*H*$_3$), 2.09, 2.06, 2.06, 2.03, 1.70, 1.52, 1.33 (7 s, 21 H, 7 C*H*$_3$). Anal. Calcd. for $C_{26}H_{38}O_{16}$: C, 51.48; H, 6.31. Found: C, 51.27; H, 5.99.



10

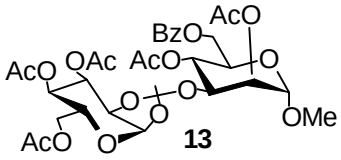
10: $[\alpha]_D$ +0.6° (c 5.8, $CHCl_3$); ^1H NMR (200Hz) δ_H 5.18-4.75 (m, 4 H, H-2', 3', 4, 4'), 4.85 (s, 1 H, H-1), 4.50 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1'), 4.24 (dd, 1 H, $J_{5',6'}$ 4.6 Hz, $J_{6',6'}$ 12.2 Hz, H-6'), 4.18-3.33 (m, 7 H, H-2, 3, 5, 5', 6, 6'), 3.30 (s, 3 H, OC*H*$_3$), 2.04, 2.04, 1.97, 1.97, 1.94 (5 s, 15 H, 5 C*H*$_3$CO), 1.47, 1.29 (2 s, 6 H, 2 C*H*$_3$). Anal. Calcd. for $C_{26}H_{38}O_{16}$: C, 51.48; H, 6.31. Found: C, 51.21; H, 6.07.



12

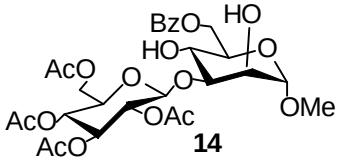
12: $[\alpha]_D$ +67.4° (c 3.1, $CHCl_3$); ^1H NMR δ_H 8.04 (d, 2 H, J 7.7 Hz, Bz-H), 7.54 (t, 1 H, J 7.7 Hz, Bz-H), 7.42 (t, 2 H, J 7.7 Hz, Bz-H), 5.84 (d, 1 H, $J_{1',2'}$ 5.3 Hz, H-1'), 5.18 (t, 1 H, $J_{2',3'}$, $J_{3',4'}$ 3.2 Hz, H-3'), 4.90 (dd, 1 H, $J_{3',4'}$ 3.2 Hz, $J_{4',5'}$ 9.6 Hz, H-4'), 4.78 (dd, 1 H, $J_{1',2'}$ 5.3 Hz, $J_{2',3'}$ 3.2 Hz, H-2'), 4.74 (s, 1 H, H-1), 4.69 (dd, 1 H, $J_{5,6a}$

4.8 Hz, $J_{6a,6b}$ 12.0 Hz, H-6_a), 4.57 (dd, 1 H, $J_{5,6b}$ 2.1 Hz, $J_{6a,6b}$ 12.0 Hz, H-6_b), 4.21 (dd, 1 H, $J_{5',6'a}$ 4.7 Hz, $J_{6'a,6'b}$ 12.4 Hz, H-6'$_a$), 4.19 (dd, 1 H, $J_{5',6'b}$ 2.8 Hz, $J_{6'a,6'b}$ 12.4 Hz, H-6'$_b$), 3.96 (d, 1 H, $J_{2,3}$ 1.6 Hz, H-2), 3.94 (dd, 1 H, $J_{2,3}$ 1.6 Hz, $J_{3,4}$ 9.6 Hz, H-3), 3.93-3.89 (m, 1 H, H-5'), 3.88-3.87 (m, 1 H, H-5), 3.81 (t, 1 H, J 9.6 Hz, H-4), 3.40 (s, 3 H, OC*H*$_3$), 2.10, 2.10, 2.09 (3 s, 9 H, C*H*$_3$CO), 1.81 (s, 3 H, C*H*$_3$CO$_3$). Anal. Calcd. for $C_{28}H_{36}O_{16}$: C, 53.50; H, 5.77. Found: C, 53.78; H, 5.99.



13

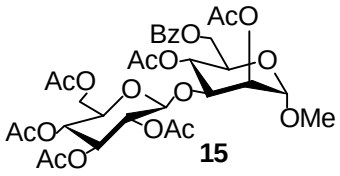
13: $[\alpha]_D$ +37.1° (c 2.0, $CHCl_3$); m.p. 116-119°C; ^{1}H NMR δ_H 8.07 (d, 2 H, J 8.0 Hz, Bz-H), 7.57 (t, 1 H, J 8.0 Hz, Bz-H), 7.44 (t, 2 H, J 8.0 Hz, Bz-H), 5.68 (d, 1 H, $J_{1',2'}$ 5.3 Hz, H-1'), 5.32 (t, 1 H, J 9.8 Hz, H-4), 5.21 (dd, 1 H, $J_{1,2}$ 1.8 Hz, $J_{2,3}$ 3.2 Hz, H-2), 5.15 (t, 1 H, J 3.5 Hz, H-3'), 4.90 (dd, 1 H, $J_{3',4'}$ 3.5 Hz, $J_{4',5'}$ 9.6 Hz, H-4'), 4.67 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 4.50 (dd, 1 H, $J_{5,6a}$ 2.5 Hz, $J_{6a,6b}$ 12.1 Hz, H-6_a), 4.40 (dd, 1 H, $J_{1',2'}$ 5.3 Hz, $J_{2',3'}$ 3.5 Hz, H-2'), 4.33 (dd, 1 H, $J_{5,6b}$ 5.5 Hz, $J_{6a,6b}$ 12.1 Hz, H-6_b), 4.21 (dd, 1 H, $J_{5',6'a}$ 6.9 Hz, $J_{6'a,6'b}$ 12.6 Hz, H-6'), 4.19 (dd, 1 H, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 9.8 Hz, H-3), 4.16 (dd, 1 H, $J_{5',6'b}$ 3.0 Hz, $J_{6'a,6'b}$ 12.6 Hz, H-6'), 4.04-4.00 (m, 1 H, H-5), 3.96-3.92 (m, 1 H, H-5'), 2.13, 2.12, 2.10, 2.09, 2.08 (5 s, 15 H, 5 C*H*$_3$CO), 1.72 (s, 3 H, C*H*$_3$CO$_3$). Anal. Calcd. for $C_{32}H_{40}O_{18}$: C, 53.93; H, 5.66. Found: C, 54.11; H, 5.79.



14

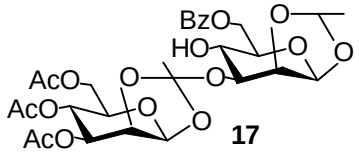
14: $[\alpha]_D$ +39.6° (c 1.0, $CHCl_3$); ^{1}H NMR δ_H 8.06 (d, 2 H, J 7.4 Hz, Bz-H), 7.56 (t, 1 H, J 7.4 Hz, Bz-H), 7.44 (t, 2 H, J 7.4 Hz, Bz-H), 5.26 (t, 1 H, J 9.6 Hz, H-3'), 5.04 (dd, 1 H, $J_{1',2'}$ 8.0 Hz, $J_{2',3'}$ 9.6 Hz, H-2'), 5.03 (t, 1 H, J 9.6 Hz, H-4'), 4.79 (s, 1 H, H-1), 4.70 (dd, 1 H, $J_{5,6a}$ 1.6 Hz, $J_{6a,6b}$ 11.9 Hz, H-6_a), 4.63 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 4.54 (dd, 1 H, $J_{5,6b}$ 5.7 Hz, $J_{6a,6b}$ 11.9 Hz, H-6_b), 4.25 (dd, 1 H, $J_{5',6'a}$ 1.8 Hz, $J_{6'a,6'b}$ 12.3 Hz, H-6'$_a$), 4.13 (dd, 1 H, $J_{5',6'b}$ 6.6 Hz, $J_{6',6'}$ 12.3 Hz, H-6'$_b$), 3.94 (t, 1 H, J 9.2

Hz, H-4), 3.89-3.85 (m, 1 H, H-5), 3.86 (d, 1 H, $J_{2,3}$ 2.9 Hz, H-2), 3.82-3.78 (m, 1 H, H-5'), 3.75 (dd, 1 H, $J_{2,3}$ 2.9 Hz, $J_{3,4}$ 9.2 Hz, H-3), 3.40 (s, 3 H, OC*H*$_3$), 2.11, 2.09, 2.05, 2.03 (4 s, 12 H, 4 C*H*$_3$CO). Anal. Calcd. for $C_{28}H_{36}O_{16}$: C, 53.50; H, 5.77. Found: C, 53.71; H, 5.52.



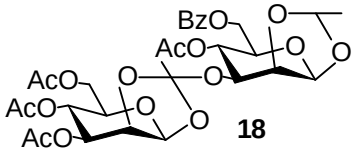
15

15: $[\alpha]_D$ +11.7° (c 1.4, $CHCl_3$); m.p. 140-144°C; ^{1}H NMR δ_H 8.07 (d, 2 H, J 7.6 Hz, Bz-H), 7.57 (t, 1 H, J 7.6 Hz, Bz-H), 7.45 (t, 2 H, J 7.6 Hz, Bz-H), 5.35 (t, 1 H, J 9.8 Hz, H-4), 5.16 (t, 1 H, J 9.1 Hz, H-3'), 5.15 (dd, 1 H, $J_{1,2}$ 1.3 Hz, $J_{2,3}$ 3.3 Hz, H-2), 5.08 (t, 1 H, J 9.1 Hz, H-4'), 4.89 (dd, 1 H, $J_{1',2'}$ 7.8 Hz, $J_{2',3'}$ 9.1 Hz, H-2'), 4.71 (d, 1 H, $J_{1,2}$ 1.3 Hz, H-1), 4.57 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1'), 4.54 (dd, 1 H, $J_{5,6a}$ 2.2 Hz, $J_{6a,6b}$ 12.0 Hz, H-6$_a$), 4.38-4.30 (m, 2 H, H-6$_b$, 6'$_a$), 4.15 (dd, 1 H, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 9.8 Hz, H-3), 4.07 (dd, 1 H, $J_{5',6'b}$ 1.9 Hz, $J_{6'a,6'b}$ 12.4 Hz, H-6'$_b$), 4.04-4.00 (m, 1 H, H-5), 3.73-3.64 (m, 1 H, H-5'), 2.08, 2.08, 2.06, 2.02, 2.01, 1.99 (6 s, 18 H, 6 C*H*$_3$CO). Anal. Calcd. for $C_{32}H_{40}O_{18}$: C, 53.93; H, 5.66. Found: C, 54.18; H, 5.88.



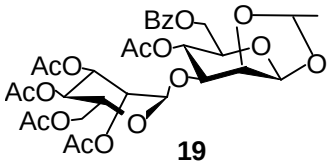
17

17: $[\alpha]_D$ –1.6° (c 0.6, $CHCl_3$); ^{1}H NMR δ_H (R) 8.05-7.39 (m, 5 H, Bz-H), 5.54 (d, 1 H, $J_{1,2}$ 2.7 Hz, H-1), 5.31 (q, 1 H, J 4.8 Hz, CH_3C*H*), 5.30 (t, 1 H, J 9.8 Hz, H-4'), 5.26 (bs, 1 H, H-1'), 5.18 (dd, 1 H, $J_{2',3'}$ 4.0 Hz, $J_{3',4'}$ 9.8 Hz, H-3'), 4.77 (dd, 1 H, $J_{1',2'}$ 2.8 Hz, H-2'), 4.64 (dd, 1 H, $J_{5,6a}$ 4.1 Hz, $J_{6a,\,6b}$ 12.0 Hz, H-6$_a$), 4.56 (dd, 1 H, $J_{5,6b}$ 2.3 Hz, H-6$_b$), 4.23 (dd, 1 H, $J_{5',6'a}$ 5.2 Hz, $J_{6'a,6'b}$ 12.2 Hz, H-6'$_a$), 4.17-4.11 (m, 2 H, H-2, 6'$_b$), 3.97-3.92 (m, 2 H, H-3,4), 3.74-3.70 (m, 1 H, H-5), 3.58-3.53 (m, 1 H, H-5'), 2.10, 2.08, 2.07 (3 s, 9 H, 3 C*H*$_3$CO), 1.88 (s, 3 H, C*H*$_3$CO$_3$), 1.48 (d, 3 H, J 4.8 Hz, C*H*$_3$CH). Anal. Calcd. for $C_{29}H_{36}O_{16}$: C, 54.37; H, 5.66. Found: C, 54.24; H, 5.41.



18

18: $[\alpha]_D$ –1.2° (c 0.4, $CHCl_3$); m.p. 156-160°C; ^{1}H NMR δ_H (R) 8.07-7.42 (m, 5 H, Bz-H), 5.51 (d, 1 H, $J_{1,2}$ 2.7 Hz, H-1), 5.33 (t, 1 H, J 9.5 Hz, H-4), 5.30 (q, 1 H, J 4.9 Hz, CH_3CH), 5.27 (bs, 1 H, H-1'), 5.28 (t, 1 H, J 9.9 Hz, H-4'), 5.18 (dd, 1 H, $J_{2',3'}$ 3.9 Hz, $J_{3',4'}$ 9.9 Hz, H-3'), 4.69 (dd, 1 H, $J_{1',2'}$ 2.9 Hz, H-2'), 4.49 (dd, 1 H, $J_{5,6a}$ 2.7 Hz, $J_{6a,6b}$ 12.1 Hz, H-6_a), 4.34 (dd, 1 H, $J_{5,6b}$ 4.8 Hz, $J_{6a,6b}$ 12.1 Hz, H-6_b), 4.24 (dd, 1 H, $J_{5',6'a}$ 5.1 Hz, $J_{6'a,6'b}$ 12.2 Hz, H-6'$_a$), 4.15 (dd, 1 H, $J_{5',6'b}$ 2.8 Hz, $J_{6'a,6'b}$ 12.2 Hz, H-6'$_b$), 4.14 (dd, 1 H, $J_{1,2}$ 2.7 Hz, $J_{2,3}$ 4.0 Hz, H-2), 4.08 (dd, 1 H, H-3), 3.78-3.70 (m, 2 H, H-5, 5'), 2.12, 2.08, 2.07,. 2.06 (4 s, 12 H, 4 CH_3CO), 1.79 (s, 3 H, CH_3CO_3), 1.51 (d, 3 H, J 4.9 Hz, CH_3CH). Anal. Calcd. for $C_{31}H_{38}O_{17}$: C, 54.55; H, 5.61. Found: C, 54.41; H, 5.74.



19

19: $[\alpha]_D$ +13.4° (c 2.6, $CHCl_3$); m.p. 133-134°C; ^{1}H NMR δ_H (R) 8.09-7.43 (m, 5 H, Bz-H), 5.48 (t, 1 H, J 9.7 Hz, H-4), 5.38-5.26 (m, 4 H, H-1, 3', 4', CH_3CH), 5.13 (dd, 1 H, $J_{1',2'}$ 1.6 Hz, $J_{2',3'}$ 3.3 Hz, H-2'), 4.98 (d, $J_{1',2'}$ 1.6 Hz, H-1'), 4.51 (dd, 1 H, $J_{5,6a}$ 2.7 Hz, $J_{6a,6b}$ 12.1 Hz, H-6_a), 4.35 (dd, 1 H, $J_{5,6b}$ 4.9 Hz, H-6_b), 4.34-4.26 (m, 3 H, H-2, 5', 6'$_a$), 4.03 (dd, 1 H, $J_{5',6'b}$ 2.0 Hz, $J_{6'a,6'b}$ 12.1 Hz, H-6'$_b$), 3.94 (dd, 1 H, $J_{2,3}$ 3.8 Hz, H-3), 3.78-3.74 (m, 1 H, H-5), 2.16, 2.12, 2.09, 2.06, 2.00 (5 s, 15 H, 5 CH_3CO), 1.53 (d, 3 H, J 4.9 Hz, CH_3CH). Anal. Calcd. for $C_{31}H_{38}O_{17}$: C, 54.55; H, 5.61. Found: C, 54.72; H, 5.71.

Di-*O*-(3,4,6-tri-*O*-acetyl-β-D-mannopyranose) 1,2-(1,2-*O*-ethylidene-β-D-mannopyranosid-3,6-yl orthoacetates) (3) $[\alpha]_D$ +5.2° (c 1.5, $CHCl_3$); m.p. 110-112°C; ^1H NMR δ_H (R) 5.54, 5.50 (2 d, J 2.7 Hz, H-1', 1''), 5.30-5.15 (m, 6 H, H-1, 3', 3'', 4', 4'', CH_3CH), 4.75, 4.63 (2 dd, $J_{2',3'}$ 3.8 Hz, $J_{2'',3''}$ 3.9 Hz, H-2', 2''), 4.23-4.13 (m, 4 H, H-6', 6''), 4.06 (dd, 1 H, $J_{1,2}$ 2.4 Hz, $J_{2,3}$ 3.6 Hz, H-2), 3.84-3.68 (m, 6 H, H-3, 4, 5', 5'', 6), 3.40-3.35 (m, 1 H, H-5), 2.11, 2.10, 2.07, 2.07, 2.06, 2.05 (6 s, 18 H, 6 CH_3CO), 1.85, 1.74 (2 s, 6 H, 2 CH_3CO), 1.47 (d, 3 H, J 5.0 Hz, CH_3CH). Anal. Calc. for $C_{36}H_{50}O_{24}$: C, 49.89; H, 5.81. Found: C, 49.96; H, 5.89.

Di-*O*-(3,4,6-tri-*O*-acetyl-β-D-mannopyranose) 1,2-(4-*O*-acetyl-1,2-*O*-ethylidene-β-D-mannopyranosid-3,6-yl orthoacetates) (4) $[\alpha]_D$ +0.4° (c 0.1, $CHCl_3$); m.p. 135-138°C; ^1H NMR δ_H (R) 5.49, 5.43 (2 d, $J_{1',2'}$, $J_{1'',2''}$ 2.8 Hz, 2.6 Hz, H-1', 1''), 5.30-5.16 (m, 6 H, H-1, 3', 3'', 4', 4'', CH_3CH), 5.12 (t, 1 H, J 9.6 Hz, H-4), 4.66 (dd, 1 H, $J_{1'',2''}$ 2.9 Hz, $J_{2'',3''}$ 3.9 Hz, H-2''), 4.58 (dd, 1 H, $J_{1',2'}$ 2.8 Hz, $J_{2',3'}$ 4.0 Hz, H-2'),4.24-4.08 (m, 5 H, H-2, 6', 6''), 4.01 (dd, 1 H, $J_{2,3}$ 4.6 Hz, $J_{3,4}$ 9.6 Hz, H-3), 3.75-3.65 (m, 2 H, H-5', 5''), 3.60 (d, 2 H, $J_{6a,6b}$ 4.5 Hz, H-6), 3.55-3.50 (m, 1 H, H-5), 2.12, 2.10, 2.07, 2.06, 2.06, 2.05, 2.04 (7 s, 21 H, 7 CH_3CO), 1.77, 1.71 (2 s, 6 H, 2 CH_3CO_3), 1.49 (d, 3 H, J 4.9 Hz, CH_3CH). Anal. Calc. for $C_{38}H_{52}O_{25}$: C, 50.22; H, 5.77. Found: C, 50.01; H, 5.94.

4-*O*-Acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-6-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-1,2-*O*-ethylidene-β-D-mannopyranoside (5) $[\alpha]_D$ +16.9° (c 0.15, $CHCl_3$);- m.p. 177-178°C; ^1H NMR δ_H (R) 5.36-5.21 (m, 8 H, H-1, 2', 3', 3'', 4, 4', 4'', CH_3CH), 5.14 (dd, 1 H, $J_{1'',2''}$ 1.9 Hz, $J_{2'',3''}$ 3.1 Hz, H-2''), 4.98 (d, 1 H, $J_{1'',2''}$ 1.9 Hz, H-1''), 4.78 (d, 1 H, $J_{1',2'}$ 1.7 Hz, H-1'), 4.34-4.27 (m, 4 H, H-2, 5', 6''), 4.10-4.01 (m, 3 H, H-5'', 6'), 3.91 (dd, 1 H, $J_{2,3}$ 3.8 Hz, $J_{3,4}$ 9.7 Hz, H-3), 3.80 (dd, 1 H, $J_{5,6a}$ 6.3 Hz, $J_{6a,6b}$ 10.4 Hz, H-6_a), 3.62-3.56 (m, 2 H, H-5, 6_b), 2.16, 2.15, 2.15, 2.11, 2.09, 2.06, 2.06, 2.00, 1.98 (9 s, 27 H, 9 CH_3CO), 1.53 (d, 3 H, J 5.0 Hz, CH_3CH). Anal. Calc. for $C_{38}H_{52}O_{25}$: C, 50.22; H, 5.77. Found: C, 50.07; H, 5.81.

Di-*O*-(3',6',2'',3'',4'',6''-hexa-*O*-acetyl-α-D-lactose) 1,2-(4-*O*-acetyl-1,2-*O*-ethylidene-β-D-mannopyranosid-3,6-yl orthoacetates) (6) $[\alpha]_D$ +2.4° (c 0.15, $CHCl_3$); ^1H NMR δ_H (R) 5.69 (d, 1 H, $J_{1B,2B}$ 5.1 Hz, H-1B), 5.65 (d, 1 H, $J_{1B',2B'}$ 5.2 Hz, H-1B'), 5.50 (dd, 1 H, $J_{2B,3B}$ 2.4 Hz, $J_{3B,4B}$ 1.2 Hz, H-3B), 5.42 (t, 1 H, J 1.9 Hz, H-3B'), 5.38 (2 d, 2 H, J 3.3 Hz, H-4C, 4C'), 5.26 (d, 1 H, $J_{1A,2A}$ = 1.6 Hz, H-1A), 5.26 (q, 1 H, J = 5.0 Hz, CH_3CH), 5.16 (2 dd, 2 H, $J_{1C(C'),2C(C')}$ 8.0 Hz, $J_{2C(C'),3C(C')}$ 9.6 Hz, H-2C, 2C'), 5.10 (t, 1 H, J = 9.5 Hz, H-4A), 5.00 (2 dd, 2 H, $J_{2C(C'),3C(C')}$ 9.6 Hz, $J_{3C(C'),4C(C')}$ = 3.4 Hz, H-3C, 3C'), 4.60, 4.55 (2 d, 2 H, $J_{1C(C'),2C(C')}$ 8.0 Hz, H-1C, 1C'), 4.41 (dd, 1 H, H-2B), 4.35 (dd, 1 H, H-2B'), 4.30-4.20 (m, 3 H, H-2A, $6B_a$, $6B'_a$), 4.13-4.05 (m, 6 H, H-$6B_b$, $6B'_b$, 6C, 6C'), 3.98-3.88 (m, 3 H, H-3A, 5C, 5C'), 3.85-3.78 (m, 2 H, H-5B, 5B'), 3.64 (2 t, 2 H, J 9.5 Hz, H-4B, 4B'), 3.60-3.58 (m, 3 H, H-5A, 6A), 2.17-1.98 (13 s, 39 H, 13 CH_3CO), 1.74, 1.68 (2 s, 6 H, 2 CH_3CO_3), 1.47 (d, 3 H, J 5.0 Hz, CH_3CH). Anal. Calc. for $C_{62}H_{84}O_{41}$: C, 50.14; H, 5.70. Found: C, 49.76; H, 5.51.

4-*O*-Acetyl-3,6-di-*O*-(2',3',6',2'',3'',4'',6''-hepta-*O*-acetyl-α-D-lactosyl)-1,2-*O*-ethylidene-β-D-mannopyranoside (7) $[\alpha]_D$ –3.6° (c 0.1, $CHCl_3$); ^1H NMR δ_H (R) 5.34 (2 d, 2 H, J 3.0 Hz, H-4C, 4C'), 4.90, 4.85, 4.81, 4.69 (4 d, J 7.9 Hz, H-1B, 1B', 1C,

1C'), 2.17-1.97 (m, 45 H, 15 CH_3CO), 1.47 (d, 3 H, J 4.9 Hz, CH_3CH). Anal. Calc. for $C_{62}H_{84}O_{41}$: C, 50.14; H, 5.70. Found: C, 50.44; H, 6.11.

Methyl 4-*O*-acetyl-2,3-*O*-isopropylidene-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-mannopyranoside (10) $[\alpha]_D$ +0.6° (c 5.8, $CHCl_3$); ^{1}H NMR (200Hz) δ_H 5.18-4.75 (m, 4H, H-2', 3', 4, 4'), 4.85 (s, 1H, H-1), 4.50 (d, 1H, $J_{1',2'}$ = 7.8Hz, H-1'), 4.24 (dd, 1H, $J_{5',6'}$ =4.6Hz, $J_{6',6'}$ =12.2Hz, H-6'), 4.18-3.33 (m, 7H, H-2, 3, 5, 5', 6, 6'), 3.30 (s, 3H, OCH_3), 2.04, 2.04, 1.97, 1.97, 1.94 (5s, 15H, 5CH_3CO), 1.47, 1.29 (2s, 6H, 2CH_3). Anal. Calc. for $C_{26}H_{38}O_{16}$: C, 51.48; H, 6.31. Found: C, 51.21; H, 6.07.

Methyl 2,4-*O*-di-acetyl-6-*O*-benzoyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-mannopyranoside (15) $[\alpha]_D$ +11.7° (c 1.4, $CHCl_3$); m.p. 140-144°C; ^{1}H NMR δ_H 8.07 (d, 2 H, J = 7.6 Hz, Bz-H), 7.57 (t, 1 H, J = 7.6 Hz, Bz-H), 7.45 (t, 2 H, J = 7.6 Hz, Bz-H), 5.35 (t, 1 H, J 9.8 Hz, H-4), 5.16 (t, 1 H, J = 9.1 Hz, H-3'), 5.15 (dd, 1 H, $J_{1,2}$ = 1.3 Hz, $J_{2,3}$ = 3.3 Hz, H-2), 5.08 (t, 1 H, J = 9.1 Hz, H-4'), 4.89 (dd, 1 H, $J_{1',2'}$ 7.8 Hz, $J_{2',3'}$ = 9.1 Hz, H-2'), 4.71 (d, 1 H, $J_{1,2}$ = ,1.3 Hz, H-1), 4.57 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1'), 4.54 (dd, 1 H, $J_{5,6a}$ 2.2 Hz, $J_{6a,6b}$ 12.0 Hz, H-6$_a$), 4.38-4.30 (m, 2 H, H-6$_b$, 6'$_a$), 4.15 (dd, 1 H, $J_{2,3}$ = 3.3 Hz, $J_{3,4}$ 9.8 Hz, H-3), 4.07 (dd, 1 H, $J_{5',6'b}$ = 1.9 Hz, $J_{6'a,6'b}$ = 12.4 Hz, H-6'$_b$), 4.04-4.00 (m, 1 H, H-5), 3.73-3.64 (m, 1 H, H-5'), 2.08, 2.08, 2.06, 2.02, 2.01, 1.99 (6 s, 18 H, 6 CH_3CO). Anal. Calc. for $C_{32}H_{40}O_{18}$: C, 53.93; H, 5.66. Found: C, 54.18; H, 5.88.