Protection of Hydroxy Groups with Diphenylmethyl and 9-Fluorenyl Trichloroacetimidates − Effect on Anomeric Stereocontrol

Ibrahim A. I. Ali,[a] El Sayed H. El Ashry,[b] and Richard R. Schmidt*[a]

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The use of *O*-diphenylmethyl (DPM) and the *O*-(9-fluorenyl) (Fl) trichloroacetimidates permitted efficient protection of alcohols. The compatibility of these groups with other chemical manipulations is demonstrated. Glucosylation of typical acceptors with an *O*-glucopyranosyl trichloroacetimidate as donor having a DPM group at 2-O afforded β-glucopyranosides, thus demonstrating anchimeric assistance of the DPM group in the anomeric stereocontrol. This effect was also observed in mannopyranoside synthesis.

Introduction

Protection/deprotection methodologies are of great significance in organic synthesis. As a consequence of the extensive use of the benzyl group as a protecting group, the diphenylmethyl (DPM) group has also found use for the protection of hydroxy groups, its hydrogenolytic cleavage being as cleanly achievable as in the case of benzyl ethers.[1] The synthesis of DPM ethers can be carried out by use of DPM chloride and bromide in the presence of a base,[2] diphenyldiazomethane,[3,4] diphenylmethyl phosphate in the presence of trifluoroacetic acid[3,4] or of diphenylmethanol in the presence of various acids such as xenon difluoride,[5] *p*-toluenesulfonic acid,[6] concentrated sulfuric acid,[7] ytterbium(III) triflate/ferric chloride,[8] ferric chloride or ferric perchlorate,[9] and ferric nitrate.[10] Direct transformation of silyl ethers or alkyl tetrahydropyranyl ethers into the corresponding DPM alkyl ethers has also been reported to take place with DPM formate in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf).[11] The DPM group was generated when orthoesters of *myo*-inositol were treated with Grignard reagents.[12] As well as for alcohol protection, the DPM group has also been used for the protection of acids.[13−15] Moreover, DPM ethers are also valuable as therapeutic agents.[16−18]

9-Fluorenyl (Fl) ethers, on the other hand, have attracted comparatively less attention, studies on them being mainly concerned with photolytic reactions.[19−22] Their synthesis has been carried out by treatment of 9-bromo- or 9-diazofluorene with alcohols.[23−25] As would be expected, the solvolysis of 9-fluorenyl ethers under acidic conditions is slower than that of the corresponding diphenylmethyl derivatives, reflecting the different stabilities of the diphenylmethyl and the fluorenyl carbenium ion intermediates.[20−22] It therefore appears worthwhile to investigate the properties of these two structurally related compounds, which might exhibit different protecting group characteristics due to their different carbenium ion stabilisation and steric demands.

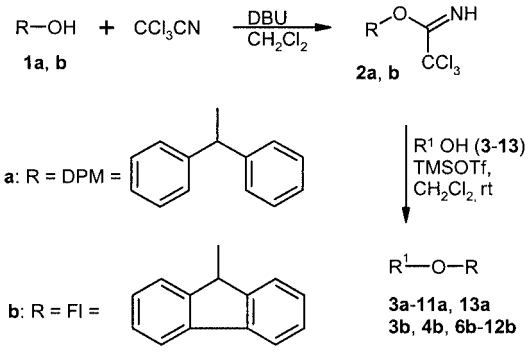
As a consequence of the interest in the DPM and Fl groups and the need for efficient methods for their introduction onto alcohols, their trichloroacetimidates were considered as donors of the DMP[26] and Fl groups, respectively. Obviously, we also had the importance of *O*-glycosyl trichloroacetimidates as glycosyl donors in mind.[27−29] Moreover, the ready formation of the trichloroacetimidates from DPM−OH and 9-Fl−OH, as well as the mild conditions usable for the introduction of these groups in the presence of acid- and base-sensitive groups should be of significance. The introduction of the DPM group and the Fl group as protecting groups, particularly in the carbohydrate field, as well as their effects on the anomeric ratios in glycosidation reactions have therefore been investigated.

Results and Discussion

The required *O*-DPM[26] and *O*-Fl trichloroacetimidates **2a** and **2b**, respectively, were prepared by treatment of diphenylmethanol (**1**) and 9-fluorenol (**1b**) with trichloroacetonitrile in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as catalyst (Scheme 1). Their formation was confirmed spectroscopically [δ(NH) = 8.4, 8.6 ppm]. The

[a] Fachbereich Chemie, Universität Konstanz,
Fach M 725, 78457 Konstanz, Germany
Fax: (internat.) + 49-7531/88-3135
E-mail: Richard.Schmidt@uni-konstanz.de
[b] Department of Chemistry, Faculty of Science, University of Alexandria,
Alexandria, Egypt
E-mail: eelashry@link.net
eelashry60@hotmail.com

trichloroacetimidates **2a** and **2b** are crystalline compounds, characterized by their stabilities at room temperature for long periods of time without detection of any decomposition. Reactions between trichloroacetimidate **2a** and **2b** and typical alcohols containing primary and secondary hydroxy groups, such as **3**−**6**, readily afforded the corresponding DPM ethers **3a**−**6a** and Fl ethers **3b**, **4b** and **6b** in high yields (Table 1). The reactions with **2a** were per-



Scheme 1

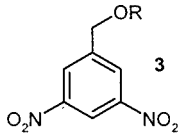
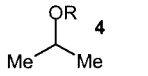
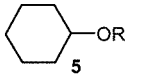
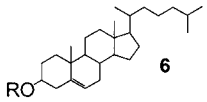
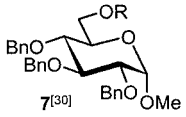
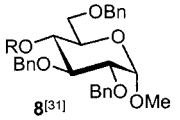
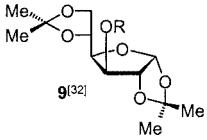
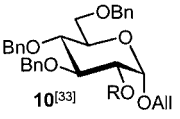
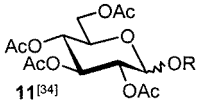
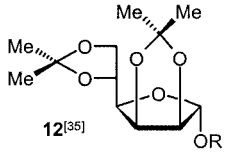
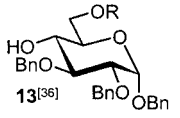
formed at room temperature and those with **2b** at −40 °C.

The etherification of primary and secondary hydroxy groups in various types of partially protected carbohydrates **7**−**13** was successfully carried out in similar fashion (Table 1). Thus, treatment of **2a** or **2b** with 6-*O*-unprotected glucoside **7**,[30] possessing a primary hydroxy group, gave **7a** or **7b**, respectively. The carbohydrate derivatives **8**−**10**,[31−33] with secondary hydroxy groups at positions 4, 3 and 2, gave the DPM and Fl derivatives **8a**−**10a** and **8b**−**10b**, respectively, under similar conditions. Ready introduction of the DPM and Fl protecting groups was even possible at the anomeric hydroxy group; thus, **11**[34] gave the corresponding α-glycosides **11a** and **11b**, while **12**[35] gave α-glycoside **12b** in high yield. For these derivatives α configurations could be assigned with the aid of NMR spectroscopic data [**11a**: δ(1-H) = 5.15 ppm, J = 3.7 Hz; **11b**: δ(1-H) = 5.30 ppm, J = 3.7 Hz]. Even regioselective introduction of DPM was possible, treatment of 4,6-*O*-unprotected glucoside **13** with DPM donor **2a**,[36] for instance, giving only 6-*O*-protected glucoside **13a** in high yield.

The DPM and Fl groups can be readily removed by hydrogenolysis, as shown for compounds **7a** and **7b**, which upon deprotection and acetylation gave the known *O*-acetyl-protected methyl glucoside **14** (Scheme 2).[37]

Stereoselective glycoside bond formation is a subject still attracting many investigators. In this respect, it was of interest to study the effects of the DPM and Fl groups on the stereoselectivity obtained during glycosylation reactions. To this end, 1-*O*-deallylation of **10a** and **10b**, with DPM and Fl groups at 2-*O*, was performed with Wilkinson's catalyst,[38] cleanly furnishing 1-*O*-unprotected compounds **15a** and **15b**, respectively (Scheme 3). Activation of their anomeric centres by treatment with trichloroacetonitrile in the presence of DBU as base gave trichloroacetimidates **16a** and **16b**. Glycosylation of methyl and octyl alcohols, as well as

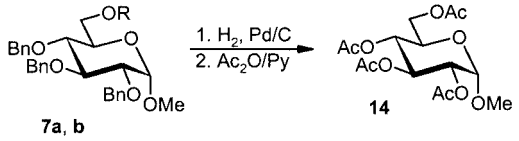
Table 1. Treatment of alcohols **3**−**13** with *O*-DPM and *O*-Fl trichloroacetimidates **2a** and **2b**[a]

Entry	Acceptor (R = H)[b]	Product	Yield
1	 **3**	**3a**: R = DPM	91%
		3b: R = Fl	88%
2	 **4**	**4a**: R = DPM	74%
		4b: R = Fl	89%
3	 **5**	**5a**: R = DPM	75%
		5b: R = Fl	[c]
4	 **6**	**6a**: R = DPM	92%
		6b: R = Fl	91%
5	 **7**[30]	**7a**: R = DPM	78%
		7b: R = Fl	79%
6	 **8**[31]	**8a**: R = DPM	83%
		8b: R = Fl	61%
7	 **9**[32]	**9a**: R = DPM	77%
		9b: R = Fl	56%
8	 **10**[33]	**10a**: R = DPM	65%
		10b: R = Fl	72%
9	 **11**[34]	**11a**: R = DPM	83%
		11b: R = Fl	76%
10	 **12**[35]	**12a**: R = DPM	[c]
		12b: R = Fl	83%
11	 **13**[36]	**13a**: R = DPM	83%
		13b: R = Fl	[c]

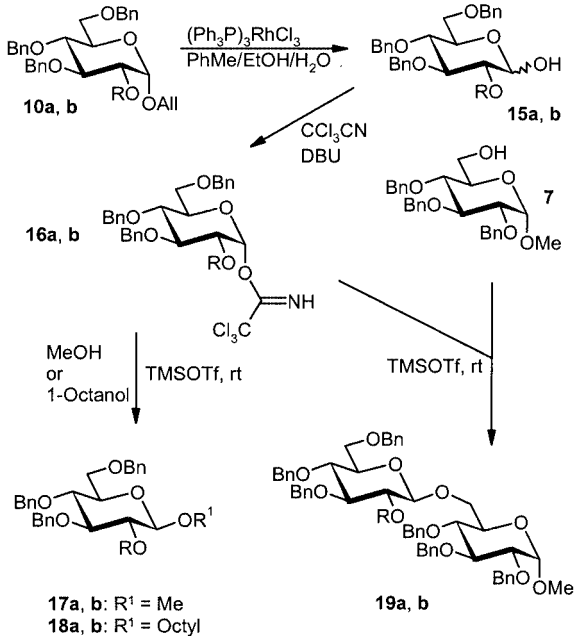
[a] For details see Scheme 1 and Exp. Sect. [b] The carbohydrate acceptors were obtained by literature procedures; see references. [c] Not investigated.

the glycosyl acceptor **7**,[30] with 2-*O*-DPM-protected **16a** gave exclusively the corresponding β-glucosides **17a**−**19a** in good yields, without any detection of the α anomers.

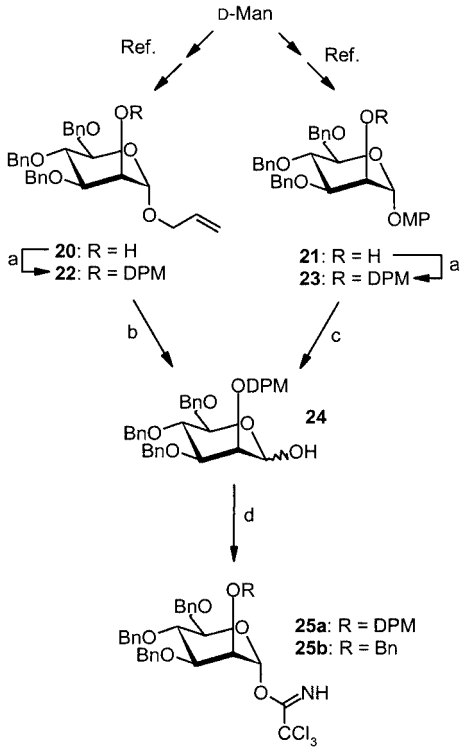
The analogous glucosyl donor **16b**, possessing an Fl group, however, predominantly gave the respective β-gluco-



Scheme 2



Scheme 3



Scheme 4. Reagents and conditions: (a) **2a**, TMSOTf, CH_2Cl_2; (b) $(Ph_3P)RhCl$, Tol, EtOH, H_2O; (c) CAN; (d) CCl_3CN, DBU

sides **17bβ**−**19bβ** on treatment with the same acceptors, but the β products were accompanied by the corresponding α-glucosides **17bα**−**19bα**, the product ratio depending on the structure of the acceptor. The presence of a DPM group at 2-O thus has a particularly favourable effect. The DPM group exhibits the desired stability under glycosylation conditions and, presumably thanks to its steric demand on the α side of the molecule, it strongly favours β-glucopyranoside formation. This is particularly worth mentioning because the corresponding 2-*O*-benzyl-protected glucosyl donor (**16**: R = Bn) provides α/β mixtures under these conditions.[27−29]

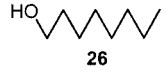
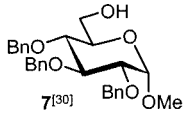
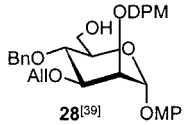
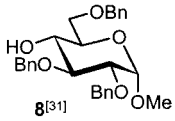
It was recently observed that the presence of sterically demanding 2-*O* substituents at mannopyranosyl donors enforces β-mannopyranoside formation rather than inhibiting it, because bulky substituents at 2-O support generation of a twist-boat intermediate, which should be preferentially attacked from the β side.[39] It was therefore of interest to investigate a 2-*O*-DPM-protected mannopyranosyl donor in glycosylation reactions (Scheme 4). To this end, mannose was transformed into the known allyl and 4-methoxyphenyl (MP) mannopyranosides **20**[40] and **21**,[41] respectively (Scheme 4).

Treatment of these with **2a** in the presence of TMSOTf as catalyst afforded 2-*O*-DPM-protected intermediates **22** and **23** in high yields. Removal of the 1-*O*-allyl group in **22** or the 1-*O*-MP group in **23** under standard conditions afforded 1-*O*-unprotected mannose derivative **24** without the DPM group being affected. Treatment of **24** with trichloroacetonitrile in the presence of DBU as base furnished the desired mannopyranosyl donor **25a** in high yield. From the NMR spectroscopic data, only the α anomer was obtained. For comparison, the corresponding known 2-*O*-benzyl-protected mannopyranosyl donor **25b**[42] was also investigated.

The results of the glycosylation reaction with **25a** and **25b** and different acceptors in dichloromethane at −40 °C in the presence of TMSOTf as catalyst are summarized in Table 2.

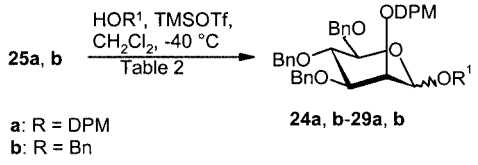
As expected, treatment of donor **25b** with octanol, 6-*O*-unprotected glucopyranoside **7**[30], 6-*O*-unprotected mannopyranoside **28**[39] and 4-*O*-unprotected glucopyranoside **8**[31] preferentially afforded α-mannopyranosides **26bα**,[43] **27bα**[44] and **28bα**. The result with the 2-*O*-DPM-protected mannosyl donor **25a**, however, was quite different. For the acceptors with primary hydroxy groups (**7**, **26**, **28**) a clear preference for the formation of β products **26aβ**−**28aβ** was observed. With less reactive acceptor **8**,[31] with a less accessible secondary hydroxy group, only the α-linked disaccharide **29aα**[44] was obtained. Obviously, this is due to some as yet unexplainable change in mechanism.

Table 2. Glycosylation results with mannosyl donors **25a** and **25b**[a]

Entry	Acceptor HOR[1]	Product	Yield	Ratio α/β
1	 **26**	**26a**	86%	1:2
		26b	75%	2:1
2	 **7**[30]	**27a**	76%	1:3
		27b	81%	2:1
3	 **28**[39]	**28a**	69%	1:3
		28b	76%	1:1
4	 **8**[31]	**29a**	67%	α
		29b	69%	3:1

[a] For details see Scheme 5 and Exp. Sect.

In conclusion, *O*-DPM and *O*-Fl protection can readily be carried out with the aid of the *O*-DPM and *O*-Fl trichloroacetimidates. These protecting groups are compatible with quite a few manipulations: at other functional groups of a sugar molecule, for instance, and also with glycoside bond formation. Of particular interest is the behaviour of DPM groups at 2-O of glucopyranosyl donors, which support β-glucopyranoside formation. The steric bulk of the DPM group thus exerts anchimeric assistance on the anomeric stereocontrol[45] through neighbouring group participation, as a 2-*O*-acyl group does. A 2-*O*-DPM group, however, affects activation of a glycosyl donor much less than a 2-*O*-acyl group. The 2-*O*-DPM group also strongly affects stereocontrol of mannopyranoside synthesis. For reactive acceptors a clear preference for β-glycoside formation is observed.



Scheme 5

Experimental Section

General Remarks: Melting points are uncorrected. Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} plastic plates (E. Merck, layer thickness 0.2 mm). Detection was achieved by treatment either with a solution of 20 g of ammonium molybdate and 0.4 g of cerium(IV) sulfate in 400 mL of 10% H_2SO_4 or with 15% H_2SO_4, and heating at 150 °C. Flash chromatography was carried out on silica gel (Baker, 30−60 μm). Optical rotations were determined at 20 °C with a Perkin−Elmer 241 MC polarimeter (1-dm cell). NMR spectra were recorded with Bruker AC 250 and 600 DRX instruments, with tetramethylsilane as an internal standard. The assignments of ^{13}C NMR spectra were based on carbon-proton shift-correlation heteronuclear multiple quantum coherence (HMQC). MALDI-MS: Kratos Compact Maldi 1; 2,5-dihydroxybenzoic acid was used as matrix. FAB-MS: Finnigan MAT 312/AMD 5000, 790 eV, 70 °C. Microanalyses were performed in the Microanalysis Unit at the Department of Chemistry, Universität Konstanz.

***O*-Diphenylmethyl Trichloroacetimidate (2a):** A mixture of diphenylcarbinol (0.92 g, 5.0 mmol), trichloroacetonitrile (5 mL, 50 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (71 μL) in dry dichloromethane (10 mL) was stirred under nitrogen at room temperature for 3 h. The reaction mixture was then concentrated in vacuo and the residue was purified by flash chromatography (3% triethylamine in petroleum ether/ethyl acetate, 80:1) to give **2a** (1.5 g, 94%) as a white powder. TLC (3% triethylamine in toluene) R_f = 0.70; m.p. 85 °C, ref.[26] 85 °C. ^1H NMR (250 MHz, $CDCl_3$): δ = 6.94 (s, 1 H, CH), 7.29−7.44 (m, 10 H, Ar-H), 8.40 (br. s, 1 H, NH) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 81.4 (CH), 91.6 (CCl_3), 126.9, 127.9, 128.5, 139.8 (C-Ar), 161.3 (CNH) ppm. EI-MS: *m*/*z* = 328.0.

***O*-(9-Fluorenyl) Trichloroacetimidate (2b):** A stirred solution of 9-hydroxyfluorene (0.91 g, 5.0 mmol) in dry dichloromethane (10 mL) and trichloroacetonitrile (5 mL, 50 mmol) was treated with DBU (71 μL) at room temperature and the mixture was then left to stand for 0.5 h. The solvent was evaporated and the product was purified by column chromatography (3% triethylamine in toluene) to give **2b** (1.4 g, 86%) as a white powder. TLC (3% triethylamine in toluene) R_f = 0.56; m.p. 59 °C. ^1H NMR (250 MHz, $CDCl_3$): δ = 6.99 (s, 1 H, CH), 7.25−7.67 (m, 8 H, Ar-H), 8.67 (br. s, 1 H, NH) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 79.6 (CH), 91.5 (CCl_3), 120.0, 126.0, 127.8, 129.6, 141.9, 141.7 (C-Ar), 163.6 (CNH) ppm. EI-MS: *m*/*z* = 326.0.

General Procedure for the Reactions between Trichloroacetimidate 2a and Alcohols: A solution of **2a** (0.2 g, 0.6 mmol) and the appropriate alcohol (0.6 mmol) in dry dichloromethane (10 mL) was stirred under nitrogen at room temperature for 5 min, and TMSOTf (13 μL, 0.06 mmol) was then added. After 45−150 min, the reaction mixture was neutralized with solid sodium hydrogencarbonate, filtered and concentrated in vacuo. The residue was purified by column chromatography.

General Procedure for the Reactions between Trichloroacetimidate 2b and Alcohols: A solution of **2b** (0.46 g, 1.4 mmol) and the appropriate alcohol (1.6 mmol) in dry dichloromethane (10 mL) was cooled to −40 °C, treated with TMSOTf (26 μL, 0.14 mmol), and the mixture was then stirred for 10−120 min. The reaction mixture was quenched by the addition of solid sodium hydrogencarbonate, filtered and concentrated. The crude residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate as eluent.

3,5-Dinitrobenzyl Diphenylmethyl Ether (3a): Yellow powder (0.2 g, 91%); R_f = 0.66 (petroleum ether/ethyl acetate, 5:1); m.p. 127 °C. ^1H NMR (250 MHz, $CDCl_3$): δ = 4.71 (s, 2 H, CH_2), 5.50 (s, 1 H, CH), 7.31−7.40 (m, 10 H, Ar-H), 8.52 (m, 2 H, Ar-H), 8.91 (t, *J* = 2.1 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 68.7 (CH_2), 84.3 (CH), 117.8, 126.9, 127.1, 128.0, 128.7, 141.0, 143.3, 148.6 (C-Ar) ppm. EI-MS: *m*/*z* = 364.0. $C_{20}H_{16}N_2O_5$ (364.36): calcd. C 65.93, H 4.43, N 7.68; found C 65.80, H 4.60, N 7.40.

9-(3,5-Dinitrobenzyloxy)fluorene (3b): Yellow powder (0.45 g, 88%); R_f = 0.47 (petroleum ether/ethyl acetate, 4:1); m.p. 108 °C. ^1H NMR (250 MHz, $CDCl_3$): δ = 4.26 (s, 2 H, CH_2), 5.89 (s, 1 H,

CH), 7.25−8.89 (m, 11 H, Ar-H) ppm. ^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 63.8 (CH_2), 81.0 (CH), 117.6, 120.3, 125.5, 127.1, 127.9, 129.7, 141.1, 141.5, 143.7, 148.4 (C-Ar) ppm. EI-MS: *m/z* = 362.0. $C_{20}H_{14}N_2O_5$ (362.34): calcd. C 66.29, H 3.89, N 7.73; found C 66.61, H 4.06, N 7.97.

Diphenylmethyl Isopropyl Ether (4a): Colourless oil (0.1 g, 73.5%); R_f = 0.76 (petroleum ether/ethyl acetate, 5:1). Compound **4a** was synthesized by a published procedure. The analytical data are identical with the published values.[46]

9-Isopropoxyfluorene (4b): White powder (0.28 g, 88.5%); R_f = 0.64 (petroleum ether/ethyl acetate, 10:1); m.p. 44 °C, refs.[23,24]: 43−44 °C.

Cyclohexyl Diphenylmethyl Ether (5a): Colourless oil (0.12 g, 75%); R_f = 0.66 (petroleum ether/ethyl acetate, 6:1). Compound **5a** was synthesized by a published procedure. The analytical data are identical with the published values.[47]

Cholesteryl Diphenylmethyl Ether (6a): White powder (0.31 g, 92%); R_f = 0.42 (petroleum ether/ethyl acetate, 10:1); m.p. 136 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.64−2.28 (m, 43 H, cholesterol), 3.31 (m, 1 H, CH), 5.30 (d, 1 H, CH), 5.61 (s, 1 H, CH), 7.20−7.52 (m, 10 H, Ar-H) ppm. EI-MS: *m/z* = 552.0. $C_{40}H_{56}O$ (552.88): calcd. C 86.80, H 10.21; found C 87.04, H 9.82.

Cholesteryl Fluorenyl Ether (6b): Colourless oil (0.70 g, 91%); R_f = 0.80 (petroleum ether/ethyl acetate, 20:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.64−2.40 (m, 43 H, cholesterol), 3.4 (m, 1 H, CH), 5.22 (d, 1 H, CH), 5.60 (s, 1 H, CH), 7.21−7.72 (m, 8 H, Ar-H) ppm. EI-MS: *m/z* = 550.0. $C_{40}H_{54}O$ (550.86): calcd. C 87.21, H 9.88; found C 87.15, H 9.81.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-diphenylmethyl-α-D-glucopyranoside (7a): Colourless oil (0.30 g, 78%); R_f = 0.51 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = −8.6 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.40 (s, 3 H, OCH_3), 3.57 (dd, $J_{1,2}$ = 3.6, $J_{2,3}$ = 9.3 Hz, 1 H, 2-H), 3.60−3.71 (m, 3 H, 4-H, 6-H, 6′-H), 3.80 (m, 1 H, 5-H), 4.04 (dd, $J_{3,2}$ = 9.3, $J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 4.50 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 4.67 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.69 (m, 2 H, 2 CHPh), 4.73 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.81 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 4.86 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 5.40 (s, 1 H, CH), 7.23−7.40 (m, 25 H, Ar-H) ppm. MS (MALDI, positive mode, matrix: DHB): *m/z* = 653.0 $[M + Na]^+$, 669.0 $[M + K]^+$. $C_{41}H_{42}O_6$ (630.78): calcd. C 78.07, H 6.71; found C 78.04, H 6.61.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-fluorenyl-α-D-glucopyranoside (7b): White foam (0.69 g, 79%); R_f = 0.52 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = 25.5 (*c* = 2.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.44 (s, 3 H, OCH_3), 3.51 (m, 2 H, 6-H, 6′-H), 3.60 (dd, $J_{4,3}$ = 9.3, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 3.63 (dd, $J_{1,2}$ = 3.1, $J_{2,3}$ = 9.2 Hz, 1 H, 2-H), 3.74 (m, 1 H, 5-H), 4.02 (dd, $J_{3,2}$ = 9.2, $J_{3,4}$ = 9.3 Hz, 1 H, 3-H), 4.50 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.72 (d, $J_{1,2}$ = 3.1 Hz, 1 H, 1-H), 4.74 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.83 (d, J_{gem} = 11.3 Hz, 1 H, CHPh), 4.86 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.88 (d, J_{gem} = 11.3 Hz, 1 H, CHPh), 5.05 (d, J_{gem} = 11.3 Hz, 1 H, CHPh), 5.74 (s, 1 H, CH), 7.05−7.42 (m, 8 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 54.9 (OCH_3), 63.4 (C-6), 70.0 (C-5), 73.1, 74.7, 75.6 (3 CH_2), 77.5 (C-4), 79.7 (C-2), 80.8 (CH), 82.0 (C-3), 97.8 (C-1), 119.8, 125.4, 127.1, 127.2, 127.4, 128.2, 129.1, 137.9, 138.6, 140.7, 142.2, 142.4 (C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): *m/z* = 650 $[M + Na]^+$. $C_{41}H_{40}O_6$ (628.76): calcd. C 78.32, H 6.41; found C 78.71, H 6.37.

Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-diphenylmethyl-α-D-glucopyranoside (8a): Colourless oil (0.32 g, 83%); R_f = 0.63 (petroleum ether/ethyl acetate, 4:1). $[\alpha]_D$ = −35.0 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.2 (dd, $J_{5,6}$ = 5.1, $J_{6,6'}$ = 10.6 Hz, 1 H, 6-H), 3.44 (s, 3 H, OCH_3), 3.55 (dd, $J_{1,2}$ = 3.6, $J_{2,3}$ = 9.6 Hz, 1 H, 2-H), 3.70 (m, 1 H, 6-H), 3.81 (m, 1 H, 5-H), 4.04 (dd, $J_{3,2}$ = 9.6, $J_{3,4}$ = 9.6 Hz, 1 H, 3-H), 4.14 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.23 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.49 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.63 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.65 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.78 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.95 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 5.91 (s, 1 H, CH) ppm. MS (MALDI, positive mode, matrix: DHB): *m/z* = 653.0 $[M + Na]^+$, 669.0 $[M + K]^+$. $C_{41}H_{42}O_6$ (630.78): calcd. C 78.07, H 6.71; found C 78.03, H 6.50.

Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(9-fluorenyl)-α-D-glucopyranoside (8b): White foam (0.54 g, 61%); R_f = 0.48 (petroleum ether/ethyl acetate, 4:1). $[\alpha]_D$ = +13.3 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.29 (m, 1 H, 6-H), 3.34 (s, 3 H, OCH_3), 3.38 (dd, $J_{6,5}$ = 3.3, J_{gem} = 10.2 Hz, 1 H, 6′-H), 3.50 (m, 2 H, 2-H, 5-H), 3.63 (dd, $J_{4,3}$ = 9.1, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 3.73 (dd, $J_{3,2}$ = 9.2, $J_{3,4}$ = 9.1 Hz, 1 H, 3-H), 4.60 (d, $J_{1,2}$ = 2.8 Hz, 1 H, 1-H), 4.62 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.64 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.66 (d, J_{gem} = 11.6 Hz, 1 H, CHPh), 4.73 (d, J_{gem} = 11.6 Hz, 1 H, CHPh), 4.76 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.97 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 5.68 (s, 1 H, CH), 7.21−7.60 (m, 23 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 55.1, (OCH_3), 63.5 (C-6), 69.8 (C-5), 70.6 (C-4), 73.1, 75.4, 77.2 (3 CH_2), 79.4 (C-2), 80.7 (CH), 81.5 (C-3), 98.1 (C-1), 119.8, 119.9, 120.2, 125.2, 125.4, 125.6, 127.3, 127.7, 127.9, 128.0, 128.4, 128.5, 129.1, 140.8, 140.9, 142.4 (C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): *m/z* = 629.0 $[M + H]^+$. $C_{41}H_{40}O_6$ (628.77): calcd. C 78.32, H 6.41; found C 78.51, H 6.49.

3-*O*-Diphenylmethyl-1:2,5:6-di-*O*-isopropylidene-α-D-glucofuranose (9a): White foam (0.20 g, 77%); R_f = 0.67 (petroleum ether/ethyl acetate, 4:1). $[\alpha]_D$ = −21.1 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.22, 1.30, 1.35, 1.40 (4 CH_3), 3.96 (m, 2 H, 6-H, 6′-H), 4.09−4.20 (m, 2 H, 4-H, 3-H), 4.31 (m, 1 H, 5-H), 4.51 (d, $J_{2,1}$ = 3.7 Hz, 1 H, 2-H), 5.60 (s, 1 H, CH), 5.87 (d, $J_{1,2}$ = 3.7 Hz, 1 H, 1-H), 7.11−7.50 (m, 10 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 25.5, 26.3, 26.7, 26.9 (4 CH_3), 67.6 (C-6), 72.7 (C-5), 80.0 (C-3), 81.6 (C-4), 82.6 (CH), 83.0 (C-2), 105.4 (C-1), 109.0, 111.8, 126.9, 127.4, 127.7, 128.4, 128.5, 141.3, 142.1 (C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): *m/z* = 449.0 $[M + Na]^+$, 465.0 $[M + K]^+$. $C_{25}H_{30}O_6$ (426.51): calcd. C 70.40, H 7.01; found C 70.26, H 7.02.

3-*O*-(9-Fluorenyl)-1:2,5:6-di-*O*-isopropylidene-α-D-glucofuranose (9b): Colourless oil (0.49 g, 82.5%); R_f = 0.38 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = +9.8 (*c* = 2.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.22, 1.42, 1.44, 1.64 (4 CH_3), 4.05 (dd, $J_{6,5}$ = 5.7, J_{gem} = 8.6 Hz, 1 H, 6-H), 4.17 (m, 2 H, 4-H, 6′-H), 4.42 (d, *J* = 2.9 Hz, 1 H, 3-H), 4.52 (dd, $J_{5,6}$ = 5.7, $J_{5,4}$ = 8.4 Hz, 1 H, 5-H), 4.55 (d, $J_{2,1}$ = 3.6 Hz, 1 H, 2-H), 5.66 (s, 1 H, CH), 5.88 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 7.27−7.70 (m, 8 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 24.1, 25.4, 27.0 (4 CH_3), 67.7 (C-6), 72.5 (C-5), 81.7 (C-3), 81.9 (C-4), 82.1 (CH), 84.1 (C-2), 105.4 (C-1), 109.0, 111.7, 119.8, 119.9, 125.1, 125.7, 127.3, 127.6, 129.0, 129.3, 140.3, 140.8, 142.6, 143.1 (C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): *m/z* = 447.0 $[M + Na]^+$. $C_{25}H_{28}O_6$ (424.49): calcd. C 70.73, H 6.65; found C 70.92, H 6.70.

Allyl 3,4,6-Tri-*O*-benzyl-2-*O*-diphenylmethyl-α-D-glucopyranoside (10a): Colourless oil (0.30 g, 76%); R_f = 0.72 (petroleum ether/ethyl

acetate, 4:1). $[\alpha]_D$ = 25.0 (c = 1.0, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$): δ = 3.62 (m, 3 H, 4-H, 5-H, 6′-H), 3.73 (dd, $J_{2,1}$ = 3.5, $J_{2,3}$ = 10.5 Hz, 1 H, 2-H), 3.80 (m, 1 H, 6-H), 3.91 (dd, J = 6.3, J = 12.9 Hz, 1 H, CH_2CH=CH$_2$), 4.10 (m, 2 H, 3-H, CH_2CH=CH$_2$), 4.44 (d, J_{gem} = 11.8 Hz, 1 H, CHPh), 4.48 (d, J_{gem} = 10.5 Hz, 1 H, CHPh), 4.58 (d, J_{gem} = 11.8 Hz, 1 H, CHPh), 4.69 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.81 (d, J_{gem} = 10.5 Hz, 1 H, CHPh), 4.86 (d, J_{gem} = 10.5 Hz, 1 H, CHPh), 4.95 (d, J_{gem} = 10.5 Hz, 1 H, CHPh), 5.21 (m, 2 H, CH=CH_2), 5.61 (s, 1 H, CH), 5.92 (m, 1 H, CH=CH$_2$), 7.14−7.39 (m, 25 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 68.3 (CH_2), 68.4 (C-6), 70.1 (CH_2−CH=CH$_2$), 73.4 (C-5), 74.9, 75.7 (2 CH_2), 78.6 (C-4), 79.7 (C-2), 82.5 (C-3), 84.9 (CH), 96.3 (C-1), 117.7 (CH=CH_2), 126.7, 127.2, 127.3, 127.4, 127.6, 127.8, 127.9, 128.3, 128.4, 133.9, 138.3, 142.1, 142.7 (HC=, C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): m/z = 680.0 $[M + Na]^+$. $C_{43}H_{44}O_6$ (656.81): calcd. C 78.63, H 6.75; found C 78.46, H 6.63.

Allyl 3,4,6-Tri-*O*-benzyl-2-*O*-(9-fluorenyl)-α-D-glucopyranoside (10b): Colourless oil (0.27 g, 66.5%); R_f = 0.54 (petroleum ether/ethyl acetate, 4:1). $[\alpha]_D$ = −5.7 (c = 2.0, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$): δ = 3.50 (m, 3 H, 6-H, 4-H, 2-H), 3.64 (dd, $J_{6',5}$ = 3.2, J_{gem} = 10.5 Hz, 1 H, 6′-H), 3.69 (m, 1 H, 5-H), 3.78 (dd, J = 6.1, J = 12.1 Hz, 1 H, CH_2CH=CH$_2$), 3.97 (dd, $J_{3,4}$ = 9.2, $J_{3,3}$ = 9.4 Hz, 1 H, 3-H), 4.01 (m, 1 H, CH_2CH=CH$_2$), 4.31 (d, $J_{1,2}$ = 2.9 Hz, 1 H, 1-H), 4.36 (d, J_{gem} = 10.5 Hz, 1 H, CHPh), 4.38 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.54 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.77 (d, J_{gem} = 12.5 Hz, 1 H, CHPh), 4.87 (d, J_{gem} = 11.2 Hz, 1 H, CHPh), 5.15 (d, J_{gem} = 11.2 Hz, 1 H, CHPh), 5.19 (d, J = 10.2 Hz, 1 H, CH_2=CH), 5.30 (d, J = 18.5 Hz, 1 H, CH_2=CH), 5.78 (s, 1 H, CH=CH$_2$), 6.01 (m, 1 H, CH=CH$_2$), 7.04−7.64 (m, 23 H, Ar-H) ppm. MS (MALDI, positive mode, matrix: DHB): m/z = 677.0 $[M + Na]^+$, 693.0 $[M + K]^+$. $C_{43}H_{42}O_6$ (654.80): calcd. C 78.87, H 6.46; found C 78.61, H 6.50.

Diphenylmethyl 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranoside (11a): White powder (0.26 g, 83%); R_f = 0.45 (petroleum ether/ethyl acetate, 2:1). $[\alpha]_D$ = +107.6 (c = 1.0, CH_2Cl_2); m.p. 127 °C. ^1H NMR (600 MHz, $CDCl_3$): δ = 2.00−2.10 (4 AcO), 3.90 (m, 1 H, 6-H), 3.97 (m, 1 H, 5-H), 4.15 (dd, $J_{6,5}$ = 3.9, J_{gem} = 12.4 Hz, 1 H, 6′-H), 4.89 (dd, $J_{1,2}$ = 3.7, $J_{2,3}$ = 9.9 Hz, 1 H, 2-H), 5.06 (dd, $J_{4,3}$ = 9.8, $J_{4,5}$ = 9.9 Hz, 1 H, 4-H), 5.15 (d, $J_{1,2}$ = 3.7 Hz, 1 H, 1-H), 5.60 (dd, $J_{3,2}$ = 9.9, $J_{3,4}$ = 9.8 Hz, 1 H, 3-H), 5.67 (s, 1 H, CH), 7.26−7.37 (m, 10 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 20.5, 20.6 (4 AcO), 61.6 (C-6), 67.7 (C-5), 68.4 (C-4), 70.2 (C-3), 70.6 (C-2), 81.0 (CH), 94.3 (C-1), 126.8, 127.1, 127.7, 128.0, 128.4, 128.5, 140.4, 141.4 (C-Ar), 169.5, 169.8, 170.1, 170.6 (4 CO) ppm. MS (MALDI, positive mode, matrix: DHB): m/z = 537.0 $[M + Na]^+$, 553.0 $[M + K]^+$. $C_{27}H_{30}O_{10}$ (514.53): calcd. C 63.02, H 5.87; found C 63.15, H 5.97.

9-Fluorenyl 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranoside (11b): Colourless foam (0.55 g, 76%); R_f = 0.37 (petroleum ether/ethyl acetate, 2:1). $[\alpha]_D$ = +17.4 (c = 1.0, CH_2Cl_2). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.90−2.11 (4 AcO), 3.90 (dd, $J_{5,4}$ = 9.5, $J_{5,6}$ = 3.9 Hz, 1 H, 5-H), 4.20 (m, 2 H, 6-H, 6′-H), 4.83 (dd, $J_{2,1}$ = 3.7, $J_{2,3}$ = 9.9 Hz, 1 H, 2-H), 5.11 (dd, $J_{4,3}$ = 9.4, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 5.30 (d, $J_{1,2}$ = 3.7 Hz, 1 H, 1-H), 5.51 (dd, $J_{3,2}$ = 9.9, $J_{3,4}$ = 9.4 Hz, 1 H, 3-H), 5.70 (s, 1 H, CH), 7.10−7.61 (m, 8 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 20.5, 20.6, 20.7 (4 AcO), 61.7 (C-6), 67.6 (C-5), 68.5 (C-4), 70.0 (C-3), 70.8 (C-2), 81.1 (CH), 95.0 (C-1), 120.1, 125.1, 125.8, 127.5, 127.6, 129.4, 129.6, 140.5, 141.1, 141.5, 142.5, 147.7 (C-Ar), 169.5, 170.0, 170.6 (CO) ppm. MS (MALDI, positive mode, matrix: DHB): m/z = 535.0 $[M + Na]^+$, 551.0 $[M + K]^+$. $C_{27}H_{28}O_{10}$·0.5H_2O (521.51): calcd. C 62.18, H 5.75; found C 61.87, H 5.77.

9-Fluorenyl 2:3,5:6-Di-*O*-isopropylidene-α-D-mannofuranoside (12b): White foam (0.33 g, 56%); R_f = 0.43 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = −3.5 (c = 1.0, CH_2Cl_2). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.30, 1.36, 1.43, 1.47 (4 CH_3), 3.71 (dd, $J_{6,5}$ = 4.4, J_{gem} = 8.6 Hz, 1 H, 6-H), 3.90 (dd, $J_{6,5}$ = 6.3, J_{gem} = 8.6 Hz, 1 H, 6′-H), 4.11 (dd, $J_{4,3}$ = 3.6, $J_{4,5}$ = 7.3 Hz, 1 H, 4-H), 4.29 (m, 1 H, 5-H), 4.67 (d, $J_{2,3}$ = 5.9 Hz, 1 H, 2-H), 4.77 (dd, $J_{3,4}$ = 3.6, $J_{3,2}$ = 5.9 Hz, 1 H, 3-H), 5.41 (s, 1 H, 1-H), 5.63 (s, 1 H, CH), 7.20−7.71 (m, 8 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 66.4 (C-6), 73.2 (C-5), 79.5 (C-3), 80.3 (C-4), 85.5 (C-2), 105.8 (C-1), 109.1, 112.6, 119.9, 120.0, 125.2, 126.1, 127.6, 127.7, 129.0, 129.2, 140.2, 140.9, 142.0, 143.7 (C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): m/z = 447.0 $[M + Na]^+$. $C_{25}H_{28}O_6$ (424.49): calcd. C 70.73, H 6.65; found C 70.91, H 6.87.

3,4,6-Tri-*O*-benzyl-2-*O*-diphenylmethyl-α/β-D-glucopyranose (15a): Wilkinson's catalyst (342 mg, 0.36 mmol) was added to a solution of **10a** (1.2 g, 1.85 mmol) in a toluene/EtOH/H_2O mixture (40:40:2 mL) and the reaction mixture was heated at reflux at 110 °C. After 10 h, the solvent was evaporated in vacuo and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 10:1) to give an α/β mixture of **15a** (0.80 g, 71%) as a colourless oil; R_f = 0.45 (petroleum ether/ethyl acetate, 3:1).$[\alpha]_D$ = 17.8 (c = 1.0, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$): δ = 3.08 (br. s, 1 H, α-OH), 3.53 (br. s, 1 H, β-OH), 3.53 (m, 2 H, β-4-H, β-5-H), 3.63 (m, 2 H, α-4-H, α-6-H), 3.72 (m, 2 H, α-2-H, β-3-H, α-6-H), 4.04 (m, 2 H, α-3-H, α-5-H), 4.46 (d, J_{gem} = 9.6 Hz, 1 H, CHPh), 4.48 (d, J_{gem} = 9.6 Hz, 1 H, CHPh), 4.51 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.75 (d, $J_{1,2}$ = 8.2 Hz, 1 H, β-1-H), 4.83 (d, J_{gem} = 9.6 Hz, 1 H, CHPh), 4.86 (d, J_{gem} = 9.6 Hz, 1 H, CHPh), 4.99 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 5.07 (d, $J_{1,2}$ = 2.9 Hz, 1 H, α-1-H), 5.72 (s, 1 H, CH), 7.16−7.38 (m, 25 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 67.0 (CH_2), 68.4 (C-6), 70.2 (C-5), 73.4, 74.7 (2 CH_2), 77.7 (C-4), 78.2 (C-2), 81.8 (C-3), 82.9 (CH), 91.1 (α-1-C), 97.6 (β-1-C), 126.6, 127.1, 127.3, 127.4, 127.6, 127.7, 127.8, 127.9, 128.0, 129.3, 128.6, 137.7, 137.9, 138.1, 138.5, 141.7, 142.3, 142.8 (C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): m/z = 639.0 $[M + Na]^+$. $C_{40}H_{40}O_6$ (616.75): calcd. C 77.89, H 6.53; found C 78.21, H 6.83.

3,4,6-Tri-*O*-benzyl-2-*O*-(9-fluorenyl)-α/β-D-glucopyranose (15b): Wilkinson's catalyst (342 mg, 0.36 mmol) was added to a solution of **10b** (1.21 g, 1.85 mmol) in a toluene/EtOH/H_2O mixture (40:40:2 mL) and the reaction mixture was heated at reflux at 110 °C for 16 h. The reaction was processed as above and the product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (8:1) as eluent to afford **15b** (0.75 g, 67%) as a colourless oil; R_f = 0.36 (petroleum ether/ethyl acetate, 2:1). $[\alpha]_D$ = 15.2 (c = 1.0, CH_2Cl_2). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.02 (br. s, 1 H, OH), 3.55 (m, 2 H, 6-H, 5-H), 3.67 (m, 2 H, 6′-H, 4-H), 4.06 (m, 1 H, 3-H), 4.51 (dd, $J_{2,1}$ = 3.8, $J_{2,3}$ = 9.8 Hz, 1 H, 2-H), 4.62 (d, J_{gem} = 11.6 Hz, 1 H, CHPh), 4.71 (d, J_{gem} = 11.6 Hz, 1 H, CHPh), 4.80 (d, J_{gem} = 9.5 Hz, 1 H, CHPh), 4.86 (d, J_{gem} = 11.6 Hz, 1 H, CHPh), 4.88 (m, 1 H, CHPh), 4.95 (d, J_{gem} = 11.6 Hz, 1 H, CHPh), 5.47 (d, $J_{1,2}$ = 3.8 Hz, 1 H, 1-H), 5.70 (s, 1 H, CH), 7.11−7.72 (m, 23 H, Ar-H) ppm. MS (MALDI, positive mode, matrix: DHB): m/z = 636.0 $[M + Na]^+$, 652.0 $[M + K]^+$. $C_{40}H_{38}O_6$ (614.74): calcd. C 78.15, H 6.23; found C 78.35, H 6.28.

***O*-(3,4,6-Tri-*O*-benzyl-2-*O*-diphenylmethyl-α-D-glucopyranosyl) Trichloroacetimidate (16a):** A stirred solution of **15a** (1.54 g, 2.5 mmol) in dry dichloromethane (40 mL) and trichloroaceto-

nitrile (2.5 mL, 25 mmol) was treated at room temperature with DBU (35 μL) and the mixture was then left to stand for 1.5 h. The solvent was evaporated and the product was purified by column chromatography (3% triethylamine in toluene) to give **16a** (1.86 g, 84%) as a yellow oil; R_f = 0.65 (3% triethylamine in toluene). $[\alpha]_D$ = 6.4 (c = 1.0, CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.56 (m, 3 H, 6-H, 6′-H, 4-H), 3.81 (dd, $J_{1,2}$ = 3.4, $J_{2,3}$ = 9.5 Hz, 1 H, 2-H), 4.02 (m, 1 H, 5-H), 4.20 (dd, $J_{3,2}$ = 9.3, $J_{3,4}$ = 9.5 Hz, 1 H, 3-H), 4.48 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.55 (d, J_{gem} = 10.3 Hz, 1 H, CHPh), 4.62 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.91 (m, 2 H, 2 CHPh), 4.97 (d, J_{gem} = 10.3 Hz, 1 H, CHPh), 5.76 (s, 1 H, CH), 6.28 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1-H), 7.01−7.53 (m, 25 H, Ar-H), 8.62 (br. s, 1 H, NH) ppm.

***O*-[3,4,6-Tri-*O*-benzyl-2-*O*-(9-fluorenyl)-α-D-glucopyranosyl] Trichloroacetimidate (16b):** A stirred solution of **15b** (1.54 g, 2.5 mmol) in dry dichloromethane (40 mL) and trichloroacetonitrile (2.5 mL, 25 mmol) was treated at room temperature with DBU (35 μL) and the mixture was then left to stand for 2 h. The reaction was processed as above and the product was purified by column chromatography (3% triethylamine in toluene) to give **16b** (1.46 g, 77%) as a yellow oil; R_f = 0.65 (3% triethylamine in toluene). $[\alpha]_D$ = −32.4 (c = 2.0, CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.51 (m, 1 H, 6-H), 3.67 (m, 2 H, 2-H, 6′-H), 3.80 (m, 1 H, 3-H), 4.05 (m, 1 H, 5-H), 4.20 (dd, $J_{4,3}$ = 9.2, $J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 4.44 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.50 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.61 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.75 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.83 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.95 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 5.69 (s, 1 H, CH), 6.01 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1-H), 7.02−7.76 (m, 23 H, Ar-H), 8.50 (br. s, 1 H, NH) ppm.

Methyl 3,4,6-Tri-*O*-benzyl-2-*O*-diphenylmethyl-β-D-glucopyranoside (17a): A solution of **16a** (0.46 g, 0.6 mmol) and methanol (0.24 mL, 6.0 mmol) in dry dichloromethane (20 mL) was treated with TMSOTf (13 μL, 0.06 mmol) and the mixture was then stirred for 1.5 h at room temperature. The reaction mixture was quenched by the addition of solid sodium hydrogencarbonate, filtered and concentrated. The crude residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as eluent to afford **17a** (0.31 g, 81%) as a colourless oil; R_f = 0.65 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = −15.6 (c = 2.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.40 (s, 3 H, OCH_3), 3.45 (m, 1 H, 5-H), 3.53 (m, 2 H, 4-H, 2-H), 3.63 (dd, $J_{6,5}$ = 4.7, J_{gem} = 10.7 Hz, 1 H, 6-H), 3.71 (m, 2 H, 3-H, 6′-H), 4.32 (d, $J_{1,2}$ = 7.6 Hz, 1 H, 1-H), 4.45 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.52 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.59 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.74 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.78 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.93 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 6.03 (s, 1 H, CH), 7.10−7.34 (m, 25 H, Ar-H) ppm. MS (MALDI, positive mode, matrix: DHB): m/z = 653.0 $[M + Na]^+$, 669.0 $[M + K]^+$. $C_{41}H_{42}O_6$ (630.78): calcd. C 78.06, H 6.71; found C 77.80, H 6.50.

Methyl 3,4,6-Tri-*O*-benzyl-2-*O*-(9-fluorenyl)-β-D-glucopyranoside (17b): Colourless oil (0.24 g, 64%); R_f = 0.54 (petroleum ether/ethyl acetate, 4:1). $[\alpha]_D$ = −5.7 (c = 2.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.54 (m, 1 H, 5-H), 3.65 (dd, $J_{3,2}$ = 9.1, $J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 3.71 (s, 3 H, OCH_3), 3.73 (m, 2 H, 6-H, 4-H), 3.79 (m, 1 H, 6′-H), 4.09 (dd, $J_{2,1}$ = 8.0, $J_{2,3}$ = 9.1 Hz, 1 H, 2-H), 4.49 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1-H), 4.50 (d, J_{gem} = 11.5 Hz, 1 H, CHPh), 4.53 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.57 (d, J_{gem} = 11.5 Hz, 1 H, CHPh), 4.59 (d, J_{gem} = 11.5 Hz, 1 H, CHPh), 4.61 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.88 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 5.96 (s, 1 H, CH), 6.98−7.63 (m, 23 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 57.2 (OCH_3), 68.8 (C-6), 73.5, 74.9, 76.0 (3 CH_2), 75.1 (C-5), 77.9 (C-4), 82.4 (CH), 83.2 (C-2), 84.5 (C-3), 105.2 (C-1), 119.7, 125.5, 127.3, 127.5, 127.7, 128.0, 128.4, 128.6, 138.1, 138.3, 140.0, 140.2, 144.3, 144.5 (C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): m/z = 652.0 $[M + Na]^+$. $C_{41}H_{40}O_6$ (628.76): calcd. C 78.32, H 6.40; found C 78.64, H 6.42.

***n*-Octyl 3,4,6-Tri-*O*-benzyl-2-*O*-diphenylmethyl-β-D-glucopyranoside (18a):** A solution of trichloroacetimidate **16a** (0.46 g, 0.6 mmol) and octanol (0.94 mL, 6.0 mmol) in dry dichloromethane (20 mL) was treated with TMSOTf (13 μL, 0.06 mmol) and the mixture was then stirred for 1 h at room temperature. The reaction mixture was processed as above and the product was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (20:1) as eluent to afford **18a** (0.37 g, 86%) as a colourless oil; R_f = 0.82 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = −27.6 (c = 2.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.87−1.55 $[CH_3(CH_2)_5]$, 3.46 (m, 2 H, CH_2), 3.54 (dd, $J_{2,1}$ = 7.6, $J_{2,3}$ = 8.7 Hz, 1 H, 2-H), 3.63 (m, 2 H, 6-H, 6′-H), 3.71 (m, 1 H, 3-H), 3.87 (m, 2 H, CH_2), 4.43 (d, $J_{1,2}$ = 7.6 Hz, 1 H, 1-H), 4.45 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.51 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.58 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.73 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.80 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.95 (d, J_{gem} = 10.6 Hz, 1 H, C*H*Ph), 6.14 (s, 1 H, CH), 7.17−7.34 (m, 25 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 14.1, 22.7, 26.2, 29.4, 29.7, 31.8 $[CH_3(CH_2)_5]$, 68.9 (CH_2), 70.0 (C-6), 73.4 (CH_2), 74.8 (C-5), 74.9, 75.7 (2 CH_2), 77.9 (C-4), 78.2 (C-2), 82.8 (CH), 84.6 (C-3), 104.1 (C-1), 126.6, 126.9, 127.4, 127.5, 127.6, 127.7, 127.9, 128.1, 128.2, 128.3, 138.1, 138.7, 141.8 (C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): m/z = 751.0 $[M + Na]^+$, 767.0 $[M + K]^+$. $C_{48}H_{56}O_6$ (728.91): calcd. C 79.09, H 7.74; found C 79.32, H 7.85.

***n*-Octyl 3,4,6-Tri-*O*-benzyl-2-*O*-(9-fluorenyl)-α/β-D-glucopyranoside (18b):** Colourless oil (0.35 g, 80%); R_f = 0.63 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = 23.5 (c = 1.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.87−1.71 $[CH_3(CH_2)_5]$, 3.49 (m, 2 H, α-2-H, α-4-H), 3.55 (m, 2 H, 5-H, α-6-H), 3.64 (dd, $J_{2,1}$ = 8.7, $J_{2,3}$ = 9.0 Hz, 1 H, β-3-H), 3.69 (m, 4 H, β-2-H, β-CH_2, β-4-H), 3.95 (m, 1 H, α-3-H), 4.09 (m, 2 H, α-CH_2), 4.27 (d, $J_{1,2}$ = 3.4 Hz, 1 H, α-1-H), 4.42 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.47 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.53 (m, 1 H, CHPh), 4.58 (d, $J_{1,2}$ = 8.1 Hz, 1 H, β-1-H), 4.60 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.64 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 4.86 (d, J_{gem} = 10.6 Hz, 1 H, CHPh), 5.77 (s, 1 H, α-CH), 6.1 (s, 1 H, β-CH), 6.93−7.38 (m, 23 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 14.1, 22.6, 26.1, 16.3, 29.1, 29.2, 31.7 $[CH_3(CH_2)_5]$, 67.7 (CH_2), 68.3 (C-6), 68.9, 69.4, 70.3 (3 CH_2), 74.9 (C-5), 76.9 (α-2-C), 77.8 (C-4), 81.8 (CH), 82.7 (β-2-C), 84.6 (C-3), 97.4 (α-1-C), 104.2 (β-1-C), 119.7, 119.8, 125.5, 125.8, 127.3, 127.4, 127.6, 127.7, 127.9, 128.2, 128.3, 128.6, 128.8, 129.1, 138.2, 140.2 (C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): m/z = 750.7 $[M + Na]^+$.

Methyl *O*-(3,4,6-Tri-*O*-benzyl-2-*O*-diphenylmethyl-β-D-glucopyranosyl)-(1−6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (19a): Colourless oil (0.43 g, 68%); R_f = 0.47 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = 34.8 (c = 1.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.27 (s, 3 H, OCH_3), 3.35 (m, 1 H, 5-H_b), 3.39 (m, 1 H, 3-H_b), 3.43 (dd, $J_{1,2}$ = 3.4, $J_{2,3}$ = 9.7 Hz, 1 H, 2-H_a), 3.47 (dd, $J_{2,1}$ = 7.8, $J_{2,3}$ = 10.1 Hz, 1 H, 2-H_b), 3.51 (m, 2 H, 6-H_b, 4-H_b), 3.56 (dd, $J_{6,5}$ = 4.8, J_{gem} = 10.2 Hz, 1 H, 6-H_a), 3.60 (m, 2 H, 6′-H_a, 4-H_a), 3.74 (m, 1 H, 5-H_a), 3.92 (dd, $J_{3,2}$ = 9.2, $J_{3,4}$ = 9.7 Hz, 1 H, 3-H_a), 4.04 (m, 1 H, 6′-H_b), 4.31 (d, $J_{1,2}$ = 7.8 Hz, 1 H, 1-H_b), 4.37 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.41 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.43 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.47 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.53 (d, $J_{1,2}$ = 3.3 Hz, 1 H, 1-H_a), 4.56 (d, J_{gem} =

10.7 Hz, 1 H, CHPh), 4.60 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.64 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.70 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.74 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.75 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.90 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.93 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 6.12 (s, 1 H, CH), 7.03−7.26 (m, 40 H, Ar-H), ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 55.0 (OCH_3), 68.2 (C_b-6), 68.9 (C_a-6), 69.0 (C_b-4), 69.6 (C_a-5), 73.2, 73.4, 73.7 (3 CH_2), 74.9 (C_b-5), 75.1, 75.5, 75.6 (3 CH_2), 77.1 (C_b-2), 77.9 (C_b-3), 79.6 (C_a-2), 81.7 (C_a-3), 82.3 (CH), 84.7 (C_a-4), 97.9 (C_a-1), 104.1 (C_b-1), 126.6, 127.3, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 138.0, 138.1, 138.3, 138.6, 138.9, 141.6, 142.9 (C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): *m/z* = 1085.9 $[M + Na]^+$, 1101.1 $[M + K]^+$. $C_{68}H_{70}O_{11}$ (1063.3): calcd. C 76.81, H 6.63; found C 76.90, H 7.01.

Methyl *O*-[3,4,6-Tri-*O*-benzyl-2-*O*-(9-fluorenyl)-α/β-D-glucopyranosyl]-(1−6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (19b): Colourless oil (0.38 g, 61%); R_f = 0.43 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = 24.6 (*c* = 2.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.37 (m, 1 H, β-2-H_a), 3.42 (s, 3 H, OCH_3), 3.45 (m, 3 H, 5-H_b, α-4-H_a, β-4-H_a), 3.54 (m, 2 H, α-3-H_b, α-2-H_b), 3.58 (m, 2 H, 6-H_a, α-2-H_a), 3.70 (m, 3 H, α-4-H_b, β-3-H_b, 6-H_b), 3.88 (m, 3 H, 5-H_a, β-3-H_a, α-3-H_a), 4.01 (m, 2 H, β-2-H_b, 6′-H_a), 4.29 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.35 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 4.43 (m, 2 H, 1-H_a, β-1-H_b), 4.47 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.58 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 4.63 (d, $J_{1,2}$ = 3.6 Hz, 1 H, α-1-H_b), 4.65 (m, 3 H, 3 CHPh), 4.76 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.81 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 4.94 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 4.98 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 5.29 (d, J_{gem} = 10.8 Hz,, 1 H, CHPh), 5.72 (s, 1 H, CH), 7.03−7.36 (m, 38 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 55.1 (OCH_3), 66.2 (C_b-6), 68.1 (C_b-5), 69.2 (C_b-4), 69.6 (C_a-6), 69.7 (C_a-5), 73.3, 73.4, 73.5, 73.8 (4 CH_2), 75.0 (β-4-C_b), 75.7, 75.8 (2 CH_2), 77.5 (α-2-C_a), 77.7 (α-4-C_a), 78.0 (α-3-C_b), 78.2 (β-4-C_b), 79.4 (β-2-C_b), 81.3 (β-2-C_b), 81.7 (α-3-C_a), 81.9 (β-3-C_a), 85.3 (β-3-C_b), 97.5 (C_a-1), 97.9 (α-1-C_b), 103.9 (β-1-C_b), 119.7, 119.8, 126.1, 127.3, 127.5, 127.6, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 138.5, 140.2, 143.9 (C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): *m/z* = 1083 $[M + Na]^+$. $C_{68}H_{68}O_{11}$ (1061.28): calcd. C 76.95, H 6.65; found C 77.27, H 6.70.

Allyl 3,4,6-Tri-*O*-benzyl-2-*O*-diphenylmethyl-α-D-mannopyranoside (22): A solution of **2a** (0.46 g, 1.4 mmol) and **20**[40] (0.69 g, 1.4 mmol) in dry dichloromethane (30 mL) was treated with TMSOTf (26 μL, 0.14 mmol) and the mixture was then stirred for 30 min. The reaction mixture was quenched by the addition of solid sodium hydrogencarbonate, filtered and concentrated. The crude residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (15:1) as eluent, to afford **22** (0.81 g, 88%) as colourless oil; R_f = 0.48 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = −12.0 (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.72 (m, 3 H, 6-H, 6′-H, 5-H), 3.91 (m, 1 H, 2-H), 4.15 (m, 2 H, 4-H, 3-H), 4.51 (m, 4 H, CH_2−CH=CH_2, 2 CHPh), 4.53 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.57 (d, J_{gem} = 11.1 Hz, 1 H, CHPh), 4.73 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.90 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.92 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1-H), 5.09 (m, 2 H, CH=CH_2), 5.71 (s, 1 H, CH), 5.80 (m, 1 H, CH=CH_2), 7.08−7.85 (m, 25 H, Ar-H) ppm. MS (MALDI, positive mode, matrix: DHB): *m/z* = 679.7 $[M + Na]^+$, 695.7 $[M + K]^+$. $C_{43}H_{44}O_6$ (656.81): calcd. C 78.63, H 6.75; found C 78.51, H 6.68.

4-Methoxyphenyl 3,4,6-Tri-*O*-benzyl-2-*O*-diphenylmethyl-α-D-mannopyranoside (23): A solution of diphenylmethyl trichloroacetimidate (**2a**, 0.46 g, 1.4 mmol) and **21**[41] (0.78 g, 1.4 mmol) in dry dichloromethane (30 mL) was treated with TMSOTf (26 μL, 0.14 mmol) and the mixture was then stirred for 1.5 h. The reaction mixture was quenched by the addition of solid sodium hydrogencarbonate, filtered and concentrated. The crude residue was purified by column chromatography on silica gel, with petroleum ether/ethyl acetate (10:1) as eluent, to afford **23** (0.90 g, 89%) as a colourless oil; R_f = 0.37 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = 32.0 (*c* = 2.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.76 (s, 3 H, OCH_3), 3.77 (m, 1 H, 6-H), 3.86 (dd, $J_{6,5}$ = 4.4, J_{gem} = 10.0 Hz, 1 H, 6′-H), 3.94 (m, 1 H, 5-H), 4.09 (m, 1 H, 2-H), 4.13 (dd, $J_{3,2}$ = 2.7, $J_{3,4}$ = 9.5 Hz, 1 H, 3-H), 4.29 (dd, $J_{4,3}$ = 9.5, $J_{4,5}$ = 9.6 Hz, 1 H, 4-H), 4.50 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.59 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.63 (d, J_{gem} = 11.9 Hz, 1 H, CHPh), 4.66 (d, J_{gem} = 11.9 Hz, 1 H, CHPh), 4.71 (d, J_{gem} = 11.9 Hz, 1 H, CHPh), 4.94 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 5.49 (d, $J_{1,2}$ = 1.1 Hz, 1 H, 1-H), 5.82 (s, 1 H, CH), 6.78 (d, *J* = 9.0 Hz, 2 H, phenol), 6.94 (d, *J* = 9.0 Hz, 2 H, phenyl), 7.23−7.37 (m, 25 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 55.6 (OCH_3), 67.1 (CH_2), 69.1 (C-6), 72.2 (CH_2), 72.4 (C-5), 72.7 (C-2), 73.2 (CH_2), 74.7 (C-4), 80.1 (C-3), 82.6 (CH), 97.2 (C-1), 114.5, 117.7, 127.3, 127.4, 127.5, 127.9, 128.2, 128.3, 128.4, 128.5, 138.4, 138.5, 142.0, 142.1, 150.1, 154.8 (C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): *m/z* = 745.0 $[M + Na]^+$, 761.0 $[M + K]^+$. $C_{47}H_{46}O_7$ (722.86): calcd. C 78.09, H 6.41; found C 78.21, H 6.50.

3,4,6-Tri-*O*-benzyl-2-*O*-diphenylmethyl-α-D-mannopyranose (24). (a) From 22: Wilkinson's catalyst (684 mg, 0.72 mmol) was added to a solution of **22** (2.4 g, 3.7 mmol) in a toluene/EtOH/H_2O mixture (80:80:5 mL) and the reaction mixture was heated at reflux at 110 °C. After 8 h, the solvent was evaporated in vacuo and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 10:1) to give an α/β mixture of **24** (1.53 g, 68%) as a colourless oil; R_f = 0.45 (petroleum ether/ethyl acetate, 3:1). $[\alpha]_D$ = 17.8 (*c* = 1.0, CH_2Cl_2). **(b) From 23:** A solution of **23** (2.4 g, 3.3 mmol) was dissolved in an acetonitrile/water mixture (60 mL, 4:1). Ammonium cerium(IV) nitrate (4.96 g, 9 mmol) was added at 0 °C; after 30 min, the mixture was diluted with dichloromethane (50 mL) and saturated $NaHCO_3$ solution. The aqueous layer was extracted twice with dichloromethane. The organic layer was dried with $MgSO_4$ and the solvents were removed in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 10:1) to give an α product of **24** (1.3 g, 63%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.96 (br. s, 1 H, OH), 3.76 (m, 2 H, 6-H, 6′-H), 4.04 (m, 1 H, 5-H), 4.07 (m, 1 H, 2-H), 4.12 (m, 2 H, 4-H, 3-H), 462 (m, 3 H, 3 CHPh), 4.65 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.69 (d, J_{gem} = 10.9 Hz, 1 H, CHPh), 4.98 (d, J_{gem} = 10.9 Hz, CHPh), 5.31 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1-H), 5.77 (s, 1 H, CH), 7.22−7.46 (m, 25 H, Ar-H) ppm. MS (MALDI, positive mode, matrix: DHB): *m/z* = 639.0 $[M + Na]^+$, 655.0 $[M + K]^+$. $C_{40}H_{40}O_6{\cdot}H_2O$ (643.75): calcd. C 74.63, H 6.70; found C 74.62, H 6.44.

3,4,6-Tri-*O*-benzyl-2-*O*-diphenylmethyl-α-D-mannopyranosyl Trichloroacetimidate (25a): A stirred solution of **24** (3.1 g, 5 mmol) in dry dichloromethane (40 mL) and trichloroacetonitrile (2.5 mL, 25 mmol) was treated at room temperature with DBU (70 μL) and the mixture was then left to stand for 2 h. The solvent was evaporated and the product was purified by column chromatography (3% triethylamine in toluene) to give **25a** (3.1 g, 82%) as a yellow oil; R_f = 0.72 (3% triethylamine in toluene). $[\alpha]_D$ = −9.5 (*c* = 2.0, CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.73 (m, 1 H, 6-H), 3.79 (m, 1 H, 6′-H), 3.91 (m, 1 H, 5-H), 3.95 (m, 1 H, 2-H), 4.01 (m, 1 H, 3-H), 4.25 (dd, $J_{4,3}$ = 9.6, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 4.46 (m, 2 H, 2 CHPh), 4.52 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.55 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.61 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.93 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 5.72 (s, 1 H, CH), 6.36 (d,

$J_{1,2}$ = 1.9 Hz, 1-H), 7.11−7.46 (m, 25 H, Ar-H), 8.51 (s, 1 H, NH) ppm.

Octyl 3,4,6-Tri-*O*-benzyl-2-*O*-diphenylmethyl-α/β-D-mannopyranoside (26a): A solution of **25a** (0.46 g, 0.6 mmol) and octanol (0.94 mL, 6.0 mmol) in dry dichloromethane (20 mL) was treated with TMSOTf (13 μL, 0.06 mmol) and the mixture was then stirred for 10 min. The reaction mixture was quenched by the addition of solid sodium hydrogencarbonate, filtered and concentrated. The crude residue was purified by column chromatography on silica gel, with petroleum ether/ethyl acetate (30:1) as eluent, to afford **26a** (0.37 g, 86%) as a colourless oil; R_f = 0.42 (petroleum ether/ethyl acetate, 10:1). $[\alpha]_D$ = 15.5 (c = 1.0, CH_2Cl_2). **26aα:** (0.12 g, 28.5%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.87−1.50 [$CH_3(CH_2)_5$], 3.36 (m, 2 H, CH_2), 3.79 (m, 2 H, 6-H, 5-H), 3.87 (dd, $J_{6',5}$ = 4.8, J_{gem} = 10.8 Hz, 1 H, 6′-H), 3.90 (d, $J_{2,1}$ = 3.6, $J_{2,3}$ = 9.3 Hz, 1 H, 2-H), 3.95 (dd, $J_{3,2}$ = 9.3, $J_{3,4}$ = 9.4 Hz, 1 H, 3-H), 4.18 (dd, $J_{4,3}$ = 9.4, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H), 4.54 (d, J_{gem} = 11.6 Hz, 1 H, CHPh), 4.58 (m, 3 H, 3 CHPh), 4.73 (d, J_{gem} = 12.1 Hz, 1 H, CHPh), 4.89 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.90 (d, J_{gem} = 11.6 Hz, CHPh), 5.75 (s, 1 H, CH), 7.25−7.36 (m, 25 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 14.1, 22.6, 26.1, 29.2, 29.3, 29.4, 31.8 [$CH_3(CH_2)_6$], 67.6 (CH_2), 69.4 (C-6), 71.9 (CH_2), 72.0 (C-5), 73.3 (C-2), 74.9 (CH_2), 75.1 (C-4), 80.5 (C-3), 82.4 (CH_2), 98.0 (C-1), 82.5 (CH), 127.2, 127.3, 127.4, 127.5, 127.6, 128.0, 128.1, 128.2, 128.3, 138.1, 138.5, 138.6, 142.2, 142.3 (C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): m/z = 751.0 [M + Na]$^+$, 767.0 [M + K]$^+$. $C_{48}H_{56}O_6$ (728.91): calcd. C 79.09, H 7.74; found C 78.72, H 7.71. **26aβ:** (0.25 g, 57%). Colourless oil; R_f = 0.38 (petroleum ether/ethyl acetate, 10:1). $[\alpha]_D$ = −27.0 (c = 2.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.92−1.68 [$CH_3(CH_2)_5$], 3.41 (m, 2 H, CH_2), 3.51 (m, 2 H, 3-H, 5-H), 3.85 (m, 2 H, 6-H, 6′-H), 4.04 (dd, $J_{2,1}$ = 2.0, $J_{2,3}$ = 9.6 Hz, 1 H, 2-H), 4.19 (dd, $J_{3,4}$ = $J_{4,5}$ = 7.5 Hz, 1 H, 4-H), 4.34 (d, J_{gem} = 11.9 Hz, 1 H, CHPh), 4.41 (d, $J_{1,2}$ = 3.0 Hz, 1 H, 1-H), 4.43 (d, J_{gem} = 11.9 Hz, 1 H, CHPh), 4.62 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.66 (d, J_{gem} = 11.9 Hz, 1 H, CHPh), 4.72 (d, J_{gem} = 11.9 Hz, 1 H, CHPh), 4.96 (d, J_{gem} = 11.9 Hz, 1 H, CHPh), 6.28 (s, 1 H, CH), 7.27−7.48 (m, 25 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 14.1, 22.7, 26.2, 29.3, 29.4, 29.7, 31.8 [$CH_3(CH_2)_5$], 69.5 (C-6), 69.9 (CH_2), 71.1 (CH_2), 71.4 (C-2), 73.3 (CH_2), 74.7 (C-4), 75.1 (CH_2), 76.0 (C-5), 82.2 (CH), 82.5 (C-3), 102.0 (C-1), 126.7, 127.3, 127.4, 127.5, 127.6, 127.7, 128.0, 128.2, 128.6, 138.3, 138.4, 138.6, 142.1, 142.9 (C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): m/z = 751.0 [M + Na]$^+$, 767.0 [M + K]$^+$. $C_{48}H_{56}O_6$ (728.91): calcd. C 79.09, H 7.74; found C 78.60, H 7.84.

***n*-Octyl 2,3,4,6-Tetra-*O*-benzyl-α/β-D-mannopyranoside (26b):** A solution of the trichloroacetimidate **25b** (0.41 g, 0.6 mmol) and *n*-octanol (0.14 mL, 0.9 mmol) in dry dichloromethane (20 mL) was treated with TMSOTf (13 μL, 0.06 mmol) and the mixture was then stirred for 45 min. The reaction mixture was processed as above and the product was purified by column chromatography on silica gel, with petroleum ether/ethyl acetate (15:1) as eluent, to afford **26b** (0.29 g, 75%) as a colourless oil; R_f = 0.63 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = 35.7 (c = 1.0, CH_2Cl_2).

Methyl *O*-(3,4,6-Tri-*O*-benzyl-2-*O*-diphenylmethyl-α/β-D-mannopyranosyl)-(1−6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (27a): Treatment of **25a** and **7** as described for **26a** gave **27a** as a colourless oil (0.48 g, 76%). **27aα:** (0.12 g, 19%). R_f = 0.41 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = 21.5 (c = 2.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.31 (s, 3 H, OCH_3), 3.39 (dd, $J_{4,5}$ = 9.5, $J_{4,3}$ = 9.6 Hz, 1 H, 4-H_a), 3.44 (dd, $J_{2,1}$ = 3.4, $J_{2,3}$ = 9.6 Hz, 1 H, 2-H_a), 3.64 (m, 3 H, 5-H_a, 6-H_a, 6-H_b), 3.73 (m, 2 H, 5-H_b, 6′-H_b), 3.83 (dd, $J_{6',5}$ = 4.1, J_{gem} = 11.5 Hz, 1 H, 6′-H_a), 3.90 (m, 2 H, 2-H_b, 3-H_b), 3.97 (dd, $J_{3,2}$ = 9.6, $J_{3,4}$ = 9.3 Hz, 1 H, 3-H_a), 4.19 (dd, $J_{4,3}$ = 9.2, $J_{4,5}$ = 9.3 Hz, 1 H, 4-H_b), 4.47 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.51 (d, J_{gem} = 11.2 Hz, 1 H, CHPh), 4.54 (m, 3 H, 3 CHPh), 4.58 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H_a), 4.66 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.70 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.79 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.83 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.87 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.90 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.99 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 5.02 (d, $J_{1,2}$ = 4.8 Hz, 1 H, 1-H_b), 5.74 (s, 1 H, CH), 7.25−7.41 (m, 40 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 55.0 (OCH_3), 65.5 (C_a-6), 68.9 (CH_2), 69.1 (C_b-6), 69.7 (C_a-5), 71.8 (CH_2), 71.9 (C_b-5), 72.5 (CH_2), 72.7 (C_b-2), 73.1, 74.4, 74.7, (3 CH_2), 74.9 (C_b-4), 75.0, 75.7 (2 CH_2), 77.5 (C_a-4), 79.7 (C_b-3), 80.0 (C_a-2), 82.0 (C_a-3), 83.3 (CH), 97.7 (C_a-1); 98.3 (C_b-1), 112.2, 114.6, 116.0, 127.3, 127.4, 127.5, 127.6, 127.8, 127.9, 128.1, 128.2, 128.3, 128.4, 138.0, 138.1, 138.3, 138.5, 142.1, 142.2 (C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): m/z = 1085.2 [M + Na]$^+$, 1102.1 [M + K]$^+$. $C_{68}H_{70}O_{11}$ (1063.30): calcd. C 76.81, H 6.63; found C 76.39, H 6.58. **27aβ:** (0.36 g, 57%). R_f = 0.38 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = 2.3 (c = 1.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.18 (s, 3 H, OCH_3), 3.29 (m, 2 H, 4-H_a, 6-H_a), 3.37 (m, 1 H, 6-H_b), 3.38 (m, 2 H, 6′-H_a, 6′-H_b), 3.64 (m, 2 H, 5-H_a, 5-H_b), 3.73 (m, 1 H, 2-H_a), 3.92 (m, 2 H, 3-H_a, 3-H_b), 4.01 (m, 2 H, 4-H_b, 2-H_b), 4.26 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.29 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.44 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.45 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1-H_b), 4.49 (m, 2 H, 2 CHPh), 4.53 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.58 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.68 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.70 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.76 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.82 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.89 (d, $J_{1,2}$ = 3.3 Hz, 1 H, 1-H_a), 4.95 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 6.06 (s, 1 H, CH), 7.09−7.23 (m, 40 H, Ar-H) ppm. MS (MALDI, positive mode, matrix: DHB): m/z = 1085.2 [M + Na]$^+$, 1102.1 [M + K]$^+$. $C_{68}H_{70}O_{11}$ (1063.30): calcd. C 76.81, H 6.63; found C 76.59, H 6.96.

Methyl (2,3,4,6-Tetra-*O*-benzyl-α/β-D-mannopyranosyl)-(1−6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (27b): A solution of trichloroacetimidate **25b** (0.41 g, 0.6 mmol) and glucose derivative **7** (0.28 mL, 0.6 mmol) in dry dichloromethane (20 mL) was treated with TMSOTf (13 μL, 0.06 mmol) and the mixture was then stirred for 30 min. The reaction mixture was processed as above and the product was purified by column chromatography on silica gel, with petroleum ether/ethyl acetate (10:1) as eluent, to afford **27b** (0.48 g, 81%) as a colourless oil; R_f = 0.37 (petroleum ether/ethyl acetate 5:1). $[\alpha]_D$ = 18.5 (c = 1.0, CH_2Cl_2).

4-Methoxyphenyl 3-*O*-Allyl-2,4-di-*O*-benzyl-α-D-mannopyranoside (28): $LiAlH_4$ (0.5 g, 13.1 mmol) was added in three portions with stirring to a solution of methoxyphenyl 3-*O*-allyl-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside[39] (1.63 g, 3.2 mmol) in diethyl ether/dichloromethane (1:1, 50 mL), and the mixture was slowly heated to its boiling point. $AlCl_3$ (1.5 g) in diethyl ether (20 mL) was added to the hot solution over 30 min. The mixture was heated at reflux for 2 h and cooled, the excess of $LiAlH_4$ was decomposed with ethyl acetate (8 mL) and addition of water (15 mL). After dilution with diethyl ether (50 mL), the organic layer was washed with water (3 × 30 mL), dried and concentrated under vacuum. The crude material was purified by flash chromatography (petroleum ether/ethyl acetate, 3:1) to obtain **28** (1.42 g, 87%) as a colourless oil; R_f = 0.34 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = 17.6 (c = 0.5, CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.30 (br. s 1 H, OH), 3.69 (s, 3 H, OCH_3), 4.02 (m, 2 H, 6-H, 5-H), 4.13 (m, 1 H, 6′-H), 4.18 (m, 3 H, 3-H, OCH_2), 4.21 (m, 1

H, 2-H), 4.72 (m, 1 H, 4-H), 4.86 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.91 (d, J_{gem} = 12.2 Hz, 1 H, CHPh), 4.97 (d, J_{gem} = 10.5 Hz, 1 H, CHPh), 5.23 (d, J_{gem} = 10.5 Hz, 1 H, CHPh), 5.36 (m, 2 H, CH=CH_2), 5.44 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1-H), 6.00 (m, 1 H, CH=CH_2), 6.75 (m, 4 H, Ar-H), 7.31 (m, 10 H, Ar-H) ppm. MS (MALDI, positive mode, matrix: DHB): *m*/*z* = 528.5 $[M + Na]^+$, 5.45 $[M + K]^+$. $C_{30}H_{34}O_7$ (506.59): calcd. C 71.13, H 6.76; found C 71.45, H 6.86.

4-Methoxyphenyl *O*-(3,4-6-Tri-*O*-benzyl-2-*O*-diphenylmethyl-α/β-D-mannopyranosyl)-(1−6)-3-*O*-allyl-2,4-di-*O*-benzyl-α-D-mannopyranoside (28a): A solution of **25a** (0.46 g, 0.6 mmol) and **28** (0.30 mL, 0.6 mmol) in dry dichloromethane (20 mL) was treated with TMSOTf (13 μL, 0.06 mmol) and the mixture was then stirred for 30 min. The reaction mixture was processed as above and the product was purified by column chromatography on silica gel, with petroleum ether/ethyl acetate (15:1) as eluent, to afford **28a** (0.47 g, 69%) as a colourless oil; R_f = 0.34 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = 30.0 (*c* = 1.0, CH_2Cl_2). **28aα:** (0.11 g, 17%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.56 (s, 3 H, OCH_3), 3.61 (m, 1 H, 6-H_a), 3.71 (m, 1 H, 6-H_b), 3.80 (m, 2 H, 5-H_a, 6′-H_b), 3.87 (m, 3 H, 3-H_b, 4-H_a, 5-H_b), 3.90 (m, 1 H, 6′-H_a), 3.93 (m, 2 H, 2-H_a, 2-H_b), 3.96 (dd, $J_{3,2}$ = 2.9, $J_{3,4}$ = 10.7 Hz, 1 H, 3-H_a), 4.13 (m, 2 H, CH_2−CH=CH_2), 4.19 (dd, $J_{4,3}$ = 9.5, $J_{4,5}$ = 9.7 Hz, 1 H, 4-H_b), 4.30 (m, 2 H, 2 CHPh), 4.48 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.52 (d, J_{gem} = 11.1 Hz, 1 H, CHPh), 4.57 (d, J_{gem} = 11.1 Hz, 1 H, CHPh), 4.69 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.71 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.74 (d, J_{gem} = 11.1 Hz, 1 H, CHPh), 4.89 (d, J_{gem} = 11.1 Hz, 1 H, CHPh), 4.94 (d, J_{gem} = 11.1 Hz, 1 H, CHPh), 4.99 (d, $J_{1,2}$ = 1.1 Hz, 1 H, 1-H_b), 5.20 (m, 2 H, CH=CH_2), 5.36 (d, $J_{1,2}$ = 1.4 Hz, 1 H, 1-H_a), 5.67 (s, 1 H, CH), 6.05 (m, 1 H, CH=CH_2), 6.75 (d, *J* = 9.0 Hz, 2 H, phenyl), 6.93 (d, *J* = 9.0 Hz, 2 H, phenyl), 7.21−7.39 (m, 35 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 55.4 (OCH_3), 66.1 (C_a-6), 67.1 (CH_2), 69.2 (C_b-6), 71.1 (CH_2−CH), 71.5 (C_a-5), 71.9 (C_b-5), 72.7 (CH_2), 72.9 (C_b-2), 73.2, 73.3, 74.4 (3 CH_2), 74.5 (C_a-4), 74.6 (CH_2), 74.7 (C_b-4), 79.8 (C_b-3), 82.2 (CH), 85.0 (CH=CH_2), 96.9 (C_a-1), 98.0 (C_b-1), 114.6 (CH_2=CH), 127.2, 127.4, 127.5, 127.6, 127.8, 127.9, 128.1, 128.2, 128.3, 128.4, 134.8, 138.6, 142.3, 142.5, 150.3, 154.8 (C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): *m*/*z* = 1128.0 $[M + Na]^+$, 1144.0 $[M + K]^+$. $C_{70}H_{72}O_{12}$ (1105.34): calcd. C 76.06, H 6.55; found C 76.48, H 6.62. **28aβ:** (0.36 g, 52%). R_f = 0.31 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = 7.9 (*c* = 2.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.34 (dd, $J_{6,5}$ = 2.5, J_{gem} = 9.4 Hz, 1 H, 6-H_b), 3.41 (m, 1 H, 5-H_b), 3.63 (s, 3 H, OCH_3), 3.64 (dd, $J_{6,5}$ = 5.3, J_{gem} = 9.8 Hz, 1 H, 6-H_a), 3.72 (m, 3 H, 3-H_b, 4-H_a, 6′-H_a), 3.79 (m, 2 H, 2-H_b, 6-H_b), 3.94 (m, 1 H, 5-H_a), 4.03 (m, 2 H, 3-H_a, 4-H_b), 4.15 (m, 1 H, 2-H_a), 4.17 (m, 2 H, CH_2−CH=CH_2), 4.18 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H_b), 4.20 (d, J_{gem} = 11.8 Hz, 1 H, CHPh), 4.27 (d, J_{gem} = 11.8 Hz, 1 H, CHPh), 4.49 (m, 3 H, 3 CHPh), 4.58 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.65 (d, J_{gem} = 11.8 Hz, 1 H, CHPh), 4.75 (d, J_{gem} = 11.8 Hz, 1 H, CHPh), 4.90 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 4.93 (d, J_{gem} = 10.7 Hz, 1 H, CHPh), 5.26 (m, 2 H, CH=CH_2), 5.38 (d, $J_{1,2}$ = 2.8 Hz, 1 H, 1-H_a), 6.15 (m, 1 H, CH=CH_2), 6.24 (s, 1 H, CH), 6.65 (d, *J* = 9.0 Hz, 2 H, phenyl), 6.90 (d, *J* = 9.0 Hz, 2 H, phenyl), 7.22−7.34 (m, 35 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 55.4 (OCH_3), 67.1, 68.0, 69.3, 70.1, 71.0 (5 CH_2), 74.4 (C_b-2), 76.4 (C_b-6), 76.5 (C_a-6), 78.0 (CH_2), 78.1 (C_a-4), 79.6 (C_a-5), 81.3 (C_a-3), 81.4 (C_b-4), 81.5 (C_a-2), 83.0 (C_b-5), 89.0 (C_b-3), 89.6 (CH), 97.4 (C_a-1), 109.1 (C_b-1), 114.5, 116.6, 117.1, 117.9, 118.1, 126.6, 127.1, 127.3, 127.4, 127.6, 127.7, 127.8, 128.0, 128.1, 128.3, 128.8, 134.6, 134.9, 138.1, 138.4, 138.6, 142.0, 143.2 (C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): *m*/*z* = 1127.3 $[M + Na]^+$, 1143.3 $[M + K]^+$. $C_{70}H_{72}O_{12}$ (1105.34): calcd. C 76.06, H 6.55; found C 76.27, H 6.57.

4-Methoxyphenyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α/β-D-mannopyranosyl)-(1−6)-3-*O*-allyl-2,4-di-*O*-benzyl-α-D-mannopyranoside (28b): A solution of trichloroacetimidate **25b** (0.41 g, 0.6 mmol) and **28** (0.30 mL, 0.6 mmol) in dry dichloromethane (20 mL) was treated with TMSOTf (13 μL, 0.06 mmol) and the mixture was then stirred for 75 min. The reaction mixture was processed as above and the product was purified by column chromatography on silica gel, with petroleum ether/ethyl acetate (15:1) as eluent, to afford **28b** (0.47 g, 76%, α:β ≈ 1:1) as a colourless oil; R_f = 0.42 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = 23.3 (*c* = 2.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.35 (m, 2 H, 3-H_b, 5-H_b), 3.57 (s, 3 H, OCH_3), 3.61 (m, 2 H, 2-H_b, 6-H_a), 3.71 (dd, $J_{6,5}$ = 5.6, J_{gem} = 10.6 Hz, 1 H, 6-H_b), 3.74 (m, 2 H, 4-H_b, 6′-H_b), 3.90 (m, 3 H, 4-H_a, 5-H_a, 2-H_a), 4.00 (m, 1 H, 3-H_a), 4.16 (m, 3 H, 6′-H_a, OCH_2), 4.19 (d, $J_{1,2}$ = 2.8 Hz, 1 H, β-1-H_b), 4.37 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.41 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.49 (d, J_{gem} = 11.0 Hz, 1 H, CHPh), 4.51 (m, 3 H, 3 CHPh), 4.66 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.76 (d, J_{gem} = 10.0 Hz, 1 H, CHPh), 4.80 (d, J_{gem} = 10.0 Hz, 1 H, CHPh), 4.83 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.86 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.90 (d, J_{gem} = 10.0 Hz, 1 H, CHPh), 5.25 (d, $J_{1,2}$ = 1.1 Hz, 1 H, α-1-H_b), 5.41 (d, $J_{1,2}$ = 1.1 Hz, 1 H, 1-H_a), 5.43 (m, 2 H, CH=CH_2), 6.01 (m, 1 H, CH=CH_2), 6.67 (d, *J* = 9.0 Hz, 2 H, Ar-H), 6.90 (d, *J* = 9.0 Hz, 2 H, Ar-H), 7.17−7.38 (m, 30 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 55.4 (OCH_3), 68.5 (C_a-6), 69.7 (C_b-6), 71.1 (OCH_2), 71.2, 71.4 (2 CH_2), 72.5 (C_a-5), 72.6, 72.8 (2 CH_2), 73.3 (C_b-2), 73.6 (CH_2), 74.4 (C_a-2), 74.8 (CH_2), 74.5 (C_a-4), 74.9 (C_b-4), 75.8 (C_b-5), 79.7 (C_a-3), 82.2 (C_b-3), 92.1 (CH=CH_2), 94.8 (α-C_b-1), 96.9 (C_a-1), 101.9 (β-C_b-1), 117.8 (CH=CH_2), 127.2, 127.3, 127.4, 127.6, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5, 134.9, 138.4, 138.8 (C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): *m*/*z* = 1052.4 $[M + Na]^+$, 1068.8 $[M + K]^+$.

Methyl *O*-(3,4,6-Tri-*O*-benzyl-2-*O*-diphenylmethyl-α-D-mannopyranosyl)-(1−4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (29a): Treatment of **25a** and **8** as described for **28a** gave **29a** as a colourless oil (0.42 g, 67%). **29aα**: R_f = 0.41 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = 36.5 (*c* = 2.0, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.37 (s, 3 H, OCH_3), 3.49 (dd, $J_{2,1}$ = 3.4, $J_{2,3}$ = 9.6 Hz, 1 H, 2-H_a), 3.62 (m, 1 H, 5-H_b), 3.69 (m, 1 H, 6-H_a), 3.72 (m, 2 H, 6′-H_a, 6-H_b), 3.75 (m, 1 H, 6′-H_b), 3.81 (m, 2 H, 3-H_a, 5-H_a), 3.83 (dd, $J_{3,2}$ = 2.8, $J_{3,4}$ = 9.4 Hz, 1 H, 3-H_b), 3.90 (m, 1 H, 2-H_b), 4.10 (dd, $J_{4,3}$ = 9.4, $J_{4,5}$ = 9.5 Hz, 1 H, 4-H_b), 4.15 (m, 1 H, 4-H_a), 4.30 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.39 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.45 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.49 (m, 2 H, 2 CHPh), 4.52 (m, 2 H, 2 CHPh), 4.55 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 4.58 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1-H_a), 4.66 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 4.87 (d, J_{gem} = 10.8 Hz, 1 H, CHPh), 4.96 (d, J_{gem} = 12.0 Hz, 1 H, CHPh), 5.40 (s, 1 H, CH), 5.41 (d, $J_{1,2}$ = 1.0 Hz, 1 H, 1-H_b), 7.12−7.31 (m, 40 H, Ar-H) ppm. ^{13}C NMR (150.8 MHz, $CDCl_3$): δ = 55.2 (OCH_3), 69.3 (C_a-6), 69.4 (C_b-6), 69.8 (C_b-5), 71.6, 72.2, 72.6 (3 CH_2), 73.0 (C_a-5), 73.2, 73.3 (2 CH_2), 73.8 (C_b-2), 74.5 (CH_2), 74.7 (C_a-4), 79.6 (C_b-3), 79.8 (C_a-2), 81.0 (C_b-4), 81.4 (C_a-3), 81.5 (CH), 97.7 (C_a-1), 99.6 (C_b-1), 126.4, 126.9, 127.2, 127.3, 127.4, 127.5, 127.6, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 137.8, 138.2, 138.6, 138.9, 142.0, 142.4 (C-Ar) ppm. MS (MALDI, positive mode, matrix: DHB): *m*/*z* = 1086.0 $[M + Na]^+$, 1102.0 $[M + K]^+$. $C_{68}H_{70}O_{11}$ (1063.30): calcd. C 76.81, H 6.63; found C 76.27, H 6.60.

Methyl (2,3,4,6-Tetra-*O*-benzyl-α/β-D-mannopyranosyl)-(1−4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (29b): A solution of trichlo-

roacetimidate **25b** (0.41 g, 0.6 mmol) and glucose derivative **8** (0.28 mL, 0.6 mmol) in dry dichloromethane (20 mL) was treated with TMSOTf (13 μL, 0.06 mmol) and the mixture was then stirred for 45 min. The reaction mixture was processed as above and the product was purified by column chromatography on silica gel, with petroleum ether/ethyl acetate (10:1) as eluent, to afford **29b** (0.41 g, 69%, α:β ≈ 3:1) as a colourless oil; R_f = 0.32 (petroleum ether/ethyl acetate, 5:1). $[\alpha]_D$ = 34.0 (c = 1.0, CH_2Cl_2).

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