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

A colourless oil; $[\alpha]_D^{27}$ +35.2 (*c*, 1.4 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 3.71 (1H, dd, $J_{5,6}$ 1.9 Hz, $J_{6,6'}$10.9 Hz, H-6), 3.67 (1H, dd, $J_{5,6'}$ 4.5 Hz, H-6'), 3.84-3.85 (1H, m, H-2), 3.86-3.98 (2H, m, H-3, H-5), 4.02 (1H, at, *J* 9.5 Hz, H-4), 4.17 (1H, dd, J_{gem} 13.1 Hz, *J* 6.0 Hz, OC<u>H</u>H'), 4.25 (1H, dd, *J* 5.7 Hz, OCH<u>H</u>'), 4.51, 4.88 (2H, ABq, J_{AB} 10.8 Hz, PhC<u>H</u>$_2$), 4.54, 4.68 (2H, ABq, J_{AB} 12.3 Hz, PhC<u>H</u>$_2$), 4.73 (2H, s, PhC<u>H</u>$_2$), 5.24 (1H, dd, J_{gem} 1.5 Hz, J_Z 10.3 Hz, $OCH_2CH=CH_E\underline{H}_Z$), 5.31 (1H, dd, J_E 17.2 Hz, $OCH_2CH=C\underline{H}_EH_Z$), 5.64 (1H, dd, $J_{1,2}$ 1.8 Hz, $J_{1,F}$ 50.6 Hz, H-1), 5.93 (1H, ddat, $OCH_2C\underline{H}=CH_2$), 7.16-7.41 (15H, m, Ar-H); δ_C ($CDCl_3$) 68.5 (t, C-6), 72.6, 72.6 (2 x t, Ph<u>C</u>H$_2$, O<u>C</u>H$_2$CH=CH$_2$), 73.3 (dd, $^2J_{C\text{-}2,F}$ 35.3 Hz, C-2), 73.4, 75.2 (2 x t, 2 x Ph<u>C</u>H$_2$), 73.9 (d, C-4), 74.0 (d, C-5), 79.0, (d, C-3), 106.4 (dd, $^1J_{C\text{-}1,H\text{-}1}$ 182.2 Hz, $^1J_{C\text{-}1,F}$ 222.6 Hz, C-1), 118.1 (t, $OCH_2CH=\underline{C}H_2$), 127.6, 127.7, 127.8, 127.9, 127.9, 128.1, 128.1, 128.3, 128.3, 128.5, 128.7 (11 x d, Ar-CH), 134.5 (d, $OCH_2\underline{C}H=CH_2$), 138.0, 138.0, 138.1 (3 x s, Ar-C); *m/z* ($APCI^+$) 515 ($M+Na^+$, 100%). (HRMS Calcd. for $C_{30}H_{37}NO_5F$ (MNH_4^+) 510.2656. Found 510.2657). (Found: C, 73.15; H, 6.86. $C_{30}H_{33}O_5F$ requires C, 73.15; H, 6.75%).

2*-O-*Allyl-3,4,6-tri*-O-*benzyl*-β-*D-glucopyranosyl fluoride 4.

A colourless oil; $[\alpha]_D^{22}$ +9.2 (*c*, 0.5 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 3.49 (1H, ddd, $J_{1,2}$ 6.9 Hz, $J_{2,3}$ 8.6 Hz, $J_{2,F}$ 12.3 Hz, H-2), 3.59 (1H, ddd, $J_{4,5}$ 9.5 Hz, $J_{5,6}$ 2.6 Hz, $J_{5,6'}$ 3.7 Hz, H-5), 3.64 (1H, at, *J* 8.7 Hz, H-3), 3.69-3.77 (3H, m, H-4, H-6, H-6'), 4.20 (1H, dd, J_{gem} 12.4 Hz, *J* 5.8 Hz, OC<u>H</u>H'), 4.34 (1H, dd, *J* 5.7 Hz, OCH<u>H</u>'), 4.54, 4.93 (2H, ABq, J_{AB} 10.8 Hz, PhC<u>H</u>$_2$), 4.55, 4.64 (2H, ABq, J_{AB} 12.2 Hz, PhC<u>H</u>$_2$), 4.80, 4.93 (2H, ABq, J_{AB} 10.8 Hz, PhC<u>H</u>$_2$), 5.21 (1H, dd, $J_{1,F}$ 52.8 Hz, H-1), 5.22 (1H, dd, J_{gem} 1.6 Hz, J_Z 10.3 Hz, $OCH_2CH=CH_E\underline{H}_Z$), 5.32 (1H, dd, J_E 17.3 Hz, $OCH_2CH=C\underline{H}_EH_Z$), 5.95 (1H, ddt, $OCH_2C\underline{H}=CH_2$), 7.14-7.38 (15H, m, Ar-H); δ_C ($CDCl_3$) 68.3, 73.3, 73.5, 75.0, 75.5 (5 x t, 3 x Ph<u>C</u>H$_2$, O<u>C</u>H$_2$CH=CH$_2$, C-6), 74.7, 76.8, 83.4 (3 x d, C-3, C-4, C-5), 81.2 (dd, $^2J_{C\text{-}2,F}$ 21.5 Hz, C-2), 109.7 (dd, $^1J_{C\text{-}1,F}$ 215.5 Hz, C-1), 117.6 (t, $OCH_2CH=\underline{C}H_2$), 127.7, 127.8, 127.8, 127.9, 127.9, 128.4, 128.4, (7 x d, Ar-CH), 134.3 (d, $OCH_2\underline{C}H=CH_2$), 137.8, 137.8, 138.2 (3 x s, Ar-C); *m/z* ($APCI^+$) 515 ($M+Na^+$, 10%). (HRMS Calcd. for $C_{30}H_{33}O_5F$ (MNH_4^+) 510.2656. Found 510.2658).

2*-O-*Acetyl-3,4,6-tri*-O-*benzyl* -α-*D-mannopyranosyl fluoride 7.

A pale yellow oil; $[\alpha]_D^{23}$ +13.3 (*c*, 1.0 in $CHCl_3$); ν_{max} (thin film) 1751 (s, C=O) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 2.17 (3H, s, CH_3), 3.72 (1H, d, $J_{6,6'}$ 10.9 Hz, H-6), 3.82 (1H, dd, $J_{5,6'}$ 2.7 Hz, H-6'), 3.97-3.99 (3H, m, H-3, H-4, H-5), 4.49, 4.87 (2H, ABq, J_{AB} 10.7 Hz, PhC<u>H</u>$_2$), 4.52, 4.69 (2H, ABq, J_{AB} 12.1 Hz, PhC<u>H</u>$_2$), 4.57, 4.72 (2H, ABq, J_{AB} 10.9 Hz, PhC<u>H</u>$_2$), 5.48 (1H, br s, H-2), 5.62 (1H, dd, $J_{1,2}$ 1.9 Hz, $J_{1,F}$ 49.1 Hz, H-1), 7.15-7.38 (15H, m, Ar-H); δ_C ($CDCl_3$) 21.0 (q, CH_3), 67.0 (dd, $^2J_{C\text{-}2,F}$ 39.9 Hz, C-2), 68.2 (t, C-6), 72.1, 73.5, 75.3 (3 x t, 3 x Ph<u>C</u>H$_2$), 73.3 (d, C-4), 73.8 (d, $^3J_{C\text{-}5,F}$ 2.0 Hz, C-5), 77.2 (d, C-3), 105.5 (dd, $^1J_{C\text{-}1,H}$ 182.6 Hz, $^1J_{C\text{-}1,F}$ 221.0 Hz, C-1), 127.8, 127.8, 127.9, 128.0, 128.1, 128.4, 128.5 (7 x d, Ar-CH), 137.6, 138.0, 138.1 (3 x s, Ar-C), 170.1 (s, <u>C</u>=O); *m/z* ($APCI^+$) 517 ($M+Na^+$, 18%). (HRMS Calcd. for $C_{29}H_{35}NO_6F$ (MNH_4^+) 512.2448. Found 512.2451). (Found: C, 70.27; H, 6.50. $C_{29}H_{31}O_6F$ requires C, 70.43; H, 6.32%).

2*-O-*Acetyl-3,4,6-tri*-O-*benzyl -β-D-glucopyranosyl fluoride 8.

A colourless oil; $[\alpha]_D^{22}$ +15.3 (*c*, 1.25 in $CHCl_3$); ν_{max} (thin film) 1750 (s, C=O) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 2.02 (3H, s, C$\underline{H}_3$), 3.67-3.75 (4H, m, H-3, H-5, H-6, H-6'), 3.86 (1H, at, *J* 9.0 Hz, H-4), 4.56, 4.78 (2H, ABq, J_{AB} 11.2 Hz, PhC$\underline{H}_2$), 456, 4.63 (2H, ABq, J_{AB} 12.1 Hz, PhC$\underline{H}_2$), 4.71, 4.78 (2H, ABq, J_{AB} 11.6 Hz, PhC$\underline{H}_2$), 5.09-5.15 (1H, m, H-2), 5.27 (1H, dd, $J_{1,2}$ 6.1 Hz, $J_{1,F}$ 52.9 Hz, H-1), 7.16-7.36 (15H, m, Ar-H); δ_C ($CDCl_3$) 20.8 (q, $\underline{C}H_3$), 68.4, 73.6, 74.4, 74.9 (4 x t, C-6, 3 x Ph$\underline{C}H_2$), 72.5 (dd, C-2), 75.0, 81.5, 81.6 (3 x d, C-3, C-4, C-5), 106.7 (dd, C-1), 127.7, 127.8, 127.8, 127.9, 128.0, 128.4, 128.4, 128.9 (8 x d, Ar-CH), 137.6, 137.8 (2 x s, Ar-C), 169.4 (s, C=O); δ_F ($CDCl_3$) -136.8 (dd, $J_{1,F}$ 52.9 Hz, $J_{2,F}$ 10.2 Hz); *m/z* ($APCI^+$) 533 ($M+K^+$, 100), 517 ($M+Na^+$, 15), 475 (M-F, 5%). (Found: C, 70.49; H, 6.48. $C_{29}H_{31}O_6F$ requires C, 70.43; H, 6.32%).

3,4,6-Tri*-O-*benzyl-α-D-mannopyranosyl fluoride 9.

A colourless oil; $[\alpha]_D^{23}$ +34.2 (*c*, 0.5 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 3.70 (1H, dd, $J_{5,6}$ 1.6 Hz, $J_{6,6'}$ 10.8 Hz, H-6), 3.78 (1H, dd, $J_{5,6'}$ 3.5 Hz, H-6'), 3.87-3.90 (1H, m, H-3), 3.94-3.96 (2H, m, H-4, H-5), 4.12-4.13 (1H, m, H-2), 4.54, 4.67 (2H, ABq, J_{AB} 12.2 Hz, PhC$\underline{H}_2$), 4.54, 4.83 (2H, ABq, J_{AB} 10.8 Hz, PhC$\underline{H}_2$), 4.71, 4.74 (2H, ABq, J_{AB} 11.4 Hz, PhC$\underline{H}_2$), 5.68 (1H, dd, $J_{1,2}$ 1.7 Hz, $J_{1,F}$ 49.5 Hz, H-1), 7.17-7.37 (15H, m, Ar-H); δ_C ($CDCl_3$) 67.1 (dd, $^2J_{C\text{-}2,F}$ 39.0 Hz, C-2), 68.2 (d, C-6), 72.4, 73.5, 75.2 (3 x t, 3 x Ph$\underline{C}H_2$), 73.2 (d, C-4), 73.4 (dd, $^3J_{C\text{-}5,F}$ 2.7 Hz, C-5), 79.1 (dd, $^3J_{C\text{-}3,F}$ 1.8 Hz, C-3), 107.2 (dd, $^1J_{C\text{-}1,H\text{-}1}$ 181.9 Hz, $^1J_{C\text{-}1,F}$ 217.7 Hz, C-1), 127.7, 127.8, 127.9, 127.9, 128.0, 128.1, 128.4, 128.6, (8 x d, Ar-CH), 137.6, 137.9, 138.0 (3 x s, Ar-C). (Found: C, 71.54; H, 6.50. $C_{27}H_{29}O_5F$ requires C, 71.66; H, 6.46%).

3,4,6-Tri*-O-*benzyl-β-D-glucopyranosyl fluoride 10.

A white crystalline solid, m.p. 84 °C (diethyl ether/petrol) [Lit 80-82 °C][A]; $[\alpha]_D^{22}$ +31.5 (*c*, 0.55 in $CHCl_3$) [Lit +25.2][8]; δ_H (400 MHz, $CDCl_3$) 3.59-3.80 (6H, m, H-2, H-3, H-4, H-5, H-6, H-6'), 4.54, 4.62 (2H, ABq, J_{AB} 12.0 Hz, PhC$\underline{H}_2$), 4.57, 4.78 (2H, ABq, J_{AB} 11.1 Hz, PhC$\underline{H}_2$), 4.81, 4.85 (2H, ABq, J_{AB} 11.5 Hz, PhC$\underline{H}_2$), 5.17 (1H, d, $J_{1,2}$ 6.5 Hz, $J_{1,F}$ 53.0 Hz, H-1), 7.17-7.40 (15H, m, Ar-H).

2*-O-*Prop-1'-enyl-3,4,6-tri*-O-*benzyl-α-D-mannopyranosyl fluoride 11.

A pale yellow oil. Partial data: δ_H (400 MHz, $CDCl_3$) (Z:E, 2.7:1) E isomer 1.55 (3H, dd, *J* 1.7 Hz, *J* 6.8 Hz, OCH=CHC$\underline{H}_3$), 5.02 (1H, dq, J_E 12.4 Hz, OCH=C$\underline{H}$CH$_3$), 5.66 (1H, dd, $J_{1,2}$ 1.9 Hz, $J_{1,F}$ 50.2 Hz, H-1), 6.12 (1H, dq, OC$\underline{H}$=CHCH$_3$); Z isomer 1.63 (3H, dd, *J* 1.6 Hz, *J* 6.9 Hz, OCH=CHC$\underline{H}_3$), 5.62 (1H, dd, $J_{1,2}$ 2.0 Hz, $J_{1,F}$ 50.5 Hz, H-1), 5.97 (1H, dq, J_Z 6.0 Hz, OC$\underline{H}$=CHCH$_3$); δ_C ($CDCl_3$) E isomer 12.3 (q, OCH=CH$\underline{C}H_3$), 102.4 (d, OCH=$\underline{C}$HCH$_3$), 105.6 (dd, $^1J_{C\text{-}1,F}$ 221.7 Hz, C-1), 145.5 (d, O$\underline{C}$H=CHCH$_3$); Z isomer 9.4 (q, OCH=CH$\underline{C}H_3$), 104.2 (d, OCH=$\underline{C}$HCH$_3$), 106.1 (dd, $^1J_{C\text{-}1,F}$ 220.7 Hz, C-1), 144.5 (d, O$\underline{C}$H=CHCH$_3$); *m/z* ($APCI^+$) 515 ($M+Na^+$, 100%). (HRMS Calcd. for $C_{30}H_{37}NO_5F$ (MNH_4^+) 510.2656. Found 510.2663).

2*-O-*Prop-1'-enyl-3,4,6-tri*-O-*benzyl-β-D-glucopyranosyl fluoride 12.

A pale yellow oil. Partial data: δ_H (400 MHz, $CDCl_3$) (E:Z, 1:2.3), E isomer 1.58 (3H, dd, *J* 1.6 Hz, *J* 7.0 Hz, OCH=CHC<u>H</u>$_3$), 5.08 (1H, dq, J_E 12.2 Hz, OCH=C<u>H</u>CH$_3$), 5.23 (1H, dd, $J_{1,2}$ 6.3 Hz, $J_{1,F}$ 52.5 Hz, H-1), 6.23 (1H, d, OC<u>H</u>=CHCH$_3$); Z isomer 1.65 (3H, dd, *J* 1.7 Hz, *J* 6.8 Hz, OCH=CH<u>C</u>H$_3$), 4.51 (1H, aquin, *J* 6.6 Hz, OCH=C<u>H</u>CH$_3$), 5.25 (1H, m, $J_{1,2}$ 6.4 Hz, $J_{1,F}$ 52.7 Hz, H-1), 6.16 (1H, dd, J_Z 6.1 Hz, OC<u>H</u>=CHCH$_3$); δ_C ($CDCl_3$) E isomer 12.2 (q, OCH=CH<u>C</u>H$_3$), 102.1 (d, OCH=<u>C</u>HCH$_3$), 108.4 (dd, $^1J_{C\text{-}1,F}$ 217.0 Hz, C-1), 146.4 (d, O<u>C</u>H=CHCH$_3$); Z isomer 9.3 (q, OCH=CH<u>C</u>H$_3$), 101.5 (d, OCH=<u>C</u>HCH$_3$), 108.5 (dd, $^1J_{C\text{-}1,F}$ 213.3 Hz, C-1), 145.6 (d, O<u>C</u>H=CHCH$_3$); *m/z* (ES^+) 510 ($M+NH_4^+$, 100%); (HRMS Calcd. for $C_{30}H_{37}NO_5F$ (MNH_4^+) 510.2656. Found 510.2663).

2*-O-(*2-Iodo-1-methoxypropyl*)-*3,4,6-tri*-O-*benzyl-α-D-mannopyranosyl fluoride 14a.

A colourless oil. *m/z* ($APCI^+$) 673 ($M+Na^+$, 100%).

2*-O-(*1-Cyclohexyloxy-2-iodopropyl*)-*3,4,6-tri*-O-*benzyl-α-D-mannopyranosyl fluoride 14b.

A colourless oil. *m/z* ($APCI^+$) 757 ($M+K^+$, 12), 741 ($M+Na^+$, 100%).

2*-O-(*2-Iodo-1-(methyl 2,3,4-tri*-O-*benzyl-α-D-mannopyranosid-6*-O-*yl)propyl*)-*3,4,6-tri*-O-*benzyl-α-D-mannopyranosyl fluoride 14d.

A colourless oil. *m/z* ($APCI^+$) 1105 ($M+Na^+$, 5%); ($APCI^-$) 1117 ($M+Cl^-$, 7%).

2*-O-(*2-Iodo-1-(methyl 2*-O-*benzyl-4,6*-O-*benzylidene-α-D-mannopyranosid-3*-O-*yl)propyl*)-*3,4,6-tri*-O-*benzyl-α-D-mannopyranosyl fluoride 14e.

A colourless oil. *m/z* ($APCI^-$) 1025 ($M+Cl^-$, 15%);

2*-O-(*2-Iodo-1-(methyl 2,3,6-tri*-O-*benzyl-α-D-mannopyranosid-4*-O-*yl)propyl*)-*3,4,6-tri*-O-*benzyl-α-D-mannopyranosyl fluoride 14f.

A colourless oil. *m/z* ($APCI^-$) 1117 ($M+Cl^-$, 8%);

2*-O-(*1-(Cholestan-3-β-yloxy)-2-iodopropyl*)-*3,4,6-tri*-O-*benzyl-α-D-mannopyranosyl fluoride 14h.

A colourless oil. *m/z* ($APCI^-$) 1041 ($M+Cl^-$, 18%);

Methyl 3,4,6-tri*-O-*benzyl-β-D-mannopyranoside 15a.

A colourless oil; $[\alpha]_D^{24}$ -13 (*c*, 0.75 in $CHCl_3$) [Lit. -13 (*c*, 1.0 in $CHCl_3$)][B]; δ_H (500 MHz, $CDCl_3$) 3.47 (1H, ddd, $J_{4,5}$ 9.5 Hz, $J_{5,6}$ 5.0 Hz, $J_{5,6'}$ 1.3 Hz, H-5), 3.57 (3H, s, OCH_3), 3.57-3.60 (1H, m, H-3), 3.74 (1H, dd, $J_{6,6'}$ 10.8 Hz, H-6), 3.80 (1H, dd, H-6'), 3.88 (1H, at, *J* 9.4 Hz, H-4), 4.11 (1H, d, $J_{2,3}$ 3.0 Hz, H-2), 4.35 (1H, s, H-1), 4.55, 4.90 (2H, ABq, J_{AB} 10.8 Hz, PhC$\underline{H}_2$), 4.58, 4.65 (2H, ABq, J_{AB} 12.3 Hz, PhC$\underline{H}_2$), 4.69, 4.78 (2H, ABq, J_{AB} 11.7 Hz, PhC$\underline{H}_2$), 7.22-7.40 (15H, m, Ar-H); δ_C (125 MHz, $CDCl_3$) $^1J_{C\text{-}1,H\text{-}1}$ 156.7 Hz.

Cyclohexyl 3,4,6-tri-O-benzyl-β-D-mannopyranoside 15b.

A colourless oil; $[\alpha]_D^{24}$ -20 (*c*, 0.4 in $CHCl_3$) [Lit. -19 (*c*, 1.6 in $CHCl_3$)][B]; δ_H (500 MHz, $CDCl_3$) 1.20-2.02 (10H, m, cyclohexyl-H), 2.50 (1H, br s, OH-2), 3.43-3.45 (1H, m, H-5), 3.58 (1H, br d, $J_{3,4}$ 8.6 Hz, H-3), 3.61-3.81 (3H, m, H-6, H-6', OC$\underline{H}$), 3.86 (1H, at, *J* 9.3 Hz, H-4), 4.08 (1H, br s, H-2), 4.56 (1H, s, H-1), 4.58, 4.63 (2H, ABq, J_{AB} 12.1 Hz, PhC$\underline{H}_2$), 4.58, 4.91 (2H, ABq, J_{AB} 10.7 Hz, PhC$\underline{H}_2$), 4.69, 4.80 (2H, ABq, J_{AB} 11.7 Hz, PhC$\underline{H}_2$), 7.23-7.41 (15H, m, Ar-H); δ_C (125 MHz, $CDCl_3$) $^1J_{C\text{-}1,H\text{-}1}$ 155.3 Hz.

3,4,6-Tri-O-benzyl-β-D-mannopyranosyl-(1→6)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose 15c.

A colourless oil; $[\alpha]_D^{22}$ -50.7 (*c*, 0.55 in $CHCl_3$) [Lit. -53 (*c*, 1.3 in $CHCl_3$)][B]; δ_H (400 MHz, $CDCl_3$) 1.32, 1.34, 1.44, 1.54 (12 H, 4 x s, 4 x CH_3), 3.42 (1H, ddd, $J_{4,5}$ 9.8 Hz, $J_{5,6}$ 2.2 Hz, $J_{5,6'}$ 4.6 Hz, H-5_b), 3.56 (1H, dd, $J_{2,3}$ 3.1 Hz, $J_{3,4}$ 9.2 Hz, H-3_b), 3.70-3.78 (3H, m, H-6_a, H-6_b, H-$6'_b$), 3.92 (1H, at, *J* 9.5 Hz, H-4_b), 4.03 (1H, dat, *J* 2.2 Hz, $J_{5,6}$ 7.8 Hz, H-5_a), 4.13 (1H, dd, $J_{5,6'}$ 2.7 Hz, $J_{6,6'}$ 11.2 Hz, H-$6'_a$), 4.22 (1H, dd, $J_{3,4}$ 7.9 Hz, $J_{4,5}$ 1.9 Hz, H-4_a), 4.22 (1H, d, H-2_b), 4.32 (1H, dd, $J_{1,2}$ 5.0 Hz, $J_{2,3}$ 2.4 Hz, H-2_a), 4.5 (1H, s, H-1_b), 4.52, 4.90 (2H, ABq, J_{AB} 10.8 Hz, PhC$\underline{H}_2$), 4.54, 4.64 (2H, ABq, J_{AB} 12.1 Hz, PhC$\underline{H}_2$), 4.60 (1H, dd, H-3_a), 4.66, 4.78 (2H, ABq, J_{AB} 12.0 Hz, PhC$\underline{H}_2$), 5.55 (1H, d, H-1_a), 7.18-7.39 (15H, m, Ar-H); δ_C (125 MHz, $CDCl_3$) $^1J_{C\text{-}1b,H\text{-}1b}$ 160.0 Hz.

Methyl 3,4,6-tri-O-benzyl-β-D-mannopyranosyl-(1→6)-2,3,4-tri-O-benzyl-α-D-mannopyranoside 15d.

A colourless oil; $[\alpha]_D^{24}$ +16.0 (*c*, 1.1 in $CHCl_3$) [Lit. +16.5 (*c*, 1.0 in $CHCl_3$)][C]; δ_H (500 MHz, $CDCl_3$) 3.30 (3H, s, CH_3), 3.40 (1H, ddd, $J_{4,5}$ 9.7 Hz, $J_{5,6}$ 4.7 Hz, $J_{5,6'}$ 2.4 Hz, H-5_b), 3.52 (1H, dd, $J_{2,3}$ 3.0 Hz, $J_{3,4}$ 9.2 Hz, H-3_b), 3.70-3.76 (3H, m, H-6_b, H-$6'_b$, H-6_a), 3.78-3.81 (3H, m, H-2_a, H-4_a, H-5_a), 3.90-3.92 (1H, m, H-3_a), 3.92 (1H, at, *J* 9.4 Hz, H-4_b), 4.06 (1H, d, H-2_b), 4.23 (1H, dd, $J_{6,6'}$ 10.0 Hz, H-$6'_a$), 4.37 (1H, s, H-1_b), 4.56, 4.93 (2H, ABq, J_{AB} 11.4 Hz, PhC$\underline{H}_2$), 4.56, 4.63 (2H, ABq, J_{AB} 13.0 Hz, PhC$\underline{H}_2$), 4.57, 4.91 (2H, ABq, J_{AB} 11.0 Hz, PhC$\underline{H}_2$), 4.62 (2H, s, PhC$\underline{H}_2$), 4.69, 4.79 (2H, ABq, J_{AB} 12.3 Hz, PhC$\underline{H}_2$), 4.71, 4.76 (2H, ABq, J_{AB} 12.7 Hz, PhC$\underline{H}_2$), 4.72 (1H, d, $J_{1,2}$ 1.7 Hz, H-1_a), 7.22-7.41 (30H, m, Ar-H); δ_C (125 MHz, $CDCl_3$) $^1J_{C\text{-}1b,H\text{-}1b}$ 157.9 Hz.

Methyl 3,4,6-tri-O-benzyl-β-D-mannopyranosyl-(1→3)-2-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside 15e.

A colourless oil; $[\alpha]_D^{22}$ +5.1 (*c*, 0.35 in $CHCl_3$); ν_{max} (thin film) 3479 (br, OH) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 3.27 (1H, dt, $J_{4,5}$ 9.6 Hz, $J_{5,6}$ 3.5 Hz, H-5_b), 3.32 (3H, s, OCH_3), 3.39 (1H, dd, $J_{2,3}$ 3.1 Hz, $J_{3,4}$ 9.0 Hz, H-3_b), 3.70 (2H, d, H-6_b, H-$6'_b$), 3.79-3.87 (3H, m, H-2_a, H-5_a, H-6_a), 3.89 (1H, at, *J* 9.1 Hz, H-4_b), 3.94 (1H, d, H-2_b), 4.19 (1H, at, *J* 9.7 Hz, H-4_a), 4.26 (1H, s, H-1_b), 4.28 (1H, dd, $J_{5,6}$ 4.2 Hz, $J_{6,6'}$ 9.6 Hz, H-$6'_a$), 4.49, 4.58 (2H, ABq, J_{AB} 12.0 Hz, PhC$\underline{H}_2$), 4.49 (1H, dd, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 10.2 Hz, H-3_a), 4.55, 4.87 (2H, ABq, J_{AB} 10.8 Hz, PhC$\underline{H}_2$), 4.62, 4.77 (2H, ABq, J_{AB} 12.2 Hz, PhC$\underline{H}_2$), 4.63, 4.73 (2H, ABq, J_{AB} 12.2 Hz, PhC$\underline{H}_2$), 4.77 (1H, d, $J_{1,2}$ 1.4 Hz, H-1_a), 5.61 (1H, s, PhC$\underline{H}$), 7.21-7.49 (25H, m, Ar-H); δ_C ($CDCl_3$) 54.9 (q, OCH_3), 64.0, 68.4, 71.8, 74.0, 75.1, 75.9, 77.2, 80.8 (8 x d, C-2_b, C-3_b, C-4_b, C-5_b, C-2_a, C-3_a, C-4_a, C-5_a), 68.8, 68.9, 71.1, 73.0, 73.5, 75.1 (6 x t, C-6_b, C-6_a, 4 x Ph$\underline{C}H_2$), 96.4 (d, $^1J_{C\text{-}1,H\text{-}1}$ 158.9 Hz, C-1_b), 99.7 (d, $^1J_{C\text{-}1,H\text{-}1}$ 168.6 Hz, C-1_a), 101.8 (d, Ph$\underline{C}$H), 126.0, 127.4, 127.6, 127.7, 127.7, 127.8, 128.0, 128.0, 128.1, 128.2, 128.2, 128.3, 128.4, 128.4, 129.0 (15 x d, Ar-CH), 137.3, 137.6, 138.1, 138.3, 138.5 (5 x s, Ar-C); *m/z* (APCI$^-$) 839 ($M+Cl^-$, 100%), (ES$^+$) 822 ($M+NH_4^+$, 100%). (HRMS Calcd. for $C_{48}H_{56}NO_{11}$ (MNH_4^+) 822.3853. Found 822.3864).

Methyl 3,4,6-tri-O-benzyl-β-D-mannopyranosyl-(1→4)-2,3,6-tri-O-benzyl-α-D-mannopyranoside 15f.

A colourless oil; $[\alpha]_D^{22}$ +21.4 (*c*, 0.35 in $CHCl_3$); ν_{max} (thin film) 3416 (br, OH) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 3.29 (1H, ddd, $J_{4,5}$ 9.7 Hz, $J_{5,6}$ 2.2 Hz, $J_{5,6'}$ 4.5 Hz, H-5_b), 3.34 (3H, s, OCH_3), 3.39 (1H, dd, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 9.2 Hz, H-3_b), 3.62 (1H, dd, $J_{6,6'}$ 11.2 Hz, H-6_b), 3.86 (1H, at, *J* 9.5 Hz, H-4_b), 3.88 (1H, dd, $J_{5,6'}$ 3.7 Hz, $J_{6,6'}$ 11.0 Hz, H-$6'_a$), 3.97 (1H, dd, $J_{2,3}$ 3.2 Hz, H-3_a), 4.01 (1H, d, H-2_b) 4.32 (1H, at, *J* 9.2 Hz, H-4_a), 4.43, 4.56 (2H, ABq, J_{AB} 12.1 Hz, PhC$\underline{H}_2$), 4.48, 4.54 (2H, ABq, J_{AB} 12.0 Hz, PhC$\underline{H}_2$), 4.51, 4.86 (2H, ABq, J_{AB} 11.1 Hz, PhC$\underline{H}_2$), 4.57, 4.71 (2H, ABq, J_{AB} 11.7 Hz, PhC$\underline{H}_2$), 4.59, 4.70 (2H, ABq, J_{AB} 11.8 Hz, PhC$\underline{H}_2$), 4.68, 4.72 (2H, ABq, J_{AB} 12.9 Hz, PhC$\underline{H}_2$), 4.69 (1H, s, H-1_b), 4.77 (1H, d, $J_{1,2}$ 1.9 Hz, H-1_a), 7.19-7.36 (30H, m, Ar-H); δ_C ($CDCl_3$) 54.7 (q, OCH_3), 67.4 (d, C-2_b), 69.0 (t, C-6_b), 69.4 (t, C-6_a), 70.9 (d, C-5_a), 70.8, 72.2, 72.5, 73.2, 73.3, 75.0 (6 x t, 6 x Ph$\underline{C}H_2$), 72.9 (d, C-4_a), 73.8 (d, C-4_b), 74.8 (d, C-2_a), 75.5 (d, C-5_b), 79.0 (d, C-3_a), 81.8 (d, C-3_b), 98.9 (d, $^1J_{C\text{-}1,H\text{-}1}$ 172.5 Hz, C-1_a), 100.0 (d, $^1J_{C\text{-}1,H\text{-}1}$ 161.5 Hz, C-1_b), 127.3, 127.4, 127.4, 127.5, 127.5, 127.5, 127.5, 127.6, 127.7, 127.9, 128.0, 128.1, 128.2, 128.2, (14 x d, Ar-CH), 137.9, 138.1, 138.2, 138.2, 138.3, 138.4 (6 x s, Ar-C); *m/z* (APCI$^-$) 931 ($M+Cl^-$, 100%), (ES$^+$) 914 ($M+NH_4^+$, 100%). (HRMS Calcd. for $C_{55}H_{64}NO_{11}$ (MNH_4^+) 914.4479. Found 914.4473).

Cholestan-3'-β-yl 3,4,6-tri-O-benzyl-β-D-mannopyranoside 15h.

Colourless crystals, m.p. 100-102 °C (ethanol); $[\alpha]_D^{24}$ -4.9 (*c*, 0.75 in $CHCl_3$); ν_{max} (thin film) 3435 (br, OH) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.58-2.00 (31H, m, steroid CH, CH_2), 0.66, 0.81 (6H, 2 x s, 2 x CH_3), 0.87 (3H, d, *J* 6.6 Hz, CH_3), 0.88 (3H, d, *J* 6.8 Hz, CH_3), 0.91, (3H, d, *J* 6.5 Hz, CH_3), 2.11 (1H, br s, OH-2), 3.43 (1H, ddd, $J_{4,5}$ 9.7 Hz, $J_{5,6}$ 5.6 Hz, $J_{5,6'}$ 1.9 Hz, H-5), 3.57 (1H, dd, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 9.1 Hz, H-3), 3.69 (1H, dd, $J_{6,6'}$ 10.7 Hz, H-6), 3.70-3.77 (1H, m, steroid OCH), 3.80 (1H, dd, H-6'), 3.84 (1H, at, *J* 9.3 Hz, H-4), 4.06 (1H, d, H-2), 4.56, 4.91 (2H, ABq, J_{AB} 10.9 Hz, PhC$\underline{H}_2$), 4.57 (1H, s, H-1), 4.58, 4.63 (2H, ABq, J_{AB} 12.1 Hz, PhC$\underline{H}_2$), 4.68, 4.79 (2H, ABq, J_{AB} 11.9 Hz, PhC$\underline{H}_2$), 7.21-

7.40 (15H, m, Ar-H); δ_C ($CDCl_3$) 12.0, 12.2, 18.7, 22.5, 22.8 (5 x q, 5 x steroid CH_3), 21.2, 23.8, 24.2, 28.2, 28.8, 29.2, 32.1, 34.2, 36.2, 37.0, 39.5, 40.0 (12 x t, 12 x steroid CH_2), 28.0, 35.6, 35.8, 44.6, 54.4, 56.2, 56.5 (7 x d, 7 x steroid CH), 35.4, 42.6 (2 x s, 2 x steroid C), 68.8 (d, C-2), 69.4 (t, C-6), 71.3, 73.4, 75.2 (3 x t, 3 x Ph<u>C</u>H_2), 74.3 (d, C-4), 75.1 (d, C-5), 77.5 (d, steroid O<u>C</u>H), 81.7 (d, C-3), 97.2 (d, $^1J_{C\text{-}1,H\text{-}1}$ 155.6 Hz, C-1), 127.5, 127.7, 127.8, 127.9, 128.1, 128.3, 128.4, 128.5, (8 x d, Ar-CH), 137.9, 138.2, 138.3 (3 x s, Ar-C); (Found: C, 78.62; H, 9.38. $C_{54}H_{76}O_6$ requires C, 78.98; H, 9.33%).

***2*-O-(*2-Iodo-1-methoxypropyl)-3,4,6-tri*-O-*benzyl*-β-*D*-glucopyranosyl fluoride 16a.**

A colourless oil. *m/z* ($APCI^+$) 673 ($M+Na^+$, 15%).

***2*-O-(*1-Cyclohexyloxy-2-iodopropyl)-3,4,6-tri*-O-*benzyl*-β-*D*-glucopyranosyl fluoride 16b.**

A colourless oil. *m/z* ($APCI^+$) 741 ($M+Na^+$, 5%).

***2*-O-(*1-(1,2:3,4-Di*-O-*isopropylidene-D-galactopyranose-6*-O-*yl-2-iodopropyl)-3,4,6-tri*-O-*benzyl*-β-*D*-glucopyranosyl fluoride 16c.**

A colourless oil. *m/z* ($APCI^-$) 913 ($M+Cl^-$, 4%); ($APCI^+$) 901 ($M+Na^+$, 5%).

***2*-O-(*2-Iodo-1-(methyl 2,3,4-tri*-O-*benzyl*-α-*D-mannopyranosid-6*-O-*yl)propyl)-3,4,6-tri*-O-*benzyl*-β-*D*-glucopyranosyl fluoride 16d.**

A colourless oil. *m/z* ($APCI^-$) 1117 ($M+Cl^-$, 92%).

***2*-O-(*2-Iodo-1-(methyl 2*-O-*benzyl-4,6*-O-*benzylidene*-α-*D-mannopyranosid-3*-O-*yl)propyl)-3,4,6-tri*-O-*benzyl*-β-*D*-glucopyranosyl fluoride 16e.**

A colourless oil. *m/z* (ES^+) 1029 ($M+K^+$, 74), 1013 ($M+Na^+$, 100), 1008 ($M+NH_4^+$, 15%).

***2*-O-(*2-Iodo-1-(methyl 2,3,6-tri*-O-*benzyl*-α-*D-glucopyranosid-4*-O-*yl)propyl)-3,4,6-tri*-O-*benzyl*-β-*D*-glucopyranosyl fluoride 16g.**

A colourless oil. *m/z* (ES^+) 1121 ($M+K^+$, 22), 1105 ($M+Na^+$, 100), 1100 ($M+NH_4^+$, 21%).

***Methyl 3,4,6-tri*-O-*benzyl*-α-*D*-glucopyranoside 17a.**

A white solid which was recrystallised from diethyl ether/petrol, m.p. 78-81 °C (diethyl ether/petrol) [Lit. 83-84 °C][1]; $[\alpha]_D^{22}$ +70.8 (*c*, 1.2 in $CHCl_3$) [Lit. +90 (*c*, 1.1 in $CHCl_3$)][B]; δ_H (400 MHz, $CDCl_3$) 2.11 (1H, d, $J_{OH,2}$ 7.4 Hz, OH-2), 3.40 (3H, s, OCH_3), 3.60-3.76 (6H, m, H-2, H-3, H-4, H-5, H-6, H-6'), 4.47, 4.79 (2H, ABq, J_{AB} 10.7 Hz, PhC<u>H</u>$_2$), 4.49,

4.62 (2H, ABq, J_{AB} 12.1 Hz, PhC$\underline{H}_2$), 4.78 (1H, d, $J_{1,2}$ 3.2 Hz, H-1), 4.83, 4.88 (2H, ABq, J_{AB} 11.2 Hz, PhC$\underline{H}_2$), 7.11-7.36 (15H, m, Ar-H).

Cyclohexyl 3,4,6-tri-O-benzyl-α-D-glucopyranoside 17b.

A white solid which was recrystallised from diethyl ether/petrol, m.p. 92-94 °C (diethyl ether/petrol); $[\alpha]_D^{22}$ +90.0 (*c*, 0.3 in $CHCl_3$) [Lit. +60 (*c*, 0.6 in $CHCl_3$)][B]; δ_H (400 MHz, $CDCl_3$) 1.24-1.92 (10H, m, cyclohexyl-H), 2.06 (1H, d, *J* 2.7 Hz, OH-2), 3.61-3.75 (5H, m, H-2, H-3, H-4, H-6, cyclohexyl OCH), 3.77 (1H, dd, $J_{5,6'}$ 3.9 Hz, $J_{6,6'}$ 10.7 Hz, H-6'), 3.87-3.90 (1H, m, H-5), 4.49, 4.83 (2H, ABq, J_{AB} 10.7 Hz, PhC$\underline{H}_2$), 4.51, 4.65 (2H, ABq, J_{AB} 12.0 Hz, PhC$\underline{H}_2$), 4.84, 4.99 (2H, ABq, J_{AB} 11.0 Hz, PhC$\underline{H}_2$), 5.03 (1H, d, $J_{1,2}$ 3.5 Hz, H-1), 7.14-7.42 (15H, m, Ar-H).

3,4,6-Tri-O-benzyl-α-D-glucopyranosyl-(1→6)-1,2:3,4-di-O-isopropylidene-D-galactopyranose 17c.

A colourless oil; $[\alpha]_D^{22}$ +27.7 (*c*, 0.35 in $CHCl_3$) [Lit. +29 (*c*, 0.9 in $CHCl_3$)][B]; δ_H (400 MHz, $CDCl_3$) 1.34, 1.35, 1.45, 1.54 (12 H, 4 x s, 4 x CH_3), 3.63-3.79 (6H, m, H-2_b, H-3_b, H-4_b, H-6_b, H-6'$_b$, H-6_a), 3.85 (1H, ddd, $J_{4,5}$ 9.9 Hz, $J_{5,6}$ 2.2 Hz, $J_{5,6'}$ 3.0 Hz, H-5_b), 3.91 (1H, dd, $J_{5,6'}$ 6.7 Hz, $J_{6,6'}$ 10.2 Hz, H-6'$_a$), 4.00 (1H, atd, *J* 6.7 Hz, $J_{4,5}$ 1.9 Hz, H-5_a), 4.25 (1H, dd, $J_{3,4}$ 7.8 Hz, H-4_a), 4.34 (1H, dd, $J_{1,2}$ 4.9 Hz, $J_{2,3}$ 2.2 Hz, H-2_a), 4.49, 4.83 (2H, ABq, J_{AB} 10.3 Hz, PhC$\underline{H}_2$), 4.50, 4.64 (2H, ABq, J_{AB} 11.7 Hz, PhC$\underline{H}_2$), 4.63 (1H, dd, H-3_a), 4.82, 4.98 (2H, ABq, J_{AB} 10.7 Hz, PhC$\underline{H}_2$), 4.93 (1H, d, H-1_b), 5.53 (1H, d, H-1_a), 7.12-7.41 (15H, m, Ar-H).

Methyl 3,4,6-tri-O-benzyl-α-D-glucopyranosyl-(1→6)-3,4,6-tri-O-benzyl-α-D-mannopyranoside 17d.

A colourless oil; $[\alpha]_D^{22}$ +65.5 (*c*, 1.1 in $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 3.30 (3H, s, OCH_3), 3.59-3.80 (8H, m, H-2_b, H-3_b, H-4_b, H-5_b, H-6_b, H-6'$_b$, H-5_a, H-6_a), 3.79 (1H, dd, $J_{1,2}$ 2.0 Hz, $J_{2,3}$ 3.0 Hz, H-2_a), 3.91 (1H, dd, $J_{3,4}$ 9.4 Hz, H-3_a), 4.04-4.10 (2H, m, H-4_a, H-6'$_a$), 4.47, 4.84 (2H, ABq, J_{AB} 10.8 Hz, PhC$\underline{H}_2$), 4.48, 4.61 (2H, ABq, J_{AB} 12.2 Hz, PhC$\underline{H}_2$), 4.62 (2H, s, PhC$\underline{H}_2$), 4.62, 4.98 (2H, ABq, J_{AB} 11.1 Hz, PhC$\underline{H}_2$), 4.70 (1H, d, H-1_a), 4.71, 4.92 (2H, ABq, J_{AB} 11.1 Hz, PhC$\underline{H}_2$), 4.72 (2H, s, PhC$\underline{H}_2$), 5.00 (1H, d, $J_{1,2}$ 2.9 Hz, H-1_b), 7.14-7.39 (30H, m, Ar-H); δ_C ($CDCl_3$) 54.9 (q, CH_3), 67.7, 68.4, 72.0, 72.8, 73.4, 75.0, 75.1, 75.2 (8 x t, 6 x Ph$\underline{C}H_2$, C-6_b, C-6_a), 70.7, 71.3, 73.8, 74.1, 74.2, 77.0, 79.9, 83.3 (8 x d, C-2_b, C-3_b, C-4_b, C-5_b, C-2_a, C-3_a, C-4_a, C-5_a), 98.9, 100.6 (2 x d, C-1_b, C-1_a), 127.4, 127.6, 127.6, 127.7, 127.8, 127.8, 127.9, 127.9, 128.0, 128.1, 128.3, 128.3, 128.4, (13 x d, Ar-CH), 138.0, 138.2, 138.3, 138.4, 138.9 (5 x s, Ar-C); *m/z* ($APCI^+$) 919 ($M+Na^+$, 55%); ($APCI^-$) 931 ($M+Cl^-$, 10%). (HRMS Calcd. for $C_{55}H_{61}O_{11}$ (MH^+) 897.4214. Found 897.4229).

Methyl 3,4,6-tri-O-benzyl-α-D-glucopyranosyl-(1→3)-2-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside 17e.

White crystals, m.p. 145-147 °C (diethyl ether/petrol); $[\alpha]_D^{22}$ +42.4 (*c*, 0.25 in $CHCl_3$); ν_{max} (thin film) 3462 (br, OH) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 2.65 (1H, d, $J_{OH,2}$ 9.8 Hz, OH-2), 3.34 (3H, s, OCH_3), 3.56 (1H, at, *J* 9.2 Hz, H-4_b), 3.65-3.68 (2H, m, H-6_b, H-$6'_b$), 3.71 (1H, atd, $J_{1,2}$ 3.4 Hz, *J* 9.6 Hz, H-2_b), 3.75 (1H, at, *J* 9.3 Hz, H-3_b), 3.81-3.88 (3H, m, H-2_a, H-5_a, H-6_a), 3.90-3.94 (1H, m, H-5_b), 4.22-4.24 (2H, m, H-4_a, H-$6'_a$), 4.28 (1H, dd, $J_{2,3}$ 3.7 Hz, $J_{3,4}$ 9.2 Hz, H-3_a), 4.47, 4.85 (2H, ABq, J_{AB} 11.0 Hz, PhC$\underline{H}_2$), 4.48, 4.57 (2H, ABq, J_{AB} 12.0 Hz, PhC$\underline{H}_2$), 4.66, 4.76 (2H, ABq, J_{AB} 12.0 Hz, PhC$\underline{H}_2$), 4.69, 4.82 (2H, ABq, J_{AB} 10.9 Hz, PhC$\underline{H}_2$), 4.69 (1H, d, $J_{1,2}$ 1.4 Hz, H-1_a), 5.21 (1H, d, H-1_b), 5.63 (1H, s, PhC$\underline{H}$), 7.14-7.49 (25H, m, Ar-H); δ_C ($CDCl_3$) 54.9 (q, OCH_3), 63.9, 71.5, 73.8, 76.1, 77.0, 77.6, 78.2, 83.4 (8 x d, C-2_a, C-3_a, C-4_a, C-5_a, C-2_b, C-3_b, C-4_b, C-5_b), 68.7, 68.8, 73.4, 73.5, 74.8, 75.2 (6 x t, C-6_a, C-6_b, 4 x Ph$\underline{C}H_2$), 100.0, 100.8, 101.8 (3 x d, C-1_a, C-1_b, Ph$\underline{C}$H), 125.6, 127.5, 127.6, 127.6, 127.7, 127.8, 127.8, 127.9, 128.0, 128.2, 128.3, 128.3, 128.3, 128.5, 129.1 (15 x d, Ar-CH), 137.0, 137.8, 137.9, 138.4, 138.7 (5 x s, Ar-C); *m/z* (ES^+) 843 ($M+K^+$, 50), 827 ($M+Na^+$, 100%). (HRMS Calcd. for $C_{48}H_{56}NO_{11}$ (MNH_4^+) 822.3853. Found 822.3842). (Found: C, 71.88; H, 6.58. $C_{48}H_{52}O_{11}$ requires C, 71.62; H, 6.51%).

Methyl 3,4,6-tri-O-benzyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-O-benzyl-α-D-glucopyranoside 17g.

A colourless oil; $[\alpha]_D^{22}$ +35.1 (*c*, 1.05 in $CHCl_3$); ν_{max} (thin film) 3418 (br, OH) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 3.38 (3H, s, OCH_3), 3.45 (1H, br d, $J_{OH,2}$ 9.1 Hz, OH-2_b), 3.55 (1H, at, *J* 9.1 Hz, H-3_b), 3.55 (1H, dd, $J_{5,6}$ 1.8 Hz, $J_{6,6'}$ 10.6 Hz, H-6_a), 3.61-3.66 (4H, m, H-2_b, H-2_a, H-3_a, H-$6'_a$), 3.68 (1H, dd, $J_{5,6}$ 1.9 Hz, $J_{6,6'}$ 11.0 Hz, H-6_b), 3.69-3.71 (1H, m, H-5_b), 3.86-3.90 (1H, m, H-5_a), 3.88 (1H, at, *J* 9.5 Hz, H-4_b), 3.93 (1H, dd, $J_{5,6'}$ 3.9 Hz, H-$6'_b$), 3.99 (1H, at, *J* 9.3 Hz, H-4_a), 4.44, 4.57 (2H, ABq, J_{AB} 12.2 Hz, PhC$\underline{H}_2$), 4.49, 4.83 (2H, ABq, J_{AB} 10.6 Hz, PhC$\underline{H}_2$), 4.49, 4.59 (2H, ABq, J_{AB} 11.6 Hz, PhC$\underline{H}_2$), 4.57, 4.69 (2H, ABq, J_{AB} 11.0 Hz, PhC$\underline{H}_2$), 4.59, 4.70 (2H, ABq, J_{AB} 12.0 Hz, PhC$\underline{H}_2$), 4.61 (1H, d, $J_{1,2}$ 3.6 Hz, H-1_b), 4.79, 5.18 (2H, ABq, J_{AB} 10.6 Hz, PhC$\underline{H}_2$), 5.19 (1H, d, $J_{1,2}$ 3.1 Hz, H-1_a), 7.16-7.36 (30H, m, Ar-H); δ_C ($CDCl_3$) 55.2 (q, OCH_3), 68.4 (t, C-6_b), 68.7 (t, C-6_a), 70.0 (d, C-5_b), 71.5 (d, C-5_a), 73.0, 73.2, 73.3, 74.9, 75.1, 75.2 (6 x t, 6 x Ph$\underline{C}H_2$), 74.0, 80.2, 83.6 (3 x d, C-2_b, C-2_a, C-3_a), 76.9 (d, C-3_b), 77.6 (d, C-4_b), 80.5 (d, C-4_a), 97.7 (d, C-1_b), 101.2 (d, C-1_a), 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 127.8, 128.0, 128.1, 128.2, 128.2, 128.3, 128.4 (13 x d, Ar-CH), 137.5, 137.7, 137.7, 137.9, 138.2, 138.7 (6 x s, Ar-C); *m/z* (ES^+) 935 ($M+K^+$, 14), 919 ($M+Na^+$, 100), 916 ($2M+K^++H^+$, 21), 914 ($M+NH_4^+$, 14%). (HRMS Calcd. for $C_{55}H_{64}NO_{11}$ (MNH_4^+) 914.4479. Found 914.4476).

Cholestan-3'-β-yl 3,4,6-tri-O-benzyl-α-D-glucopyranoside 17h.

White crystals, m.p. 108-109 °C; $[\alpha]_D^{24}$ +98.5 (*c*, 0.20 in $CHCl_3$); ν_{max} (thin film) 3487 (br, OH) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.59-1.99 (31H, m, steroid CH, CH_2), 0.66, 0.81 (6H, 2 x s, 2 x CH_3), 0.88 (3H, d, *J* 6.5 Hz, CH_3), 0.89 (3H, d, *J* 6.5 Hz, CH_3), 0.91, (3H, d, *J* 6.6 Hz, CH_3), 2.10 (1H, br d, $J_{OH,2}$ 8.0 Hz, OH-2), 3.57-3.79 (4H, m, H-2, H-3, H-4, OCH), 3.68 (1H, dd, $J_{5,6}$ 2.0 Hz, $J_{6,6'}$ 10.5 Hz, H-6), 3.77 (1H, dd, $J_{5,6'}$ 4.0 Hz, H-6'), 3.89-3.92 (1H, m, H-5), 4.49, 4.84 (2H, ABq, J_{AB} 10.7 Hz, PhC$\underline{H}_2$), 4.51, 4.65 (2H, ABq, J_{AB} 11.9 Hz, PhC$\underline{H}_2$), 4.84, 4.99 (2H, ABq, J_{AB} 11.2 Hz, PhC$\underline{H}_2$), 5.04 (1H, d, $J_{1,2}$ 3.6 Hz,

H-1), 7.14-7.41 (15H, m, Ar-H); δ_C ($CDCl_3$) 12.0, 12.3, 18.6, 22.6, 22.8, (5 x q, 5 x steroid CH_3), 21.2, 23.8, 24.2, 27.8, 28.2, 28.7, 32.0, 36.0, 36.1, 36.8, 39.5, 40.0 (12 x t, 12 x steroid $\underline{C}H_2$), 28.0, 35.5, 35.8, 44.9, 54.2, 56.2, 56.4 (7 x d, 7 x steroid CH), 35.4, 42.6 (2 x s, 2 x steroid C), 68.6, 73.4, 75.0, 75.3 (4 x t, 3 x Ph$\underline{C}H_2$, C-6), 70.4, 73.0, 77.3, 77.3, 83.8 (5 x d, C-2, C-3, C-4, C-5, steroid OCH), 96.9 (d, C-1), 127.6, 127.7, 127.7, 127.9, 127.9, 128.3, 128.3, (7 x d, Ar-CH), 137.9, 138.2, 138.8 (3 x s, Ar-C). (Found: C, 79.25; H, 9.52. $C_{54}H_{76}O_6$ requires C, 78.98; H, 9.33%).

2*-O-*(2-Iodo-1-(succinimid*-N-*yl)propyl)-3,4,6-tri*-O-*benzyl-α-D-mannopyranosyl fluoride 18.

A single isomer, as a colourless oil; $[\alpha]_D^{22}$ +60.0 (*c*, 0.75 in $CHCl_3$); ν_{max} (thin film) 1709 (s, C=O) cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.98 (3H, d, *J* 6.8 Hz, CH_3), 2.76 (4H, s, COC$\underline{H}_2$C$\underline{H}_2$CO), 3.66-3.73 (2H, m, H-6, H-6'), 3.90 (3H, br s, H-3, H-4, H-5), 3.99 (1H, br s, H-2), 4.51, 4.62 (2H, ABq, J_{AB} 12.2 Hz, PhC$\underline{H}_2$), 4.51, 4.82 (2H, ABq, J_{AB} 11.0 Hz, PhC$\underline{H}_2$), 4.68, 4.90 (2H, ABq, J_{AB} 11.0 Hz, PhC$\underline{H}_2$), 5.12 (1H, dq, *J* 10.2 Hz, C$\underline{H}$I), 5.39 (1H, dd, $J_{1,2}$ 2.0 Hz, $J_{1,F}$ 50.5 Hz, H-1), 5.72 (1H, d, C$\underline{H}$N), 7.15-7.47 (15H, m, Ar-H); δ_C ($CDCl_3$) 23.2, 25.0 (d, q, $\underline{C}H_3$, $\underline{C}$HI), 27.9 (t, CO$\underline{C}H_2\underline{C}H_2$CO), 68.4, 73.0, 73.4, 75.1 (4 x t, C-6, 3 x Ph$\underline{C}H_2$), 72.7 (dd, $^2J_{C\text{-}2,F}$ 6.6 Hz, C-2), 73.6, 74.2, 78.9 (3 x d, C-3, C-4, C-5), 86.4 (d, $\underline{C}$HN), 106.3 (dd, $^1J_{C\text{-}1,F}$ 221.0 Hz, C-1), 127.6, 127.8, 127.8, 128.0, 128.0, 128.3, 128.4, 128.5, 128.6 (9 x d, Ar-CH), 137.5, 137.8, 138.0, (3 x s, Ar-C); . *m/z* (ES^+) 735 ($M+NH_4^+$, 100%); (HRMS Calcd. for $C_{34}H_{41}N_2O_7FI$ (MNH_4^+) 735.1943. Found 725.1949).

A Gordon, D. M.; Danishefsky, S. J. *Carbohydr. Res.*, **1990**, *206*, 361-366

B Ennis, S.C.; Fairbanks, A.J.; Slinn, C.A.; Tennant-Eyles, R.J.; Yeates, H.S. *Tetrahedron*, **2001,** *57*, 4221-4230.

C Stork, G.; Kim, G. *J. Am. Chem. Soc.*, **1992,** *114*, 1087-1088.