Subtle Stereochemical and Electronic Effects in Iridium-Catalyzed Isomerization of *C*-Allyl Glycosides

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SUPPORTING INFORMATION

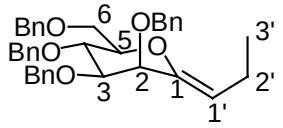
Experimental Section

General Information. All the chemicals were purchased from Aldrich Chemicals and used as they were without further purification. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. NMR spectra were recorded on a Bruker AMX-500 spectrometer or Bruker AV-300 spectrometers. EI MS spectra were recorded on Kratos Concepts IIH mass spectrometer. Thin layer chromatography (TLC) was performed on silica gel F_{254} (Merck) precoated aluminium sheets and spots were visualized under UV and by spraying with molybdenum solution and heating.

General method for isomerization of C-allyl glycosides with 1,5-cyclooctadiene-bis[methyldiphenylphosphine]-iridium hexafluorophosphate

The iridium catalyst $(Ph_2MeP)_2Ir(cod)PF_6$ (0.1 mmol) was stirred in degassed THF (6 ml) and activated under an H_2 atmosphere, until the orange red suspension became a clear slightly orange solution. The solution was bubbled with N_2 for 15 minutes to remove the excess H_2. The activated catalyst was then added to the C-allyl glycoside (1 mmol) in degassed THF (6 ml) and the reaction mixture was stirred for 48 h. at room temperature. The solution was evaporated and the residue was purified by flash column chromatography on silica gel using gradient elution of hexane and ethyl acetate.

(1(1')Z)-2,3,4,6-Tetra-O-benzyl-1-deoxy-1-propylidene-D-mannopyranose (8)



Yield: 80 %

R_f: 0.6 (Hexane : EtOAc, 4 : 1)

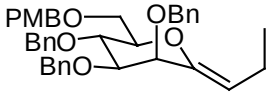
$[\alpha]^{20}_D$ +10.4 (*c* = 1, $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46-7.20 (20H, m, PhCH_2), 5.01 (1H, d, *J* = 10.8 Hz, PhCH_2), 4.82 (1H, t, *J* = 7.2 Hz, H-1'), 4.81-4.43 (7H, m, PhCH_2), 4.24 (1H, t, *J* = 9.4 Hz, H-4), 4.01 (1H, d, *J* = 3.3 Hz, H-2), 3.88 (2H, m, H-6), 3.67 (1H, dd, *J* = 3.3, 9.2 Hz, H-3), 3.58 (1H, ddd, *J* = 3.3, 3.3, 9.6 Hz, H-5), 2.22 (2H, m, H-2'), 1.00 (3H, t, *J* = 7.4 Hz, H-3').

^{13}C NMR (75 MHz, $CDCl_3$): δ 147.0 (s, C-1), 139.0 (s, PhCH_2), 138.9 (s, PhCH_2), 128.7 (d, PhCH_2), 128.7 (d, PhCH_2), 128.7 (d, PhCH_2), 128.3 (d, PhCH_2), 128.2 (d, PhCH_2), 128.1 (d, PhCH_2), 128.0 (d, PhCH_2), 127.9 (d, PhCH_2), 127.92 (d, PhCH_2), 119.4 (d, C-1'), 82.6 (d, C-4), 80.7 (d, C-5), 75.6 (t, PhCH_2), 74.8 (d, C-2), 74.4 (d, C-3), 73.8 (t, PhCH_2), 71.5 (t, PhCH_2), 69.9 (t, PhCH_2), 69.3 (t, C-6), 18.6 (t, C-2'), 14.9 (q, C-3').

MS (ESI): 565.2 $[M+H]^+$; calcd. 564.3 for $C_{37}H_{40}O_5$

(1(1')Z)-2,3,4-Tri-O-benzyl-1-deoxy-6-O-(*p*-methoxybenzyl)-1-propylidene-D-mannopyranose (9)



Yield: 77 %

R_f: 0.5 (Hexane : EtOAc, 2 : 1)

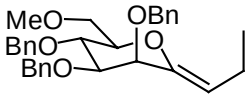
$[\alpha]^{20}_D$ +17.5 (*c* = 1, $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 (17H, m, PhCH_2), 6.81 (2H, d, *J* = 8.8 Hz, PhCH_2(PMB)), 4.91 (1H, d, *J* = 10.7 Hz, PhCH_2), 4.74 (1H, t, *J* = 7.1 Hz, H-1'), 4.74 – 4.35 (7H, m, PhCH_2), 4.14 (1H, t, *J* = 9.3 Hz, H-4), 3.93 (1H, d, *J* = 3.3 Hz, H-2), 3.78 (2H, d, *J* = 3.3 Hz, H-3, H-5), 3.74 (3H, s, OCH_3), 3.58 (1H, dd, *J* = 9.1, 3.3 Hz, H-6a), 3.47 (1H, dt, *J* = 9.6, 3.3 Hz, H-6b), 2.15 (2H, m, H-2'), 0.95 (3H, t, *J* = 7.4 Hz, H-3').

^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1 (s, PhCH_2), 146.6 (s, C-1), 138.5 (s, PhCH_2), 138.3 (s, PhCH_2), 130.4 (s, PhCH_2), 129.4 (d, PhCH_2), 128.3 (d, PhCH_2), 128.2 (d, PhCH_2), 128.15 (d, PhCH_2), 127.9 (d, PhCH_2), 127.7 (d, PhCH_2), 127.5(d, PhCH_2), 127.45 (d, PhCH_2), 118.9 (d, C-2'), 113.6 (d, PhCH_2), 82.2 (d, C-4), 80.2 (d, C-5), 75.1 (t, PhCH_2), 74.4 (d, C-2), 74.0 (d, C-3), 73.0 (t, PhCH_2), 71.1 (t, PhCH_2), 69.0 (t, PhCH_2), 68.8 (t, C-6), 55.2 (q, OCH_3), 18.1 (t, C-2'), 14.4 (q, C-3').

MS (ESI): 595.3 $[M+H]^+$; calcd. 594.3 for $C_{38}H_{42}O_6$

(1(1')Z)-2,3,4-Tri-O-benzyl-1-deoxy-6-O-methyl-1-propylidene-D-mannopyranose (10)



Yield: 77 %

R_f: 0.6 (Hexane : EtOAc, 3 : 1)

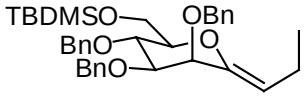
$[\alpha]^{20}_D$ +3.75 (*c* = 1, $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 – 7.19 (15H, m, PhCH_2), 4.95 (1H, d, *J* = 10.9 Hz, PhCH_2), 4.71 (1H, t, *J* = 7.4 Hz, H-1'), 4.72 – 4.32 (5H, m, PhCH_2), 4.09 (1H, t, *J* = 9.3 Hz, H-4), 3.90 (1H, d, *J* = 3.3 Hz, H-2), 3.66 (2H, m, H-6), 3.56 (1H, dd, *J* = 9.1, 3.3 Hz, H-3), 3.43 (1H, m, H-5), 3.37 (3H, s, OMe), 2.11 (2H, m, H-2'), 0.92 (3H, t, *J* = 7.7 Hz, H-3').

^{13}C NMR (75 MHz, $CDCl_3$): δ 146. 5 (s, C-1), 138.6 (s, PhCH_2), 138.2 (s, PhCH_2), 128.3 (d, PhCH_2), 128.26 (d, PhCH_2), 128.24 (d, PhCH_2), 128.2 (d, PhCH_2), 127.9 (d, PhCH_2), 127.6 (d, PhCH_2), 127.5 (d, PhCH_2), 119.1 (d, C-1'), 82.1 (d, C-4), 79.9 (d, C-5), 75.2 (t, PhCH_2), 74.4 (d, C-2), 73.8 (C-3), 71.8 (t, PhCH_2), 71.0 (t, PhCH_2), 68.8 (t, C-6), 59.3 (q, OMe), 18.0 (t, C-2'), 14.4 (q, C-3').

MS (ESI): 489.3 $[M+H]^+$; calcd. 488.3 for $C_{31}H_{36}O_5$

(1(1')Z)-2,3,4-Tri-O-benzyl-6-O-(*t*-butyldimethylsilyl)-1-deoxy-1-propylidene-D-mannopyranose (11)



Yield: 38 %

R_f: 0.55 (Hexane : EtOAc, 6.5 : 1)

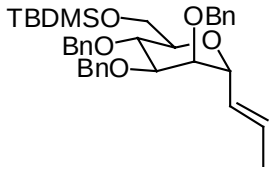
$[\alpha]^{20}_D$ +5.6 (*c* = 1, $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 – 7.18 (15H, m, PhCH_2), 4.93 (1H, d, *J* = 10.9 Hz, PhCH_2), 4.67 (1H, t, *J* = 7.4 Hz, H-1'), 4.67 – 4.29 (5H, m, PhCH_2), 4.09 (1H, t, *J* = 9.3 Hz, H-4), 3.87 – 3.82 (3H, m, H-2, H-6), 3.54 (1H, dt, *J* = 3.3, 9.3 Hz, H-3), 3.27 (1H, dt, *J* = 4.1, 9.3 Hz, H-5), 2.05 (2H, m, H-2'), 0.90 (3H, *J* = 7.7 Hz, H-3').

^{13}C NMR (75 MHz, $CDCl_3$): δ 146.7 (s, C-1), 138.4 (s, PhCH_2), 138.3 (s, PhCH_2), 128.3 (d, PhCH_2), 128.28 (d, PhCH_2), 128.23 (d, PhCH_2), 128.1 (d, PhCH_2), 128.0 (d, PhCH_2), 127.7 (d, PhCH_2), 127.6 (d, PhCH_2), 127.5 (d, PhCH_2), 127.4 (d, PhCH_2), 118.6 (d, C-1'), 82.1 (d, C-4), 81.2 (d, C-5), 75.2 (t, PhCH_2), 74.2 (d, C-2), 73.9 (d, C-3), 71.2 (t, PhCH_2), 68.6 (t, PhCH_2), 62.7 (t, C-6), 25.9 (q, C-TBDMS), 18.0 (t, C-2'), 14.5 (q, C-3'), -4.1 (q, C- TBDMS), –4.3 (q, C-TBDMS).

MS (ESI): 589.1 $[M+H]^+$; calcd. 588.3 for $C_{36}H_{48}O_5Si$

***Trans*-2,3,4-Tri-O-benzyl-6-O-(t-butyldimethylsilyl)-1-deoxy-1'-prop-1-enyl-α-D-mannopyranose (11a)**



Yield: 53 %

R_f: 0.5 (Hexane : EtOAc, 6.5 : 1)

$[\alpha]^{20}_D$ +17.4 (*c* = 1, $CHCl_3$)

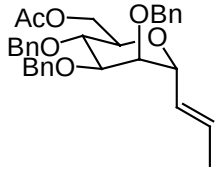
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 – 7.17 (15H, m, PhCH_2), 5.65 – 5.53 (1H, m, H-1'), 5.42 – 5.33 (1H, m, H-2'), 4.74 (1H, d, *J* = 10.9 Hz, PhCH_2), 4.60 – 4.54 (5H, m, PhCH_2), 4.43 (1H, m, H-1), 3.87 – 3.82 (3H, m, H-2, H-4, H-6a), 3.71 (1H, dd, *J* = 7.7, 3.0 Hz, H-3), 3.62 – 3.59 (2H, m, H-5, H-6b), 1.62 (3H, dd, *J* = 6.6, 1.4 Hz, H-3').

^{13}C NMR (75 MHz, $CDCl_3$): δ 138.5 (s, PhCH_2), 138.4 (s, PhCH_2), 138.38 (s, PhCH_2) 129.5 (d, C-1'), 128.4 (d, PhCH_2), 128.3(d, PhCH_2), 128.2 (d, PhCH_2), 128.0 (d, PhCH_2), 127.9 (d, PhCH_2), 127.8 (d, PhCH_2), 127.6 (d, PhCH_2), 127.58 (d, PhCH_2), 127.5 (d, PhCH_2), 127.3 (d, PhCH_2), 78.1 (d, C-4), 76.5 (d, C-2), 75.1 (d, C-3), 74.4 (t, PhCH_2),

74.2 (d, C-1), 73.1 (d, C-5), 72.1 (t, Ph$\underline{CH_2}$), 71.5 (t, Ph$\underline{CH_2}$), 63.7 (t, C-6), 25.9 (q, C-TBDMS), 18.1 (q, C-3'), -5.2 (q, C- TBDMS), –5.3 (q, C-TBDMS).

MS (ESI): 589.3 $[M+H]^+$; calcd. 588.3 for $C_{36}H_{48}O_5Si$

***Trans*-6-Acetoxy-2,3,4-tri-O-benzyl-1-deoxy-1'-prop-1-enyl-α-D-manopyranose (12)**



Yield: 81 %

R_f: 0.5 (Hexane : EtOAc, 3 : 2)

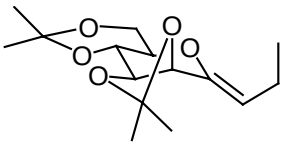
$[\alpha]^{20}_D$ +18.2 (*c* = 1, $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40 – 7.24 (15H, m, Ph$\underline{CH_2}$), 5.59 –5.54 (1H, m, H-1'), 5.45 – 5.38 (1H, m, H-2'), 4.86 (1H, d, *J* = 10.7 Hz, Ph$\underline{CH_2}$), 4.74 – 4.54 (6H, m, H-1, 5 x Ph$\underline{CH_2}$), 4.38 – 4.27 (2H, m, H-6), 3.88 – 3.69 (4H, m, H-2, H-3, H-4, H-5), 2.06 (3H, s, $\underline{CH_3}$CO), 1.65 (3H, d, *J* = 6.3 Hz, H-3').

^{13}C NMR (75 MHz, $CDCl_3$): δ 171.0 (s, $CH_3\underline{CO}$), 138.2 (s, $\underline{Ph}CH_2$), 138.1 (s, $\underline{Ph}CH_2$), 138.03 (s, $\underline{Ph}CH_2$), 130.1 (d, C-1'), 128.4 (d, $\underline{Ph}CH_2$), 128.36 (d, $\underline{Ph}CH_2$), 128.3 (d, $\underline{Ph}CH_2$), 128.1 (d, $\underline{Ph}CH_2$), 127.9 (d, $\underline{Ph}CH_2$), 127.85 (d, $\underline{Ph}CH_2$), 127.8 (d, $\underline{Ph}CH_2$), 127.7 (d, $\underline{Ph}CH_2$), 127.6 (d, $\underline{Ph}CH_2$), 126.5 (d, C-2'), 78.6 (d, C-3), 75.9 (d, C-2), 75.0 (d, C-4), 74.6 (t, Ph$\underline{CH_2}$), 73.9 (d, C-1), 72.1 (t, Ph$\underline{CH_2}$), 72.0 (d, C-5), 71.6 (t, C-Ph$\underline{CH_2}$), 63.8 (t, C-6), 20.9 (q, $\underline{CH_3}$CO), 18.1 (q, C-3').

MS (ESI): 517.2 $[M+H]^+$; calcd. 516.2 for $C_{32}H_{36}O_6$

(1(1')Z)-2,3:4,6-Di-O-isopropylidene-1-deoxy-1-propylidene-D-mannopyranose (13)



Yield: 88 %

R_f: 0.5 (Hexane : EtOAc, 3 : 1)

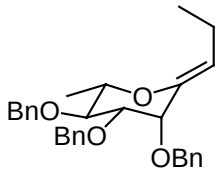
$[\alpha]^{20}_D$ +45.8 (*c* = 1, $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.03 (1H, t, *J* = 7.14 Hz, H-1'), 4.58 (1H, d, *J* = 6.04 Hz, H-4), 4.11 (1H, dd, *J* = 7.7, 6.0 Hz, H-3), 3.99 (1H, dd, *J* = 10.9, 5.8 Hz, H-6a), 3.89 – 3.78 (2H, m, H-2, H-6b), 3.31 (1H, dt, *J* = 10.2, 5.7 Hz, H-5), 2.13 (2H, m, H-2'), 1.55 (3H, s, CH_3), 1.53 (3H, s, CH_3), 1.43 (3H, s, CH_3), 1.39 (3H, s, CH_3), 0.96 (3H, t, *J* = 7.7 Hz, H-3').

^{13}C NMR (75 MHz, $CDCl_3$): δ 145.5 (s, C-1), 118.1 (d, C-1'), 110.0 (s, $C(CH_3)_2$), 99.3 (s, $C(CH_3)_2$), 76.4 (d, C-4), 74.8 (d, C-3), 72.6 (d, C-2), 68.9 (d, C-5), 62.1 (t, C-6), 28.9 (q, CH_3), 28.1 (q, CH_3), 26.1 (q, CH_3), 18.8 (q, CH_3), 18.0 (t, C-2'), 13.9 (q, C-3').

MS (ESI): 285.0 $[M+H]^+$; calcd. 284.2 for $C_{15}H_{24}O_5$

(1(1')Z)-2,3,4-Tri-O-benzyl-1-deoxy-1-propylidene-L-rhamnopyranose (14)



Yield: 92 %

R_f: 0.6 (Hexane : EtOAc, 3 : 1)

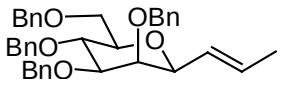
$[\alpha]^{20}_D$ – 5.95 (*c* = 0.9, $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 – 7.20 (15H, m, $\underline{Ph}CH_2$), 4.98 (1H, d, *J* = 10.7 Hz, $Ph\underline{CH_2}$), 4.69 (1H, t, *J* = 7.2 Hz, H-1'), 4.68 – 4.32 (5H, m, $Ph\underline{CH_2}$), 3.89 (1H, d, *J* = 3.3 Hz, H-2), 3.74 (1H, t, *J* = 9.2 Hz, H-4), 3.53 (1H, dd, *J* = 9.2, 3.6 Hz, H-3), 3.36 (1H, m, H-5), 2.09 (2H, m, H-2'), 1.39 (3H, d, *J* = 6.0 Hz, H-6), 0.92 (3H, t, *J* = 7.4 Hz, H-3').

^{13}C NMR (75 MHz, $CDCl_3$): δ 146.7 (s, C-1), 138.6 (s, $\underline{Ph}CH_2$), 138.2 (s, $\underline{Ph}CH_2$), 138.2 (s, $\underline{Ph}CH_2$), 1283 (d, $\underline{Ph}CH_2$), 128.2 (d, $\underline{Ph}CH_2$), 128.22 (d, $\underline{Ph}CH_2$), 128.15 (d, $\underline{Ph}CH_2$), 127.9 (d, $\underline{Ph}CH_2$), 127.6 (d, $\underline{Ph}CH_2$), 127.56 (d, $\underline{Ph}CH_2$), 127.5 (d, $\underline{Ph}CH_2$), 127.46 (d, $\underline{Ph}CH_2$), 118.7 (d, C-1'), 82.0 (d, C-5), 79.9 (d, C-4), 76.7 (d, $Ph\underline{CH_2}$), 75.4 (d, $Ph\underline{CH_2}$), 74.0 (d, $Ph\underline{CH_2}$), 71.0 (d, C-3), 68.7 (d, C-2), 18.5 (t, C-2'), 17.95 (t, C-6), 14.4 (q, C-3').

MS (ESI): 459.2 $[M+H]^+$; calcd. 458.2 for $C_{30}H_{34}O_4$

***Trans*-2,3,4,6-tetra-O-benzyl-1-deoxy-1'- prop-1-enyl -*β*–D-mannopyranose (24)**



Yield: 65 %

R_f: 0.5 (Hexane : EtOAc, 3 : 2)

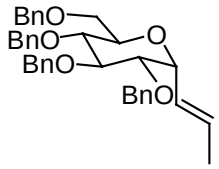
$[\alpha]^{20}_D$ +4.5 (*c* = 1, $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.16 (20H, m, PhCH_2), 5.76-5.63 (1H, m, H-1'), 5.61-5.56 (1H, m, H-2'), 4.95 (1H, d, *J* = 12.1 Hz, PhCH_2), 4.89 (1H, d, *J* = 10.7 Hz, PhCH_2), 4.78-4.56 (7H, m, H-1, PhCH_2), 3.96 (1H, t, *J* = 9.6 Hz, H-4), 3.81-3.75 (3H, m, H-2, H-6), 3.64 (1H, dd, *J* = 2.8, 9.6 Hz, H-3), 3.49 (1H, m, H-5), 1.68 (3H, d, *J* = 6.0 Hz, H-3').

^{13}C NMR (75 MHz, $CDCl_3$): δ 138.4 (s, PhCH_2), 138.41 (s, PhCH_2), 138.38 (s, PhCH_2), 128.5 (d, PhCH_2), 128.4 (d, PhCH_2), 128.3(d, PhCH_2), 128.2 (d, PhCH_2), 128.15 (d, PhCH_2), 128.1 (d, PhCH_2), 128.0 (d, PhCH_2), 127.6 (d, PhCH_2), 127.5 (d, PhCH_2), 127.4 (d, PhCH_2), 84.7 (d, C-3), 79.5 (d, C-1), 79.3 (d, C-5), 75.2 (d, C-4), 75.1 (d, C-2), 75.14 (t, PhCH_2), 74.3 (t, PhCH_2), 73.4 (t, PhCH_2), 72.2 (t, PhCH_2), 69.6 (t, C-6), 17.9 (q, C-3').

MS (ESI): 582.4 $[M+NH_4]^+$; calcd. 564.3 for $C_{37}H_{40}O_5$

***Trans*-2,3,4,6-tetra-O-benzyl-1-deoxy-1'- prop-1-enyl -α-D-glucopyranose (25)**



Yield: 89 %

R_f: 0.55 (Hexane : EtOAc, 4 : 1)

$[\alpha]^{20}_D$ +50.5 (*c* = 1, $CHCl_3$)

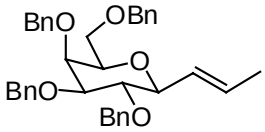
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 – 7.24 (18H, m, PhCH_2), 7.15 – 7.09 (2H, m, PhCH_2), 5.93 – 5.76 (2H, m, H-1', H-2'), 4.96 (1H, d, *J* = 10.1 Hz, PhCH_2), 4.91 – 4.77 (2H, m, PhCH_2), 4.64 – 4.44 (6H, m, H-1, 5 x PhCH_2), 3.82 – 3.61 (6H, m, H-2, H-3, H-4, H-5, H-6), 1.76 (3H, d, *J* = 5.8 Hz, H-3').

^{13}C NMR (75 MHz, $CDCl_3$): δ 138.7 (s, PhCH_2), 138.1 (s, PhCH_2), 138.0 (s, PhCH_2), 137.9 (s, PhCH_2), 131.9 (d, C-1'), 128.2 (d, PhCH_2), 128.2 (d, PhCH_2), 128.0 (d, PhCH_2),

127.8 (d, PhCH_2), 127.78 (d, PhCH_2), 127.76 (d, PhCH_2), 127.7 (d, PhCH_2), 127.6 (d, PhCH_2), 127.55 (d, PhCH_2), 127.5 (d, PhCH_2), 127.4 (d, PhCH_2), 124.5 (d, C-2'), 82.7 (d, C-2), 79.9 (d, C-3), 78.2 (d, C-1), 75.4 (t, PhCH_2), 75.0 (t, PhCH_2), 73.9 (d, C-5), 73.86 (t, PhCH_2), 72.5 (t, PhCH_2), 71.7 (d, C-4), 68.8 (t, C-6), 18.3 (q, C-3').

MS (ESI): 565.2 $[M+H]^+$; calcd. 564.3 for $C_{37}H_{40}O_5$

***Trans*-2,3,4,6-tetra-O-benzyl-1-deoxy-1'- prop-1-enyl -β-D-galactopyranose (27)**



Yield: 90 %

R_f: 0.4 (Hexane : EtOAc, 3 : 1)

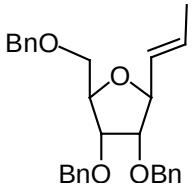
$[\alpha]^{20}_D$ +8.7 (*c* = 1, $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.22 (20H, m, PhCH_2), 5.87-5.77 (1H, m, H-1'), 5.56-5.48 (1H, m, H-2'), 4.94 (1H, d, *J* = 11.8 Hz, PhCH_2), 4.78 - 4.40 (8H, m, H-1, 7 x PhCH_2), 3.97 (1H, d, *J* = 2.8 Hz, H-4), 3.74-3.64 (2H, m, H-2, H-3) 3.58-3.51 (3H, m, H-5, H-6), 1.71 (3H, dd, *J* = 1.4, 6.3 Hz, H-3').

^{13}C NMR (75 MHz, $CDCl_3$): δ 138.8 (s, PhCH_2), 138.5 (s, PhCH_2), 138.4 (s, PhCH_2), 137.9 (s, PhCH_2), 130.6 (d, C-1'), 128.6 (d, C-2'), 128.4 (d, PhCH_2), 128.3 (d, PhCH_2), 128.25 (d, PhCH_2), 128.2 (d, PhCH_2), 128.0 (d, PhCH_2), 127.7 (d, PhCH_2), 127.6 (d, PhCH_2), 127.55 (d, PhCH_2), 127.5 (d, PhCH_2), 84.1 (d, C-3), 80.9 (d, C-2), 79.0 (d, C-5), 75.6 (d, C-1), 75.2 (t, PhCH_2), 74.5 (t, PhCH_2), 73. 9 (d, C-4), 73.5 (t, PhCH_2), 72.5 (t, PhCH_2), 68.8 (t, C-6), 18.0 (q, C-3').

MS (ESI): 565.2 $[M+H]^+$; calcd. 564.3 for $C_{37}H_{40}O_5$

***Trans*-2,3,5-tri-O-benzyl-1-deoxy-1'- prop-1-enyl -β-D-ribofuranose (28)**



Yield: 77 %

R_f: 0.45 (Hexane: EtOAc, 3 : 2)

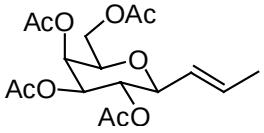
$[\alpha]^{20}_{D}$ +16.9 (*c* = 1, $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27 – 7.17 (15H, m, PhCH_2), 6.01 – 5.93 (1H, m, H-1'), 5.68-5.61 (1H, m, H-2'), 4.72 – 4.54 (6H, m, PhCH_2), 4.02 – 3.98 (1H, m, H-1), 3.91 (1H, m, H-3), 3.74 (1H, m, H-2), 3.55 (2H, m, H-4, H-5a), 3.41-3.37 (1H, m, H-5b), 1.63 (3H, d, *J* = 6.0 Hz, H-3').

^{13}C NMR (75 MHz, $CDCl_3$): δ 138.7 (s, PhCH_2), 138.5 (s, PhCH_2), 129.4 (d, C-1'), 128.2 (d, PhCH_2), 128.1 (d, PhCH_2), 127.9 (d, PhCH_2), 127.7 (d, PhCH_2), 127.4 (d, PhCH_2), 127.39 (d, PhCH_2), 77.2 (d, C-1, C-4), 76.5 (d, C-3), 73.4 (d, C-2), 72.5 (t, PhCH_2), 71.9 (t, PhCH_2), 71.4 (t, C-5), 18.0 (q, C-3').

MS (ESI): 445.3 $[M+H]^+$; calcd. 444.2 for $C_{29}H_{32}O_4$

***Trans*-2,3,4,6-tetra-acetyl-1-deoxy-1'- prop-1-enyl -β-D-galactopyranose (30)**



Yield: 92 %

R_f: 0.45 (Hexane : EtOAc, 2 :3)

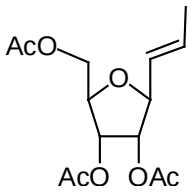
$[\alpha]^{20}_{D}$ + 41.1 (*c* = 0.91, $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.83 – 5.72 (1H, m, H-1'), 5.45 – 5.37 (2H, m, H-2', H-4), 5.12 – 4.98 (2H, m, H-2, H-3), 4.34 – 4.05 (2H, m, H-6), 3.87 (1H, t, *J* = 6.3, H-5), 3.75 (1H, t, *J* = 8.5 Hz, H-1), 2.12 (3H, s, CH_3CO), 2.00 (3H, s, CH_3CO), 1.96 (3H, s, CH_3CO), 1.95 (3H, s, CH_3CO), 1.67 (3H, d, *J* = 5.6 Hz, H-3').

^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3 (s, CH_3CO), 170.2 (s, CH_3CO), 170.1 (s, CH_3CO), 169.6 (s, CH_3CO), 132.3 (d, C-1'), 126.4 (d, C-2'), 79.9 (d, C-1), 73.8 (d, C-2), 71.6 (d, C-3), 68.6 (d, C-5), 67.6 (d, C-4), 61.7 (t, C-6), 20.7 (q, CH_3CO), 20.6 (q, CH_3CO), 20.58 (q, CH_3CO), 20.5 (q, CH_3CO), 17.8(q, C-3').

MS (ESI): 373.2 $[M+H]^+$; calcd. 372.1 for $C_{17}H_{24}O_9$

2,3,5-Tri-acetoxy-1-deoxy-1'- prop-1-enyl -β-D-ribofuranose (31)



Yield: 89 %

R_f: 0.6 (EtOAc)

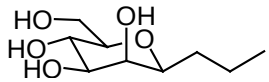
$[\alpha]^{20}_D$ +37.9 (*c* = 1, $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.87 – 5.76 (1H, m, H-1'), 5.56 – 5.47 (1H, m, H-2'), 5.41 (1H, t, *J* = 3.8 Hz, H-1), 5.26 (1H, dd, *J* = 4.7, 8.4 Hz, H-3), 4.59 (1H, dd, *J* = 3.8, 7.9 Hz, H-2), 4.33 – 4.22 (1H, m, H-4, H-5a), 4.11 (1H, dd, *J* = 4.1, 11.8 Hz, H-5b), 2.12 (6H, s, 2 x $\underline{CH_3}CO$), 2.09 (3H, s, $\underline{CH_3}CO$), 2.05 (3H, s, $\underline{CH_3}CO$), 1.73 (3H, dd, *J* = 1.1, 6.6 Hz, H-3').

^{13}C NMR (75 MHz, $CDCl_3$): δ 170.7 (s, $CH_3\underline{CO}$), 169.8 (s, $CH_3\underline{CO}$), 169.77 (s, $CH_3\underline{CO}$), 132.5 (d, C-1'), 124.7 (d, C-2'), 80.6 (d, C-4), 76.8 (d, C-1), 73.1 (d, C-2), 72.3 (d, C-3), 63.8 (t, C-5), 20.8 (q, $\underline{CH_3}CO$), 20.6 (q, $\underline{CH_3}CO$), 20.5 (q, $\underline{CH_3}CO$), 17.9 (q, C-3').

MS (ESI): 301.0 $[M+H]^+$; calcd. 300.1 for $C_{14}H_{20}O_7$

1-Deoxy-1-propyl-*β*-D-mannopyranose (32)



To a solution of compound **8** (56.4 mg, 0.1 mmol) in MeOH (1 ml) was added Pd/C (10 mg) and the reaction mixture was stirred under a H_2 (1 atm) atmosphere at room temperature for 6 h, during this period 1 drop of AcOH was added and the reaction was monitored by TLC. After completion of reaction, the catalyst was filtered off over celite and the filtrate concentrated to afford fully deprotected mannoside (**32**) (19.4 mg).

Yield: 95 %

R_f: 0.45 ($CHCl_3$: MeOH, 7 : 3)

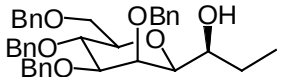
$[\alpha]^{20}_D$ – 5.7 (*c* = 1, D_2O)

^{1}H NMR (300 MHz, D_2O): δ 3.90 (2H, m, H-1, H-2), 3.69 – 3.53 (4H, m, H-3, H-4, H-6, H-5), 3.35 – 3.29 (1H, m, H-6), 1.61 – 1.51 (2H, m, H-1'), 1.38 – 1.29 (2H, m, H-2'), 0.91 (3H, t, *J* = 7.4 Hz, H-3').

^{13}C NMR (75 MHz, D_2O): δ 82.9 (d, C-4), 80.8 (d, C-5), 77.3 (d, C-2), 73.3 (d, C-3), 70.3 (d, C-1), 64.2 (t, C-6), 35.0 (t, C-1'), 211 (t, C-2'), 16.2 (q, C-3').

MS (ESI): 205.1 $[M+H]^+$; calcd. 204.1 for $C_9H_{16}O_5$

2,3,4,6-Tetra-O-benzyl-1-deoxy-1-(1'-hydroxy-propyl)-β-D-mannopyranose (33)



A solution of borane in THF (1 M, 1.3 mL, 1.3 mmol) was added to a solution of the *exo*-glycal **8** (56.4 mg, 0.1 mmol) in THF (5 ml) and the mixture was stirred for three days. The reaction was quenched by the addition of aq.NaOH (1M, 1ml), followed by aq. H_2O_2 (ca. 30 % v/v, 1 mL). After stirring for 30 min. at room temperature, the mixture was partitioned between brine (25 mL) and EtOAc (25 mL), the aqueous layer was extracted with EtOAc (2 x 25 ml), dried, and concentrated in vacuo. Column chromatography (hexane/EtOAc, gradient elution) gave first unchanged starting material **8** (5.6 mg), followed by **33** (25.0 mg).

Yield: 43 %

R_f: 0.45 (Hexane : EtOAc, 1 : 1)

$[\alpha]^{20}_D$ – 2.8 (*c* = 1, $CHCl_3$)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 – 7.12 (20H, m, PhCH_2), 4.98 (1H, d, *J* = 11.5 Hz, PhCH_2), 4.86 – 4.67 (4H, m, PhCH_2), 4.59 – 4.48 (3H, m, PhCH_2), 4.09 (1H, d, *J* = 1.9 Hz, H-1'), 3.89 (1H, t, *J* = 9.6 Hz, H-4), 3.73 – 3.56 (4H, m, H-2, H-3, H-1, H-6a), 3.42 – 3.35 (1H, m, H-6b), 2.98 (1H, d, *J* = 7.9 Hz, H-5), 1.62 (1H, m, H-2a'), 1.34 (1H, m, H-2b'), 0.86 (3H, t, *J* = 6.3 Hz, H-3').

^{13}C NMR (75 MHz, $CDCl_3$): δ 138.6 (s, PhCH_2), 138.4 (s, PhCH_2), 138.3 (s, PhCH_2), 128.5 (d, PhCH_2), 128.46 (d, PhCH_2), 128.3 (d, PhCH_2), 128.2 (d, PhCH_2), 128.0 (d, PhCH_2), 127.95 (d, PhCH_2), 127.8 (d, PhCH_2), 127.7 (d, PhCH_2), 127.6 (d, PhCH_2), 127.56 (d, PhCH_2), 127.4 (d, PhCH_2), 85.3 (d, C-1'), 80.4 (d, C-4), 80.0 (d, C-5), 75.4 (t,

Ph$\underline{CH_2}$), 75.2(d, C-2), 73.9 (d, C-3), 73.4 (t, Ph$\underline{CH_2}$), 72.5 (t, Ph$\underline{CH_2}$), 72.1 (t, Ph$\underline{CH_2}$), 70.6 (d, C-1), 69.7 (t, C-6), 26.75 (t, C-2'), 9.5 (q, C-3').

MS (ESI): 583.2 $[M+H]^+$; calcd. 582.3 for $C_{37}H_{42}O_6$

(*R*)-MTPA ester of 33

To a solution of **33** (7 mg, 0.012 mmol) in CH_2Cl_2 (1ml) were added DMAP (3 mg), Et_3N (5 µl), and (*R*)-MTPACl (5 µl) at room temperature, and stirring was continued for 18 h. N,N-Dimethyl-1,3-propanediamine (5 µl) was added, and the reaction mixture was stirred for 10 min. After addition of phosphate buffer (pH 6.85), the reaction mixture was extracted with $CHCl_3$, and then the organic layer was evaporated. The residue was purified by flash CC to afford (*R*)-MTPA ester of **33** (8 mg).

Yield: 84 %

R_f: 0.45 (Hexane : EtOAc, 7 : 3)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 – 7.57 (2H, m, Ar-H), 7.41-7.19 (23H, m, 20x Ph$\underline{CH_2}$, 3xAr-H), 5.37 (1H, m, H-1'), 4.93 (1H, d, *J* = 10.7 Hz, Ph$\underline{CH_2}$), 4.87 (1H, d, *J* = 10.7 Hz, Ph$\underline{CH_2}$), 4.73 – 4.43 (6H, m, Ph$\underline{CH_2}$), 3.94 (1H, t, *J* = 9.3 Hz, H-4), 3.77 – 3.66 (3H, m, H-2, H-3, H-1), 3.60 – 3.57 (2H, m, H-1, H-6), 3.47 (3H, s, O$\underline{CH_3}$), 3.42 (1H, m, H-5), 1.92 (1H, m, H-2a'), 1.76 (1H, m, H-2b'), 0.79 (3H, t, *J* = 7.4 Hz, H-3').

MS (ESI): 799.3 $[M+H]^+$; calcd. 798.3 for $C_{47}H_{49}F_3O_8$

(S)-MTPA ester of 33

The (*S*)-MTPA ester of **33** (9.5 mg) was obtained from **33** (9 mg, 0.015 mmol) through the same procedure as described for preparation of the (*R*)-MTPA ester of **33**.

Yield: 80 %

R_f: 0.45 (Hexane : EtOAc, 7 : 3)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (2H, m, Ar-H), 7.41-7.17 (23H, m, 20x Ph$\underline{CH_2}$, 3xAr-H), 5.45 (1H, m, H-1'), 4.91 (1H, d, *J* = 11.0 Hz, Ph$\underline{CH_2}$), 4.85 (1H, d, *J* = 11.0 Hz, Ph$\underline{CH_2}$), 4.67 – 4.38 (6H, m, Ph$\underline{CH_2}$), 3.91 (1H, t, *J* = 9.9 Hz, H-4), 3.74 – 3.66 (3H, m, H-2, H-3, H-1), 3.57 (3H, s, O$\underline{CH_3}$), 3.51 (1H, m, H-6a), 3.41 (1H, m, H-6b), 3.33 (1H, m, H-5), 1.98 (1H, m, H-2a'), 1.81 (1H, m, H-2b'), 0.91 (3H, t, *J* = 7.4 Hz, H-3').

MS (ESI): 799.4 $[M+H]^+$; calcd. 798.3 for $C_{47}H_{49}F_3O_8$