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Supporting Information

for

Direct Synthesis of β-Mannopyranosides by the Sulfoxide Method

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Ethyl 3-O-Benzyl-4,6-O-benzylidene-2-O-trimethylsilyl-1-deoxy-1-thio-α-D-mannopyranoside S-Oxide (7).

$[\alpha]_D^{20}$ = +7.6 (c = 3.1, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 0.18 (s, 9H), 1.39 (t, J = 7.5 Hz, 3H), 2.61-2.77 (m, 1H), 2.90-3.04 (m, 1H), 3.63-3.72 (m, 1H), 3.81 (t, J = 10.0 Hz, 1H), 4.01 (dd, J = 3.1, 10.0 Hz, 1H), 4.19 (dd, J = 4.6, 10.0 Hz, 1H), 4.29 (t, J = 10.0 Hz, 1H), 4.45 (bs, 1H), 4.76 (d, J = 11.8 Hz, 1H), 4.78 (s, 1H), 4.85 (d, J = 11.8 Hz, 1H), 5.63 (s, 1H), 7.24-7.49 (m, 10H); ^{13}C-NMR ($CDCl_3$), δ: 0.3, 5.7, 43.8, 67.2, 68.1, 70.2, 73.3, 75.5, 77.7, 95.2, 101.5, 125.9, 127.7, 127.9, 128.1, 128.2, 128.9, 137.1, 137.7.

Ethyl 2,3-Di-O-benzyl-4,6-O-benzylidene-1-deoxy-1-thio-α-D-mannopyranoside S-Oxide (8).

mp: 110-113°C. $[\alpha]_D^{20}$ = +10.4 (c = 0.5, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 1.35 (t, J = 7.5 Hz, 3H), 2.55-2.70 (m, 1H), 2.84-2.96 (m, 1H), 3.66-3.84 (m, 2H), 4.11 (dd, J = 3.4, 10.0 Hz, 1H), 4.20 (dd, J = 4.1, 10.0 Hz, 1H), 4.34 (t, J = 10.0 Hz, 1H), 4.51 (dd, J = 1.3, 3.4 Hz, 1H), 4.61 (d, J = 1.3 Hz, 1H), 4.64-4.87 (m, 4H), 5.63 (s, 1H), 7.24-7.50 (m, 15H); ^{13}C-NMR ($CDCl_3$), δ: 5.8, 43.9, 68.1, 70.0, 72.9, 73.1, 74.0, 76.0, 77.8, 92.6, 101.5, 125.9, 127.6, 127.9, 128.2, 128.3, 128.4, 129.0, 137.0, 137.4, 138.0; IR,

υ: 1454, 1374, 1209, 1104, 1028, 740, 698 cm^{-1}; Anal. Calcd. for $C_{29}H_{32}O_6S$: C, 68.48; H, 6.34. Found: C, 68.14; H, 6.57.

Phenyl 2,3-Di-O-benzyl-4,6-O-benzylidene-1-deoxy-1-thio-α-D-mannopyranoside S-Oxide (10).

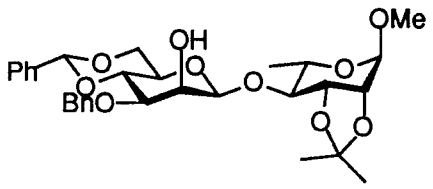
mp: 136-139°C. $[\alpha]_D^{20}$ = -52.7 (c = 1.0, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 3.76 (t, J = 10.0 Hz, 1H), 4.05-4.17 (m, 1H), 4.22 (dd, J = 4.8, 10.0 Hz, 1H), 4.29-4.42 (m, 3H), 4.51 (bs, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.61 (d, J = 12.0 Hz, 1H), 4.67 (d, J = 12.0 Hz, 1H), 4.83 (d, J = 12.0 Hz, 1H), 5.64 (s, 1H), 7.21-7.55 (m, 15H); ^{13}C-NMR ($CDCl_3$), δ: 68.1, 70.0, 72.7, 73.2, 73.4, 77.9, 97.5, 101.6, 124.3, 126.1, 127.6, 127.8, 127.9, 128.2, 128.3, 129.0, 129.4, 131.6, 137.2, 138.2, 141.4; IR, υ: 1454, 1373, 1314, 1214, 1100, 1037, 911, 747, 697 cm^{-1}; Anal. Calcd. for $C_{33}H_{32}O_6S$: C, 71.20; H, 5.79. Found: C, 70.90; H, 5.92.

Ethyl 2,3-Di-O-allyl-4,6-O-benzylidene-1-deoxy-1-thio-α-D-mannopyranoside S-Oxide (11).

mp: 59-62°C. $[\alpha]_D^{20}$ = +52.0 (c = 1.3, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 1.41 (t, J = 7.5 Hz, 3H), 2.65-2.78 (m, 1H), 2.93-3.06 (m, 1H), 3.65-3.82 (m, 2H), 4.02 (dd, J = 3.3, 10.1 Hz, 1H), 4.17-4.42 (m, 7H), 4.62 (s, 1H), 5.16-5.39 (m, 4H), 5.60 (s, 1H), 5.85-6.03 (m, 2H), 7.34-7.49 (m, 5H); ^{13}C-NMR ($CDCl_3$), δ: 5.9, 44.0, 68.1, 69.9, 72.2, 72.9, 73.3, 75.4, 77.9, 92.8, 101.5, 117.2, 118.3, 125.9, 128.2, 129.0, 134.1, 134.3,

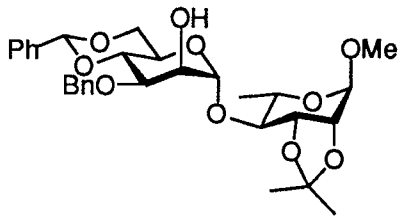
137.0; IR, υ: 1457, 1380, 1217, 1129, 1100, 1046, 1024, 968, 923, 751, 699 cm^{-1}; Anal. Calcd. for $C_{21}H_{28}O_6S$: C, 61.74; H, 6.91. Found: C, 61.74; H, 6.96.

Methyl 4-O-(3-O-benzyl-4,6-O-benzylidene-β-D-mannopyranosyl)-(1→4)-2,3-O-isopropylidene-α-L-rhamnoside.[1] (After removal of TMS group).



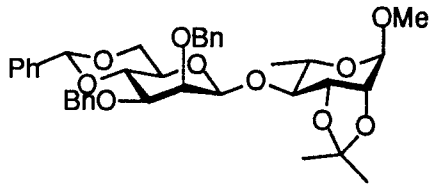
The TMS group was removed for easier purification. $[\alpha]_D^{20}$ = -21.1 (c = 1.5, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 1.30 (d, J = 5.6 Hz, 3H), 1.34 (s, 3H), 1.51 (s, 3H), 2.48 (bs, 1H), 3.29-3.40 (m, 5H), 3.62-3.70 (m, 2H), 3.90 (t, J = 10.3 Hz, 1H), 4.08-4.21 (m, 4H), 4.29 (dd, J = 4.9, 10.4 Hz, 1H), 4.76-4.90 (m, 3H), 5.02 (s, 1H), 5.61 (s, 1H), 7.24-7.44 (m, 8H),7.45-7.54 (m, 2H); ^{13}C-NMR ($CDCl_3$), δ: 17.5, 26.3, 27.7, 54.7, 63.8, 66.9, 68.5, 69.9, 72.3, 76.0, 76.7, 78.1, 78.14, 78.4, 97.7, 98.7, 101.5, 109.3, 125.9, 127.7, 128.2, 128.4, 128.9, 137.3, 137.9; IR, υ: 3573, 2909, 1454, 1384, 1094 cm^{-1}; MS (EI): m/z 558 (M), 543 (M-CH_3), 527 (M-OCH_3), 526 (M-1-OCH_3); HRMS calcd. For $C_{30}H_{38}O_{10}$ (M): 558.2465. Found: 558.2461.

Methyl 4-O-(3-O-benzyl-4,6-O-benzylidene-α-D-mannopyranosyl)-(1→4)-2,3-O-isopropylidene-α-L-rhamnoside.[1] (After removal of TMS group).



The TMS group was removed for easier purification. $[\alpha]_D^{20}$ = +25.0 (c = 1.20, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 1.25 (d, J = 5.6 Hz, 3H), 1.33 (s, 3H), 1.51 (s, 3H), 2.71 (s, 1H), 3.34-3.42 (m, 4H), 3.61-3.67 (m, 1H), 3.79-3.93 (m, 2H), 4.05-4.16 (m, 5H), 4.26-4.31 (m, 1H), 4.73 (d, J = 11.9 Hz, 1H), 4.84 (s, 1H), 4.88 (d, J = 11.9 Hz, 1H), 4.94 (d, J = 1.2 Hz, 1H), 5.62 (s, 1H), 7.24-7.40 (m, 8H), 7.50-7.54 (m, 2H); ^{13}C-NMR ($CDCl_3$), δ: 17.4, 26.3, 28.0, 54.8, 63.2, 64.6, 68.8, 69.9, 72.9, 75.4, 75.9, 76.7, 78.7, 80.6, 97.8, 100.6, 101.4, 109.1, 126.0, 127.7, 127.8, 128.1, 128.4, 128.8, 137.5, 137.9; IR, υ: 3573, 2936, 1454, 1383, 1094, 1046, 1028 cm^{-1}; MS (EI): m/z 558 (M), 543 (M-CH_3), 527 (M-OCH_3), 526 (M-1-OCH_3).

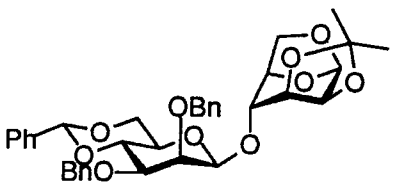
Methyl 4-O-(2,3-Di-O-benzyl-4,6-O-benzylidene-β-D-mannopyranosyl)-(1→4)-2,3-O-isopropylidene-α-L-rhamnoside.



$[\alpha]_D^{20}$ = -61.0 (c = 2.6, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 1.33 (s, 3H), 1.34 (d, J = 5.7 Hz, 3H), 1.50 (s, 3H), 3.27-3.38 (m, 1H), 3.40 (s, 3H), 3.60-3.72 (m, 3H), 3.91-4.00 (m, 2H), 4.06-4.15 (m, 2H), 4.21 (t, J = 9.6 Hz, 1H), 4.27 (dd, J = 4.9, 10.4 Hz, 1H), 4.60 (d, J = 12.6 Hz, 1H), 4.68 (d, J = 12.6 Hz, 1H), 4.82 (d, J = 12.2 Hz, 1H), 4.87

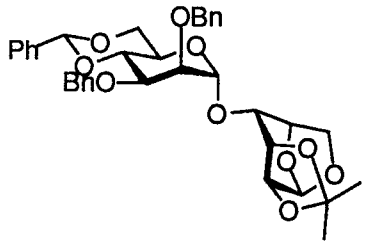
(s, 1H), 4.93 (d, J = 12.2 Hz, 1H), 5.00 (s, 1H), 5.63 (s, 1H), 7.24-7.55 (m, 15H); ^{13}C-NMR ($CDCl_3$), δ: 17.6, 26.3, 27.7, 54.8, 64.1, 67.6, 68.5, 72.0, 74.8, 76.0, 76.2, 77.6, 77.9, 78.3, 78.6, 97.8, 100.0, 101.3, 109.3, 125.9, 127.3, 127.4, 128.1, 128.2, 128.3, 128.8, 137.5, 138.3, 138.5; IR, υ: 1451, 1386, 1372, 1090, 1020, 857 cm^{-1}; MS (EI): m/z 648 (M), 633 (M-CH_3), 617 (M-OCH_3), 616 (M-1-OCH_3), 557 (M-$PhCH_2$); HRMS calcd. For $C_{37}H_{44}O_{10}$ (M): 648.2934. Found: 648.2928.

1,6-Anhydro-4-O-(2,3-di-O-benzyl-4,6-O-benzylidene-β-D-mannopyranosyl)-(1→4)-2,3-O-isopropylidene-β-D-mannopyranose.



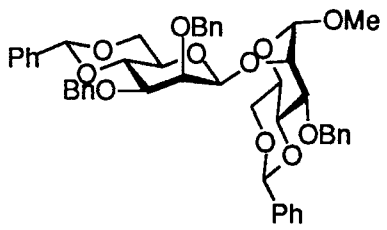
$[\alpha]_D^{20}$ = -48.8 (c = 6.4, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 1.32 (s, 3H), 1.54 (s, 3H), 3.29-3.39 (m, 1H), 3.60 (dd, J = 3.1, 9.9 Hz, 1H), 3.76 (t, J = 6.6 Hz, 1H), 3.90-4.08 (m, 5H), 4.24 (t, J = 9.9 Hz, 1H), 4.30 (dd, J = 4.9, 10.4 Hz, 1H), 4.37 (bd, J = 6.2 Hz, 1H), 4.54 (bd, J = 6.2 Hz, 1H), 4.61 (d, J = 12.6 Hz, 1H), 4.68 (s, 1H), 4.70 (d, J = 12.6 Hz, 1H), 4.92 (d, J = 12.3 Hz, 1H), 4.98 (d, J = 12.3 Hz, 1 H), 5.38 (d, J = 2.8 Hz, 1 H), 5.63 (s, 1H), 7.24-7.53 (m, 15H); ^{13}C-NMR ($CDCl_3$), δ: 25.6, 25.9, 64.2, 67.7, 68.3, 72.1, 72.4, 72.6, 74.9, 75.4, 75.7, 77.6, 78.4, 99.3, 100.4, 101.4, 109.8, 126.0, 127.5, 127.6, 127.7, 128.1, 128.2, 128.3, 128.7, 128.9, 137.3, 138.1 (2); IR, υ: 1378, 1151, 1091, 994, 916 cm^{-1}; MS (EI): m/z 632 (M), 617 (M-CH_3), 542 (M+1-$PhCH_2$), 541 (M-$PhCH_2$); HRMS calcd. For $C_{36}H_{40}O_{10}$ (M): 632.2621. Found: 632.2622.

1,6-Anhydro-4-O-(2,3-di-O-benzyl-4,6-O-benzylidene-α-D-mannopyranosyl)-(1→4)-2,3-O-isopropylidene-β-D-mannopyranose.



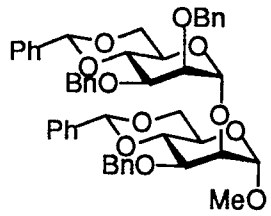
$[\alpha]_D^{20}$ = +25.0 (c = 0.5, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 1.31 (s, 3H), 1.52 (s, 3H), 3.74 (t, J = 7.1 Hz, 1H), 3.84-4.05 (m, 8H), 4.20-4.32 (m, 2H), 4.59 (bd, J = 6.2 Hz, 1H), 4.68 (d, J = 12.1 Hz, 1H), 4.69 (d, J = 12.1 Hz, 1H), 4.90 (d, J = 12.1 Hz, 2H), 4.91 (d, J = 1.5 Hz, 1H), 5.33 (d, J = 2.9 Hz, 1H), 5.65 (s, 1H), 7.24-7.52 (m, 15H); ^{13}C-NMR ($CDCl_3$), δ: 25.9, 64.5, 64.8, 68.5, 72.0, 73.3, 73.5, 73.9, 74.3, 74.6, 79.1, 99.0, 99.1, 101.4, 110.0, 125.9, 127.3, 127.4, 127.9, 128.1, 128.2, 128.4, 128.8, 137.4, 137.9, 138.6; IR, υ: 1370, 1124, 1096, 990, 924 cm^{-1}; MS (EI): m/z 632 (M), 617 (M-CH_3), 542 (M+1-$PhCH_2$), 541 (M-$PhCH_2$).

Methyl 3-O-Benzyl-2-O-(2,3-di-O-benzyl-4,6-O-benzylidene-β-D-mannopyranosyl)-(1→2)-4,6-O-benzylidene-α-D-mannopyranoside.



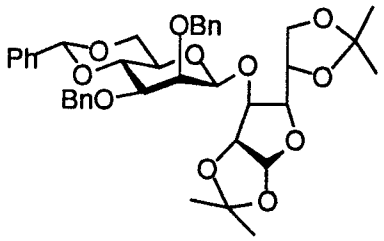
$[\alpha]_D^{20}$ = -44.8 (c = 3.9, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 3.28-3.37 (m, 4H), 3.59 (dd, J = 3.2, 9.9 Hz, 1 H), 3.74-4.00 (m, 5H), 4.07-4.15 (m, 1H), 4.20-4.31 (m, 4H), 4.59-4.81 (m, 6H), 4.98 (d, J = 12.3 Hz, 1H), 5.07 (d, J = 12.3 Hz, 1H), 5.52 (s, 1H), 5.61 (s, 1H), 7.24-7.56 (m, 25H); ^{13}C-NMR ($CDCl_3$), δ: 54.9, 64.0, 67.7, 68.5, 68.9, 71.3, 72.2, 74.0, 74.5, 75.1, 75.8, 77.5, 78.4, 78.6, 99.4, 100.8, 101.3, 101.6, 126.0, 126.1, 127.2, 127.5, 128.1, 128.2, 128.3, 128.6, 128.7, 137.5, 138.3, 138.4, 138.8; IR, υ: 1604, 1091, 1003, 976 cm^{-1}; MS (EI): m/z 802 (M), 712 (M+1-$PhCH_2$), 711 (M-$PhCH_2$).

Methyl 3-O-Benzyl-2-O-(2,3-di-O-benzyl-4,6-O-benzylidene-α-D-mannopyranosyl)-(1→2)-4,6-O-benzylidene-α-D-mannopyranoside.



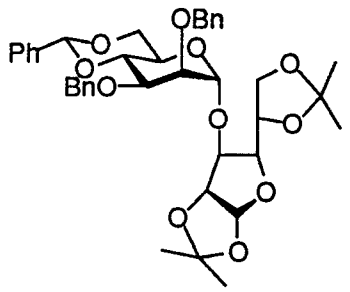
$[\alpha]_D^{20}$ = -0.9 (c = 0.4, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 3.35 (s, 3H), 3.71-4.07 (m, 9H), 4.20-4.30 (m, 3H), 4.50 (d, J = 12.2 Hz, 1H), 4.56 (d, J = 12.2 Hz, 1H), 4.59-4.68 (m, 3H), 4.80 (d, J = 11.7 Hz, 1H), 4.86 (d, J = 12.1 Hz, 1H), 5.23 (d, J = 1.5 Hz, 1H), 5.62 (s, 1H), 5.65 (s, 1H), 7.24-7.54 (m, 25H); ^{13}C-NMR ($CDCl_3$), δ: 54.8, 63.6, 64.6, 68.6, 68.7, 73.0, 73.4, 75.8, 75.9, 79.1, 79.2, 100.8, 100.9, 101.3, 101.4, 125.9, 126.0, 127.3, 127.5, 127.6, 127.7, 127.8, 128.2, 128.3, 128.8, 128.9, 137.5, 138.1, 138.3, 138.7; IR, υ: 1600, 1124, 1091, 1003, 966 cm^{-1}; MS (EI): m/z 803 (M+1), 802 (M), 801 (M-1), 711 (M-$PhCH_2$).

3-O-(2,3-Di-O-benzyl-4,6-O-benzylidene-β-D-mannopyranosyl)-(1→3)-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose.



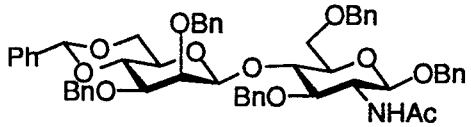
$[\alpha]_D^{20}$ = -38.6 (c = 2.9, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 1.31 (s, 3H), 1.34 (s, 3H), 1.43 (s, 3H), 1.50 (s, 3H), 3.28-3.37 (m, 1H), 3.61 (dd, J = 3.0, 9.8 Hz, 1H), 3.87 (d, J = 3.0 Hz, 1H), 3.92 (t, J = 10.2 Hz, 1H), 4.02-4.15 (m, 2H), 4.22 (t, J = 9.8 Hz, 1H), 4.27-4.33 (m, 3H), 4.38-4.45 (m, 2H), 4.56 (bs, 1H), 4.63 (d, J = 12.5 Hz, 1H), 4.76 (d, J = 12.5 Hz, 1H), 4.82 (d, J = 11.9 Hz, 1H), 4.88 (d, J = 11.9 Hz, 1H), 5.63 (s, 1H), 5.89 (d, J = 3.8 Hz, 1H), 7.24-7.53 (m, 15H); ^{13}C-NMR ($CDCl_3$), δ: 25.3, 26.2, 26.5, 26.7, 66.1, 67.7, 68.3, 72.5, 72.9, 74.8, 76.1, 77.9, 78.5, 80.4, 80.8, 82.7, 100.1, 101.3, 104.9, 108.6, 111.9, 125.9, 127.5, 127.6, 127.7, 128.1, 128.3, 128.4, 128.8, 137.4, 138.0, 138.2; IR, υ: 1451, 1377, 1090, 1024 cm^{-1}; MS (EI): m/z 690 (M), 676 (M+1-CH_3), 675 (M-CH_3), 600 (M+1-$PhCH_2$), 599 (M-$PhCH_2$); HRMS calcd. For $C_{39}H_{46}O_{11}$ (M): 690.3040. Found: 690.3047.

3-O-(2,3-Di-O-benzyl-4,6-O-benzylidene-α-D-mannopyranosyl)-(1→3)-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose.



$[\alpha]_D^{20}$ = +15.7 (c = 1.1, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 1.31 (s, 3H), 1.34 (s, 3H), 1.41 (s, 3H), 1.50 (s, 3H), 3.77-3.98 (m, 4H), 4.00-4.15 (m, 4H), 4.23-4.37 (m, 3H), 4.54 (d, J = 3.6 Hz, 1H), 4.60 (d, J = 12.1 Hz, 1H), 4.72 (d, J = 12.3 Hz, 1H), 4.77 (d, J = 12.3 Hz, 1H), 4.79 (d, J = 12.1 Hz, 1H), 5.22 (d, J = 1.4 Hz, 1H), 5.67 (s, 1H), 5.84 (d, J = 3.6 Hz, 1H), 7.24-7.55 (m, 15H); ^{13}C-NMR ($CDCl_3$), δ: 25.5, 26.2, 26.7, 26.8, 65.0, 67.8, 68.7, 72.4, 73.0 (2), 75.6, 75.8, 78.9, 80.0, 81.3, 83.9, 99.8, 101.3, 105.2, 109.3, 112.1, 125.8, 127.4, 127.8, 127.9, 128.1, 128.2, 128.3, 128.8, 137.4, 137.7, 138.4; IR, υ: 1452, 1373, 1094, 1017 cm^{-1}; MS (EI): m/z 600 (M+1-$PhCH_2$), 599 (M-$PhCH_2$).

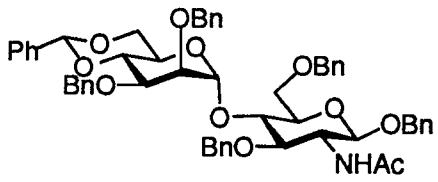
Benzyl 2-N-Acetylamino-2-deoxy-3,6-di-O-benzyl-4-O-(2,3-di-O-benzyl-4,6-O-benzylidene-β-D-mannopyranosyl)-(1→4)-β-D-glucopyranoside.



$[\alpha]_D^{20}$ = -38.7 (c = 1.1, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 1.73 (s, 3H), 3.08-3.19 (m, 1H), 3.45 (dd, J = 3.0, 9.8 Hz, 1H), 3.51-3.69 (m, 4H), 3.70-3.80 (m, 2H), 3.92 (t, J = 7.2 Hz, 1H), 4.02-4.18 (m, 3H), 4.35-4.65 (m, 6H), 4.72-4.98 (m, 6H), 5.54 (s, 1H), 5.76 (d, J = 8.0 Hz, 1H), 7.20-7.50 (m, 30H); ^{13}C-NMR ($CDCl_3$), δ: 23.2, 54.9, 67.2, 68.5, 69.1, 70.7, 72.5, 73.4, 73.6, 75.0, 75.2, 77.9, 78.1, 78.6, 99.1, 101.3, 101.7, 126.0,

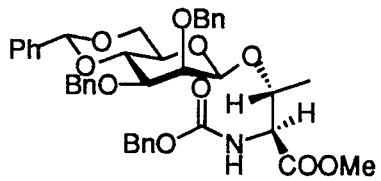
127.0, 127.4, 127.5, 127.7, 127.8, 127.9, 128.1, 128.3, 128.4, 128.8, 137.5, 137.8, 138.2, 138.4, 138.7, 170.1; MS (EI): m/z 921 (M), 829 (M+1-$PhCH_2$).

Benzyl 2-N-Acetylamino-2-deoxy-3,6-di-O-benzyl-4-O-(2,3-di-O-benzyl-4,6-O-benzylidene-α-D-mannopyranosyl)-(1→4)-β-D-glucopyranoside.



$[\alpha]_D^{20}$ = +2.67 (c = 0.3, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 1.77 (s, 3H), 3.40-3.50 (m, 1H), 3.51-3.59 (m, 1H), 3.71-3.93 (m, 7H), 4.05-4.18 (m, 2H), 4.25 (t, J = 9.7 Hz, 1H), 4.37 (d, J = 12.1 Hz, 1H), 4.50-4.67 (m, 7H), 4.79-4.91 (m, 3H), 5.28 (d, J = 1.5 Hz, 1H), 5.40 (d, J = 7.9 Hz, 1H), 5.63 (s, 1H), 7.20-7.53 (m, 30H); ^{13}C-NMR ($CDCl_3$), δ: 23.4, 30.9, 56.9, 65.1, 68.6, 69.1, 70.8, 73.0, 73.2, 73.3, 73.4, 74.3, 76.1, 76.2, 78.9, 80.7, 98.6, 100.5, 101.3, 126.0, 127.0, 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.5, 128.7, 137.3, 137.6, 137.9, 138.1, 138.6, 170.4.

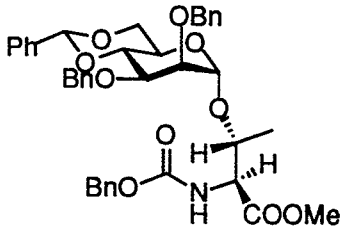
N-Benzyloxycarbonyl-O-(2,3-di-O-benzyl-4,6-O-benzylidene-β-D-mannopyranosyl)-L-threonine methyl ester.



$[\alpha]_D^{20}$ = -29.7 (c = 5.8, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 1.22 (d, J = 6.3 Hz, 3H), 3.18-3.28 (m, 1H), 3.56 (dd, J = 3.1, 9.9 Hz, 1 H), 3.73 (s, 3H), 3.80-3.90 (m, 2H), 4.15 (t,

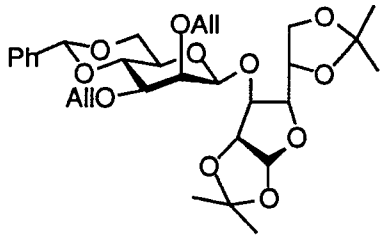
J = 9.9 Hz, 1H), 4.24 (dd, J = 4.9, 10.5 Hz, 1H), 4.37 (dd, J = 2.3, 9.3 Hz, 1H), 4.44-4.52 (m, 2H), 4.62 (d, J = 12.5 Hz, 1H), 4.72 (d, J = 12.5 Hz, 1H), 4.78 (d, J = 12.2 Hz, 1H), 4.87 (d, J = 12.2 Hz, 1 H), 5.15 (s, 2H), 5.55 (d, J = 9.2 Hz, 1H), 5.59 (s, 1H), 7.24-7.55 (m, 20H); ^{13}C-NMR ($CDCl_3$), δ: 17.4, 52.5, 58.4, 67.1, 67.4, 68.4, 72.3, 74.1, 74.6, 76.2, 77.7, 78.4, 99.7, 101.3, 126.0, 127.5, 128.0, 128.1, 128.3, 128.5, 128.8, 136.2, 137.4, 138.2, 138.3, 156.7, 170.7; IR, υ: 1725, 1515, 1309, 1100, 911 cm^{-1}; MS (EI): m/z 697 (M), 606 (M-$PhCH_2$), 562 (M-$PhCH_2OCO$); HRMS calcd. For $C_{33}H_{36}NO_{10}$ (M-$PhCH_2$): 606.2313. Found: 606.2310.

N-Benzyloxycarbonyl-O-(2,3-di-O-benzyl-4,6-O-benzylidene-α-D-mannopyranosyl)-L-threonine methyl ester.



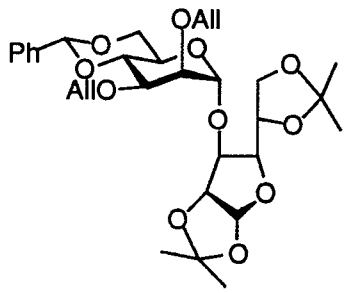
$[\alpha]_D^{20}$ = +45.6 (c = 0.2, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 1.27 (d, J = 6.4 Hz, 3H), 3.56 (s, 3H), 3.59-3.62 (m, 1H), 3.78-3.90 (m, 3H), 4.17-4.39 (m, 4H), 4.62 (d, J = 12.1 Hz, 1H), 4.68 (d, J = 12.4 Hz, 1H), 4.75 (d, J = 12.4 Hz, 1H), 4.76 (d, J = 1.4 Hz, 1H), 4.82 (d, J = 12.1 Hz, 1H), 5.14 (s, 2H), 5.26 (d, J = 9.7 Hz, 1H), 5.63 (s, 1H), 7.24-7.52 (m, 20H); ^{13}C-NMR ($CDCl_3$), δ: 18.4, 52.3, 58.4, 64.7, 67.3, 68.5, 73.2, 73.3, 75.9, 76.0, 76.2, 78.9, 100.7, 101.3, 125.9, 127.5, 127.7, 128.0, 128.1, 128.2, 128.3, 128.5, 128.7, 137.4, 137.8, 138.4, 156.4, 170.8; IR, υ: 1725, 1507, 1096, 1011 cm^{-1}; MS (EI): m/z 697 (M), 607 (M+1-$PhCH_2$), 606 (M-$PhCH_2$).

3-O-(2,3-Di-O-allyl-4,6-O-benzylidene-β-D-mannopyranosyl)-(1→3)-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose.



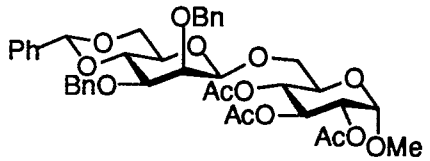
$[\alpha]_D^{20}$ = -43.5 (c = 2.6, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 1.32 (s, 3H), 1.36 (s, 3H), 1.44 (s, 3H), 1.50 (s, 3H), 3.20-3.40 (m, 1H), 3.55 (dd, J = 3.0, 9.8 Hz, 1H), 3.81 (bd, J = 3.0 Hz, 1H), 3.89 (t, J = 10.3 Hz, 1H), 4.00-4.42 (m, 11H), 4.50 (d, J = 3.8 Hz, 1H), 4.57 (bs, 1H), 5.10-5.36 (m, 4H), 5.58 (s, 1H), 5.82-6.02 (m, 3H), 7.34-7.50 (m, 5H); ^{13}C-NMR ($CDCl_3$), δ: 25.4, 26.2, 26.4, 26.7, 65.7, 67.6, 68.3, 71.8, 73.4, 74.3, 76.3, 77.9, 78.4, 80.2, 80.6, 82.7, 99.7, 101.3, 104.9, 108.3, 111.9, 116.8, 117.4, 125.9, 128.1, 128.8, 134.7, 135.1, 137.3; IR, υ: 1455, 1383, 1217, 1087, 754, 699 cm^{-1}; MS (EI): m/z 590 (M), 576 (M+1-CH_3), 575 (M-CH_3); HRMS calcd. For $C_{31}H_{42}O_{11}$ (M): 590.2727. Found: 590.2730.

3-O-(2,3-Di-O-allyl-4,6-O-benzylidene-α-D-mannopyranosyl)-(1→3)-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose.



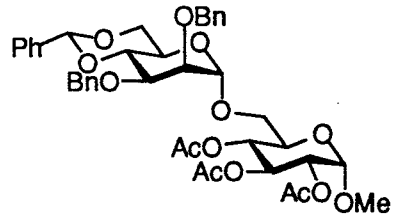
$[\alpha]_D^{20}$ = +20.1 (c = 1.0, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 1.32 (s, 3H), 1.35 (s, 3H), 1.41 (s, 3H), 1.50 (s, 3H), 3.75-4.39 (m, 16H), 4.56 (d, J = 3.6 Hz, 1H), 5.15-5.35 (m, 4H), 5.63 (s, 1H), 5.85-6.00 (m, 3H), 7.34-7.51 (m, 5H); ^{13}C-NMR ($CDCl_3$), δ: 25.3, 26.2, 26.8 (2), 64.9, 67.8, 68.7, 72.2, 72.4, 72.7, 75.3, 75.8, 79.0, 80.0, 81.4, 84.0, 100.2, 101.3, 105.2, 109.4, 112.1, 116.5, 117.8, 125.8, 128.1, 128.8, 134.6, 134.8, 137.4; IR, υ: 1456, 1374, 1217, 1073, 1021, 755 cm^{-1}; MS (EI): m/z 591 (M+1), 590 (M), 576 (M+1-CH_3), 575 (M-CH_3).

Methyl 2,3,4-Tri-O-acetyl-6-O-(2,3-di-O-benzyl-4,6-O-benzylidene-β-D-mannopyranosyl)-(1→6)-α-D-glucopyranoside.



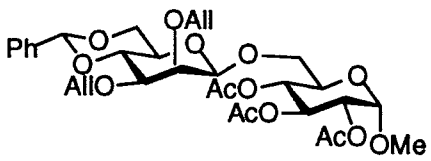
$[\alpha]_D^{20}$ = +16.8 (c = 1.4, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 2.02 (s, 3H), 2.03 (s, 3H), 2.08 (s, 3H), 3.26-3.35 (m, 1H), 3.37 (s, 3H), 3.50 (dd, J = 6.7, 10.8 Hz, 1H), 3.59 (dd, J = 3.1, 9.9 Hz, 1H), 3.92 (t, J = 10.3 Hz, 1H), 3.96-4.05 (m, 3H), 4.20 (t, J = 9.9 Hz, 1H), 4.30 (dd, J = 4.9, 10.3 Hz, 1H), 4.48 (d, J = 0.6 Hz, 1H), 4.57 (d, J = 12.5 Hz, 1H), 4.67 (d, J = 12.5 Hz, 1H), 4.83-5.02 (m, 5H), 5.50 (t, J = 10.1 Hz, 1H), 5.61 (s, 1H), 7.24-7.52 (m, 15H); ^{13}C-NMR ($CDCl_3$), δ: 20.7 (3), 55.2, 67.5, 68.2, 68.4 (2), 68.9, 70.0, 70.8, 72.2, 75.0, 75.9, 77.6, 78.4, 96.4, 101.3, 102.4, 126.0, 127.5, 128.1, 128.2, 128.4, 128.8, 137.4, 138.2, 138.3, 169.8, 170.0, 170.1; IR, υ: 1748, 1452, 1369, 1258, 1040 cm^{-1}; MS (EI): m/z 750 (M), 660 (M+1-$PhCH_2$), 659 (M-$PhCH_2$); HRMS calcd. For $C_{33}H_{39}O_{14}$ (M-$PhCH_2$): 659.2340. Found: 659.2264.

Methyl 2,3,4-Tri-O-acetyl-6-O-(2,3-di-O-benzyl-4,6-O-benzylidene-α-D-mannopyranosyl)-(1→6)-α-D-glucopyranoside.



$[\alpha]_D^{20}$ = +92.2 (c = 0.6, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 1.99 (s, 3H), 2.02 (s, 3H), 2.08 (s, 3H), 3.30 (s, 3H), 3.46 (dd, J = 2.2, 11.4 Hz, 1H), 3.67-3.76 (m, 3H), 3.79-3.96 (m, 4H), 4.16-4.27 (m, 2H), 4.65-4.89 (m, 6H), 5.01 (t, J = 9.9 Hz, 1H), 5.44 (t, J = 9.9 Hz, 1H), 5.62 (s, 1H), 7.24-7.52 (m, 15H); ^{13}C-NMR ($CDCl_3$), δ: 20.7 (3), 55.2, 64.2, 65.2, 67.7, 68.7, 70.2, 70.7, 73.2, 73.5, 75.9, 76.2, 78.9, 96.5, 99.3, 101.4, 126.0, 127.4, 127.6, 128.0, 128.1, 128.2, 128.3, 128.7, 137.6, 138.0, 138.5, 169.4, 170.1 (2); IR, υ: 1748, 1456, 1369, 1096 cm^{-1}; MS (EI): m/z 751 (M+1), 750 (M), 749 (M-1), 660 (M+1-$PhCH_2$), 659 (M-$PhCH_2$).

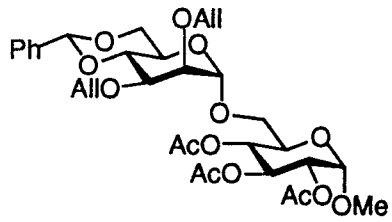
Methyl 2,3,4-Tri-O-acetyl-6-O-(2,3-di-O-allyl-4,6-O-benzylidene-β-D-mannopyranosyl)-(1→6)-α-D-glucopyranoside.



$[\alpha]_D^{20}$ = +36.2 (c = 5.0, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 2.00 (s, 3H), 2.02 (s, 3H), 2.06 (s, 3H), 3.24-3.34 (m, 1H), 3.39 (s, 3H), 3.43-3.55 (m, 2H), 3.83-4.39 (m, 10H), 4.46 (bs, 1H), 4.81-5.00 (m, 3H), 5.13-5.33 (m, 4H), 5.48 (t, J = 9.9 Hz, 1H), 5.55 (s, 1H),

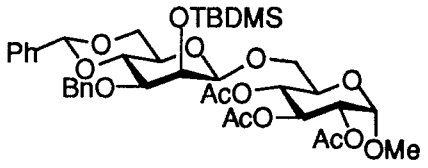
5.82-6.04 (m, 2H), 7.30-7.49 (m, 5H); ^{13}C-NMR ($CDCl_3$), δ: 20.6 (3), 55.0, 67.4, 68.1, 68.4, 68.5, 68.9, 70.0, 70.8, 71.7, 74.4, 75.7, 77.6, 78.4, 96.3, 101.3, 102.0, 116.7, 117.4, 125.9, 128.1, 128.7, 134.7, 135.4, 137.4, 169.8, 169.9, 170.1; IR, υ: 1750, 1370, 1226, 1043, 754 cm^{-1}; MS (EI): m/z 650 (M), 609 (M-$CH_2CH{=}CH_2$); HRMS calcd. For $C_{32}H_{42}O_{14}$ (M): 650.2574. Found: 650.2558.

Methyl 2,3,4-Tri-O-acetyl-6-O-(2,3-di-O-allyl-4,6-O-benzylidene-α-D-mannopyranosyl)-(1→6)-α-D-glucopyranoside.



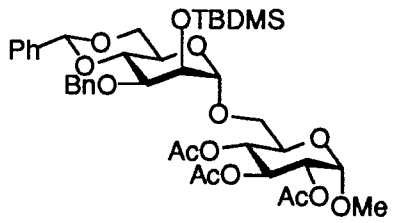
$[\alpha]_D^{20}$ = +96.9 (c = 0.5, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 2.01 (s, 3H), 2.03 (s, 3H), 2.08 (s, 3H), 3.41 (s, 3H), 3.53 (dd, J = 2.2, 11.3 Hz, 1H), 3.70-3.87 (m, 5H), 3.91-3.99 (m, 1H), 4.07-4.38 (m, 6H), 4.83-4.96 (m, 3H), 5.08 (t, J = 9.5 Hz, 1H), 5.12-5.36 (m, 4H), 5.47 (t, J = 9.5 Hz, 1H), 5.58 (s, 1H), 5.85-6.01 (m, 2H), 7.33-7.51 (m, 5H); ^{13}C-NMR ($CDCl_3$), δ: 20.6 (3), 55.3, 64.1, 65.3, 67.8, 68.6, 68.8, 70.2, 70.7, 72.2, 73.0, 75.6, 78.9, 96.6, 99.5, 101.5, 116.5, 117.7, 126.0, 128.1, 128.7, 134.7, 134.9, 169.4, 170.1 (2); IR, υ: 1753, 1371, 1225, 1038, 757 cm^{-1}; MS (EI): m/z 650 (M).

Methyl 2,3,4-Tri-O-acetyl-6-O-[3-O-benzyl-4,6-O-benzylidene-2-O-(t-butyldimethylsilyl)-β-D-mannopyranosyl]-(1→6)-α-D-glucopyranoside.[1]



$[\alpha]_D^{20}$ = +40.0 (c = 0.6, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 0.13 (s, 3H), 0.16 (s, 3H), 1.25 (s, 9H), 2.01 (s, 3H), 2.04 (s, 3H), 2.07 (s, 3H), 3.25-3.34 (m, 1H), 3.40 (s, 3H), 3.43-3.55 (m, 2H), 3.84-4.10 (m, 3H), 4.09 (t, J = 9.4 Hz, 1H), 4.17 (d, J = 2.6 Hz, 1H), 4.26-4.32 (m, 2H), 4.72 (d, J = 12.4 Hz, 1H), 4.78 (d, J = 12.4 Hz, 1H), 4.85 (dd, J = 3.6, 9.8 Hz, 1H), 4.93 (d, J = 3.6 Hz, 1H), 5.05 (t, J = 9.8 Hz, 1H), 5.50 (t, J = 9.8 Hz, 1H), 5.60 (s, 1H), 7.24-7.41 (m, 8H), 7.48-7.52 (m, 2H); ^{13}C-NMR ($CDCl_3$), δ: -4.9, -4.2, 18.5, 20.7, 25.9, 55.5, 67.6, 68.3, 68.6, 68.7, 68.8, 70.0, 70.8, 71.1, 72.1, 77.7, 78.7, 96.5, 101.4, 102.5, 126.0, 127.4, 127.7, 128.1, 128.13, 128.8, 137.5, 138.3, 169.7, 170.1; IR, υ: 2932, 1749, 1602 cm^{-1}; Anal. Calcd for $C_{39}H_{54}O_{14}Si$: C, 60.45; H, 7.02. Found: C, 60.12; H, 7.02.

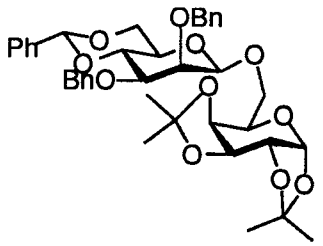
Methyl 2,3,4-Tri-O-acetyl-6-O-[3-O-benzyl-4,6-O-benzylidene-2-O-(t-butyldimethylsilyl)-α-D-mannopyranosyl]-(1→6)-α-D-glucopyranoside.[1]



$[\alpha]_D^{20}$ = +69.7 (c = 1.4, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 0.07 (s, 3H), 0.09 (s, 3H), 0.90 (s, 9H), 2.02 (s, 6H), 2.08 (s, 3H), 3.33 (s, 3H), 3.52 (dd, J = 2.2, 11.4 Hz, 1H), 3.66-3.86 (m, 4H), 3.86-3.96 (m, 1H), 4.04 (dd, J = 1.5, 2.9 Hz, 1H), 4.10 (t, J = 9.4 Hz, 1H), 4.19 (dd, J = 4.4, 9.8 Hz, 1H), 4.69 (d, J = 1.5 Hz, 1H), 4.70 (d, J = 12.0 Hz, 1H), 4.81 (d, J = 12.0 Hz, 1H), 4.85-4.92 (m, 2H), 5.06 (t, J = 9.8 Hz, 1H), 5.46 (t, J =

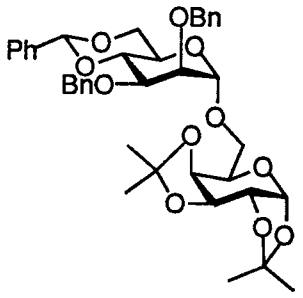
9.8 Hz, 1H), 5.60 (s, 1H), 7.24-7.39 (m, 8H), 7.47-7.51 (m, 2H); ^{13}C-NMR ($CDCl_3$), δ: -5.2, -4.5, 18.1, 20.6, 25.7, 55.2, 64.4, 65.0, 67.9, 68.8, 70.3, 70.7, 71.1, 72.9, 75.2, 79.0, 96.5, 101.5, 126.1, 127.3, 127.9, 128.0, 128.7, 137.7, 138.6, 169.4, 170.1; IR, υ: 2955, 1751, 1465 cm^{-1}. Anal. Calcd for $C_{39}H_{54}O_{14}Si$: C, 60.45; H, 7.02. Found: C, 60.18; H, 6.97.

6-O-(2,3-Di-O-benzyl-4,6-O-benzylidene-β-D-mannopyranosyl)-(1→6)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose.



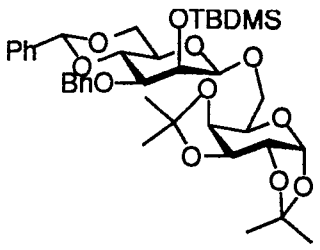
$[\alpha]_D^{20}$ = -79.2 (c = 3.3, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 1.33 (s, 3H), 1.35 (s, 3H), 1.45 (s, 3H), 1.51 (s, 3H), 3.26-3.36 (m, 1H), 3,54 (dd, J = 3.0, 10.0 Hz, 1H), 3.64 (dd, J = 8.3, 10.7 Hz, 1H), 3.93 (t, J = 10.3 Hz, 1H), 4.03 (d, J = 3.0 Hz, 1H), 4.07-4.12 (m, 1H), 4.15-4.24 (m, 3H), 4.30 (dd, J = 4.9, 10.3 Hz, 1H), 4.35 (dd, J = 2.5, 5.0 Hz, 1H), 4.50-4.65 (m, 4H), 4.91 (d, J = 12.3 Hz, 1H), 5.03 (d, J = 12.3 Hz, 1H), 5.59 (d, J = 5.0 Hz, 1H), 5.62 (s, 1H), 7.19-7.54 (m, 15H); ^{13}C-NMR ($CDCl_3$), δ: 24.3, 25.0, 25.9, 26.0, 67.5, 67.9, 68.5, 70.0, 70.4, 70.7, 71.5, 72.0, 74.5, 74.7, 78.4, 96.3, 101.3, 102.8, 108.7, 109.5, 126.0, 127.4, 128.1, 128.2, 128.7, 137.5, 138.1, 138.2; IR, υ: 1600, 1498, 1456, 1378, 1096, 1003 cm^{-1}; MS (EI): m/z 690 (M), 676 (M+1-CH_3), 675 (M-CH_3), 600 (M+1-$PhCH_2$), 599 (M-$PhCH_2$); HRMS calcd. For $C_{39}H_{46}O_{11}$ (M): 690.3040. Found: 690.3043.

6-O-(2,3-Di-O-benzyl-4,6-O-benzylidene-α-D-mannopyranosyl)-(1→6)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose.



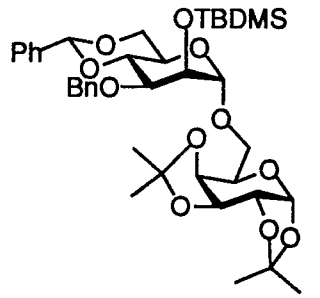
$[\alpha]_D^{20}$ = -5.3 (c = 1.3, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 1.34 (s, 6H), 1.44 (s, 3H), 1.52 (s, 3H), 3.65-3.93 (m, 5H), 3.95-4.00 (m, 2H), 4.15-4.29 (m, 3H), 4.33 (dd, J = 2.4, 5.0 Hz, 1H), 4.59-4.65 (m, 2H), 4.72-4.84 (m, 3H), 4.93 (d, J = 1.4 Hz, 1H), 5.53 (d, J = 5.0 Hz, 1H), 5.64 (s, 1H), 7.24-7.53 (m, 15H); ^{13}C-NMR ($CDCl_3$), δ: 24.5, 24.8, 25.9, 26.0, 64.3, 65.3, 65.7, 68.7, 70.5, 70.6, 70.8, 73.0, 73.3, 76.2, 76.3, 79.0, 96.3, 98.9, 101.3, 108.5, 109.3, 126.0, 127.3, 127.4, 127.6, 127.9, 128.1, 128.2, 128.3, 128.7, 137.6, 138.0, 138.6; IR, υ: 1600, 1498, 1447, 1373, 1100, 1003 cm^{-1}; MS (EI): m/z 600 (M+1-$PhCH_2$), 599 (M-$PhCH_2$).

6-O-[3-O-Benzyl-4,6-O-benzylidene-2-O-(t-butyldimethylsilyl)-β-D-mannopyranosyl]-(1→6)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose.[1]



$[\alpha]_D^{20}$ = -69.7 (c = 1.1, $CHCl_3$); ^{1}H-NMR ($CDCl_3$), δ: 0.13 (s, 6H), 0.92 (s, 9H), 1.32 (s, 3H), 1.33 (s, 3H), 1.45 (s, 3H), 1.51 (s, 3H), 3.25-3.34 (m, 1H), 3.51 (dd, J = 3.2, 9.5 Hz, 1H), 3.64 (dd, J = 7.9, 11.4 Hz, 1H), 3.86 (t, J = 10.1 Hz,1H), 3.95-4.15 (m, 3H), 4.17-4.22 (m, 2H), 4.25-4.34 (m, 2H), 4.42 (s, 1H), 4.60 (dd, J = 3.0, 7.9 Hz, 1H), 4.74 (s, 2H), 5.56 (d, J = 5.4 Hz, 1H), 5.61 (s, 1H), 7.24-7.42 (m, 8H), 7.46-7.55 (m, 2H); ^{13}C-NMR ($CDCl_3$), δ: -4.9, -3.7, 18.5, 24.3, 24.9, 26.0 (3), 67.4, 67.6, 68.9, 69.9, 70.2, 70.8, 71.0, 71.5, 72.0, 77.6, 78.8, 96.4, 101.5, 102.5, 108.5, 109.3, 126.1, 127.5, 127.8, 128.1, 128.2, 128.8, 137.7, 138.4; IR, υ: 2931, 1602, 1472, 1376, 1256, 1212, 1098, 1073, 1008 cm^{-1}; MS (EI): m/z 714 (M), 699 (M-CH_3), 657 (M-Bu^t); HRMS calcd. For $C_{37}H_{51}O_{11}Si$ (M-CH_3): 699.3201. Found: 699.3208.

6-O-[3-O-Benzyl-4,6-O-benzylidene-2-O-(t-butyldimethylsilyl)-α-D-mannopyranosyl]-(1→6)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose.[1]



$[\alpha]_D^{20}$ = -21.8 (c = 0.5, $CHCl_3$); ^{1}H-NMR, δ: 0.05 (s, 3H), 0.07 (s, 3H), 0.89 (s, 9H), 1.33 (s, 6H), 1.44 (s, 3H), 1.53 (s, 3H), 3.65-3.90 (m, 5H), 3.91-4.00 (m, 1H), 4.05-4.18 (m, 2H), 4.20-4.28 (m, 2H), 4.33 (dd, J = 2.5, 5.1 Hz, 1H), 4.62 (dd, J = 2.4, 7.9Hz, 1H), 4.68 (d, J = 12.0 Hz, 1H), 4.74 (d, J = 1.6 Hz, 1H), 4.81 (d, J = 12.0 Hz, 1H), 5.53 (d, J = 5.0 Hz, 1H), 5.62 (s, 1H), 7.24-7.36 (m, 8H), 7.47-7.50 (m, 2H); ^{13}C-NMR ($CDCl_3$), δ: -5.5, -4.4, 18.2, 24.5, 24.9, 25.8, 25.9, 26.2, 64.5, 65.5, 65.7, 69.0, 70.5, 70.7, 70.9, 71.2, 72.9, 75.8, 79.2, 96.3, 101.4, 101.6, 108.6, 109.4, 126.1, 127.3, 127.7, 128.1, 128.7, 137.7, 138.8; IR, υ: 2930, 1601, 1475, 1374, 1255, 1212, 1132, 1072, 1010 cm^{-1}; MS (EI): m/z 714 (M), 699 (M-CH_3), 657 (M-Bu^t); Anal. Calcd. For $C_{38}H_{54}O_{11}Si$: C, 63.84; H, 7.61. Found: C, 64.26; H, 7.70.

Reference

1) Crich, D.; Sun, S. *J. Org. Chem.* **1996**, *61*, 4506-4507.