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Direct Chemical Synthesis of β-Mannopyranosides and Other Glycosides via Glycosyl Triflates

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Abstract: **High yield, highly stereoselective methods for the synthesis of β-mannopyranosides of primary, secondary, and tertiary alcohols are presented. Activation of mannosyl sulfoxides or mannosyl thioglycosides with trifluoromethanesulfonic anhydride or benzenesulfenyl triflate, respectively, leads to the efficient formation of α-mannosyl triflates at -78 °C in dichloromethane, in the presence of 2,6-di-*tert*-butyl-4-methylpyridine. These triflates then react S_N2-like with alcohols to give the β-mannosides. The use of a 4,6-*O*-benzylidene protected mannose is required for high selectivity, as is the use of non-participating protecting groups on *O*-2 and *O*-3 of the donors. It is further demonstrated that the thioglycoside/benzenesulfenyl triflate activation is applicable in the glucoside series, when both armed and disarmed protecting groups are tolerated.** © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Carbohydrates; Glycosidation; Stereoselection; Inversion Reactions

INTRODUCTION

The diastereoselective synthesis of β-mannopyranosides has long been recognized as one of the most challenging problems in carbohydrate chemistry[1,2]. The goal in the direct coupling of any glycosyl donor with a glycosyl acceptor to give an equatorial glycoside is essentially one of favoring an S_N2-like displacement of an axial glycosyl donor over and above the S_N1-type process which, for stereoelectronic reasons, provides mainly the axial glycoside (Scheme 1). In the mannose series the problem is compounded by the presence of the axial C-O bond adjacent to the reaction site which retards the equatorial approach of the acceptor and which, in the case of ester protecting groups, actively promotes axial glycoside formation through anchimeric assistance. Axial glycoside formation through S_N2-like displacement of a less stable but more reactive equatorial glycosyl donor is a further problem to be addressed under conditions when equilibration of the axial and equatorial donors is possible[3]. In essence, the problem can be solved by the use of an axial mannosyl donor, bearing non-participating protecting groups under conditions likely to promote concerted rather than stepwise mechanisms and retard equilibration of the axial and equatorial donors. In practice this rather black and white picture is blurred by the spectrum of intermediate ion pair mechanisms possible, separated only by incremental changes in activation energies but leading to significant changes in stereoselectivity.

In line with the above analysis the use of non-participating protecting groups for *O*-2, chiefly the 2,3-*O*-cyclic carbonate[4], 2,3-*O*-acetals[5] and simple 2-*O*-benzyl ethers[6], afforded considerable success for early workers in the field when applied in conjunction with the activation of anomeric halides by insoluble silver salts. However selectivities were less than ideal with the less reactive, more hindered acceptors and competing hydrolysis was a problem with all but the most reactive acceptors. Thus, the introduction of silver silicate as a combined insoluble silver promoter and desiccant by Paulsen[7] was a considerable advance and permitted the synthesis of numerous β-mannoside-containing oligosaccharides. Nevertheless, coupling to poorly nucleophilic acceptors remained a problem as did irreproducibility owing to the heterogeneous nature of the reaction. Schuerch introduced the use of the sulfonates as non-participating protecting groups for *O*-2 in combination with a second α-sulfonate as leaving group at the anomeric center[8,9].

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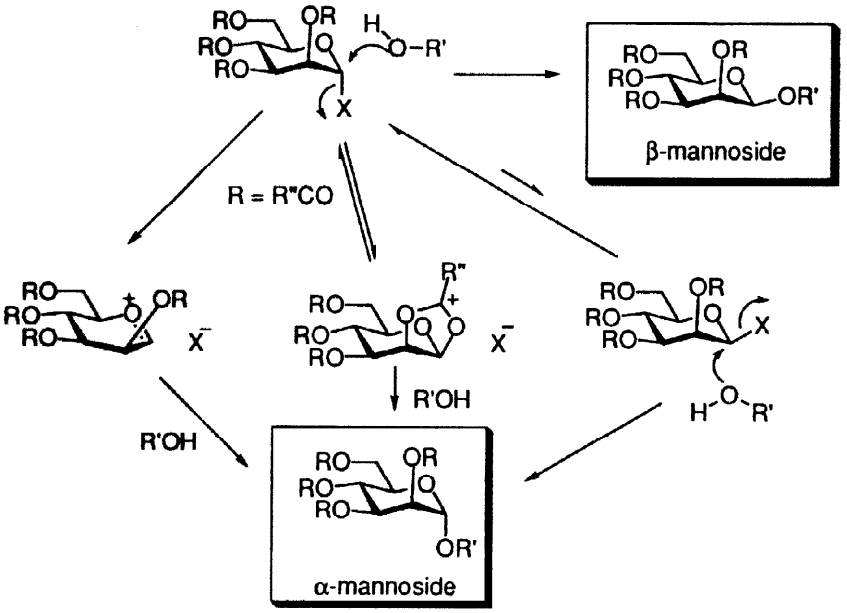
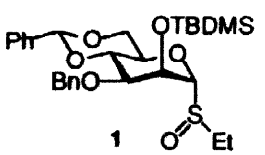


Scheme 1

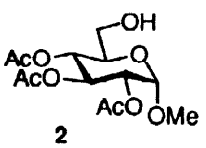
A second widely applied approach has been the synthesis of the more tractable β-glucosides followed by inversion of stereochemistry at *C*-2. This may be achieved by oxidation to the 2-ulose followed by stereoselective reduction[10-12] and by simple nucleophilc displacement, be it inter[13,14] or intramolecular[15]. A recent variant on this theme, introduced by Lichtenthaler, has been the use of α-2-ulosyl bromides as glycosyl donors leading directly to the β-2-ulosyl glycoside ready for subsequent reduction to the β-mannoside[16]. The most notable successes in totally selective β-mannoside synthesis have involved intramolecular aglycone transfer; a technique introduced by Hindsgaul[17-19] closely followed by Stork[20,21] and, later, Ogawa[22,23]. In this method the glycosyl acceptor is attached to *O*-2 of the donor in a temporary fashion by means of a mixed acetal or silylene group. As such it is poised for completely β-selective intramolecular delivery on activation of the anomeric center. Spectacular successes were recorded by all three of these groups, however, the formation of the required mixed acetal or silylene ether was not always straightforward, especially with the more hindered acceptors. Alongside these variants of the essentially classical theme of coupling of an activated glycosyl donor to a nucleophilc acceptor alcohol, several groups have sought to develop *de novo* entries into the β-mannoside linkage. These have included the α-selective quenching of 1-alkoxy-1-mannosyl radicals by suitable hydrogen atom donors[24-27] and the insertion of glycosyl carbenes into the O-H bonds of acceptor alcohols[28]. The radical method in particular gives excellent selectivity for β-mannosides but is unfortunately rendered impractical by the circuitous methods needed for generation of the key anomeric radical. Mannosyl carbenes insert into alcohol O-H bonds but unfortunately give primarily the α-mannoside[28]. Yet another approach, again pioneered by Schuerch, involves the β-selective alkylation of 1,2-*O*-dibutylstannylene derivatives of mannose[29-31]. This method, which provides pure β-mannosides, is very attractive but suffers from long reaction times with all but the simplest electrophiles. The parallel alkylation of alkali metal anomeric alkoxides with suitable electrophiles has been investigated by Schmidt[32]. Against this background of considerable ingenuity, we set out here full details of a new method developed recently in our laboratory for the facile, direct synthesis of β-mannopyransides by means of the S_N2-like displacement of α-mannosyl triflates generated *in situ* from simple thioglycosides or glycosyl sulfoxides[33-35].

RESULTS AND DISCUSSION

In pursuit of our theme of α-to β-mannoside inversion via the 1-mannosyl radical[25] we had previously synthesized the α-mannoside **4** by addition of triflic anhydride (Tf_2O) to a preformed mixture of donor **1**, acceptor **2**, and 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) in ether at -78 °C. We had anticipated that this relatively minor modifcation, involving the first use of the 4,6-benzylidene protecting group and the first documented application in the mannose series, of Kahne's excellent sulfoxide method[36,37] would lead to the α-mannoside **4** as the major product. In this we were not disappointed as **4** was isolated in 58% yield together with 6% of the β-anomer **3**[26]. Subsequently, when the need for more of **4** arose, we repeated the experiment with the, at first sight, trivial variation that the sulfoxide **1** was activated with Tf_2O at -78 °C before the acceptor **2** was added. Indeed, in his various papers on his sulfoxide glycosylation Kahne had reported both modes of addition without comment. We were therefore surprised to isolate the β-mannoside **3** as the major product (85%) together with only a minor proportion of the α-anomer (8%). Careful experimentation revealed that the reversal of stereoselectivity was simply a function of the order of addition with premixing of the two sugars and base followed by dropwise addition of Tf_2O (Protocol B) giving mainly the α-mannoside and prior activation of the sulfoxide with Tf_2O before dropwise addition of the acceptor (Protocol A) giving predominantly the β-anomer[34].



1



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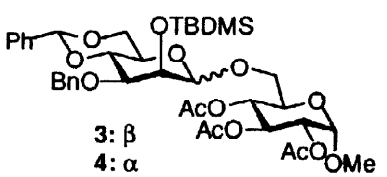
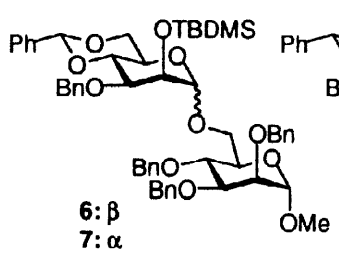
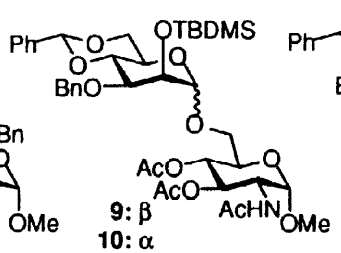


3: β
4: α

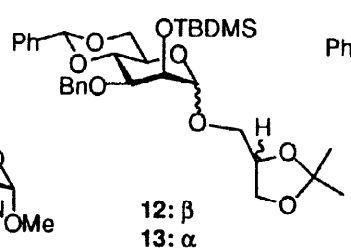
We capitalized on our discovery by coupling a number of other primary alcohols to donor **1** under the conditions of protocol A, obtaining in each case good selectivity for the β-mannoside as reported in Table 1. In certain cases we also verified that the selectivity could be reversed by use of protocol B. Furthermore, we noted that the β-selectivity under protocol A could be moderately improved in some cases by working in the presence of several equivalents of benzene, or 1,4-dimethoxybenzene, or even a slight excess of DTBMP as base (Table 1). The precise reason for the effect of these additives was unclear. Moreover, in the light of subsequent improved selectivities in dichloromethane (*vide infra*) they were insignificant and so not investigated further.



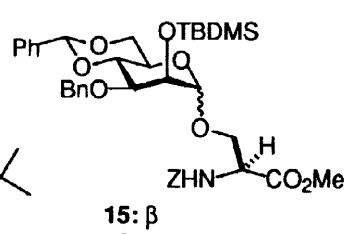
6: β
7: α



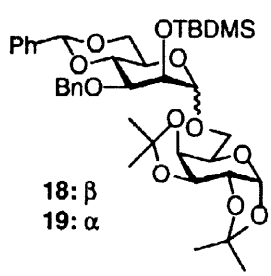
9: β
10: α



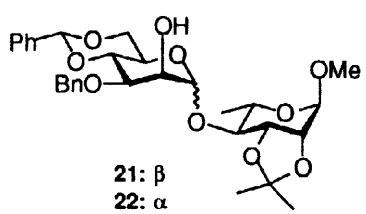
12: β
13: α



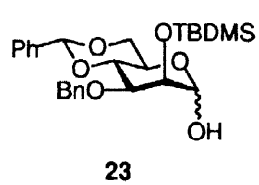
15: β
16: α



18: β
19: α

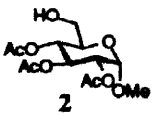
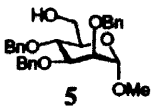
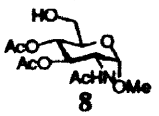
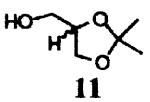
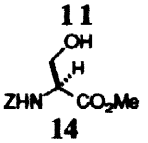
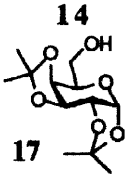
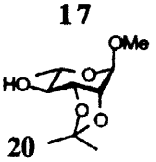


21: β
22: α



23

Table 1. Coupling of Aglycones with 1.

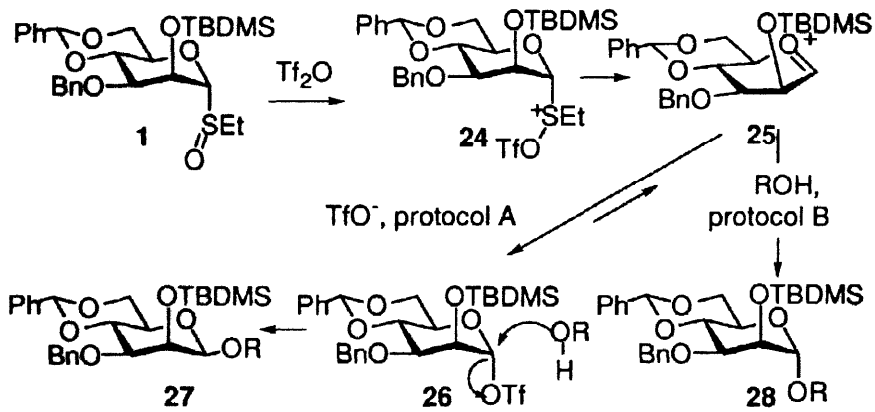
Entry	Glycosyl Acceptor	Protocol[a]	Additive	DTBMP (Equivs)	% Yield β-mannoside	% Yield α-mannoside	% Yield 23	β:α Ratio[b]
1	 2	A	C_6H_6	2	**3** (86)	**4** (8)	-	10.7:1
2	**2**	A	none	2	**3** (69)	**4** (15)	-	4.5:1
3	**2**	A	none	1	**3** (75)	**4** (15)	-	5:1
4	**2**	B	none	1	**3** (9)	**4** (71)	7	0.12:1
5	**2**	B	none	2.3	**3** (65)	**4** (22)	7	3.0:1
6	**2**	C	DMB[c]	2	**3** (82)	**4** (8)	-	10.2:1
7	 5	A	C_6H_6	2	**6** (84)	**7** (10)	-	8.6:1
8	**5**	C	DMB[c]	2	**6** (67)	**7** (8)	12	8.4:1
9	 8	A	C_6H_6	2	**9** (50)	**10** (0)	15	>20:1
10	**8**	C	DMB[c]	2	**9** (51)	**10** (0)	30	>20:1
11	 **11**	A	C_6H_6	2	**12** (64)	**13** (10)	23	6.4:1
12	**11**	C	DMB[c]	2	**12** (80)	**13** (0)	3	>20:1
13	 **14**	A	C_6H_6	2	**15** (60)	**16** (6)	25	10.0:1
14	**14**	C	DMB[c]	2	**15** (70)	**16** (7)	16	10.0:1
15	 **17**	A	C_6H_6	2	**18** (69)	**19** (12)	10	5.6:1
16	**17**	A	none	1	**18** (41)	**19** (41)	7	1.0:1
17	**17**	B	none	1	**18** (10)	**19** (72)	10	0.14:1
18	**17**	C	DMB[c]	2	**18** (61)	**19** (14)	15	4.3:1
19	 **20**	A	C_6H_6	2	**21**[d] (49)	**22**[d] (30)	20	1.6:1
20	**20**	B	none	1	**21**[d] (16)	**22**[d] (55)	13	0.29:1
21	**20**	C	DMB[c]	2	**21**[d] (50)	**22**[d] (33)	10	1.5:1

a) A: Protocol A: addition of ROH to premixed **1**, Tf_2O, and DTBMP in ether/benzene. Protocol B: addition of Tf_2O to premixed **1**, ROH and DTBMP in ether. Protocol C: as protocol A with DMB replacing benzene. b) Anomeric ratios were assigned by integration of ^{1}H-NMR spectra of crude reaction mixtures. c) DMB: 1,4-dimethoxybenzene. d) Isolated after treatment of the reaction mixture with TBAF.

Attempted coupling of **1** to the secondary glycosyl acceptor **20** was disappointing under all conditions in ether, giving both low yields and selectivites (Table 1, entries 19 -21). Furthermore, significant yields of the hydrolysis product **23** were obtained in the attempted couplings to **20**, as in several other reactions (Table 1).

We reasoned that the unanticipated reversal of selectivity with the sequence of mixing of reagents could best be interpreted as outlined in Scheme 2[33]. According to this rationale, Tf_2O serves to activate **1** in the form of **24** which rapidly expels a sulfenate ester to give the oxacarbenium cation **25**. In protocol A, in the absence of other nucleophiles, **25** is trapped axially by triflate anion to give the glycosyl triflate **26**. On addition of the acceptor ROH an S_N2-like reaction then occurs to give the β-mannoside **27**. Under the conditions of protocol B, oxacarbenium cation **25** is simply trapped preferentially by ROH along the axial direction to give the α-mannoside **28**. When ROH is a secondary alcohol the direct displacement of TfO^- from **26** is retarded for steric reasons and leads to the formation of **28**, via **25**, even with protocol A.

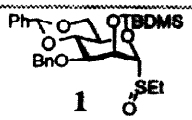
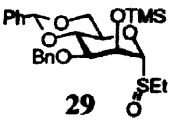
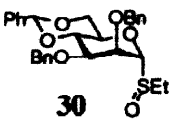
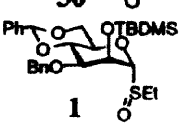
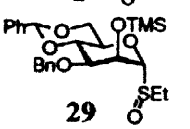
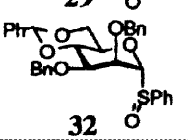
On the basis of this hypothesis it was predicted that reducing the bulk of the *O*-2 protecting group would lead to greater β:α-ratios for secondary glycosyl acceptors. Therefore, glycosyl donors **29** and **30** were prepared and reacted with the secondary glycosyl acceptor **20** under the conditions of protocol A in ether giving rise to the formation of the corresponding β- and α-mannopyranoside in the yields and ratios indicated in Table 2, entries 1-3. Clearly, reducing the steric bulk of the *O*-2 protecting group does indeed lead to enhanced β-selectivity.



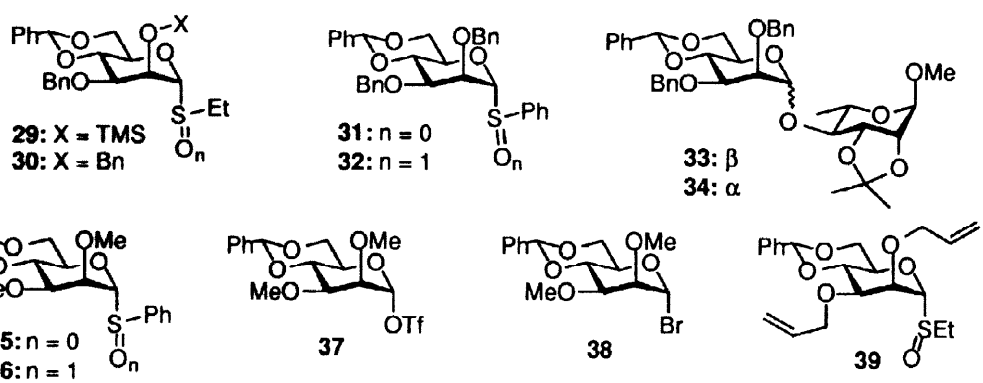
Scheme 2

A further prediction of the hypothetical mechanism set out in Scheme 2 is that going from ether to a less ionizing solvent such as dichloromethane should lead to a futher enhancement in selectivity. Hence a series of reactions were conducted in which donors **1**, **29**, and **32** were activated with Tf_2O in dichloromethane in the presence of DTBMP at -78 °C, followed by addition of the acceptor (Protocol D). As is seen from Table 2, entries 4 - 6 the yields and selectivities were indeed improved over and above those from comparable reactions in ether, with a simlar trend of increased selectivity with diminishing size of the *O*-2 protecting group being observed.

Table 2. **Reaction of Glycosyl Donors with 20** in Ether and Dichloromethane.

Entry	Donor	Solvent	Protocol[a]	% Yield β-mannoside	% Yield α-mannoside	β:α Ratio[b]
1	 **1**	Et_2O	A	(**21**)[c] 49	(**22**)[c] 30	1.6:1
2	 **29**	Et_2O	A	(**21**)[c] 76	(**22**)[c] 15	5.1:1
3	 **30**	Et_2O	A	(**33**) 74	(**34**) 11	6.7:1
4	 **1**	CH_2Cl_2	D	(**21**)[c] 82	(**22**)[c] 11	7.5:1
5	 **29**	CH_2Cl_2	D	(**21**)[c] 92	(**22**)[c] 7	13.1:1
6	 **32**	CH_2Cl_2	D	(**33**) 90	(**34**) 0	>25:1

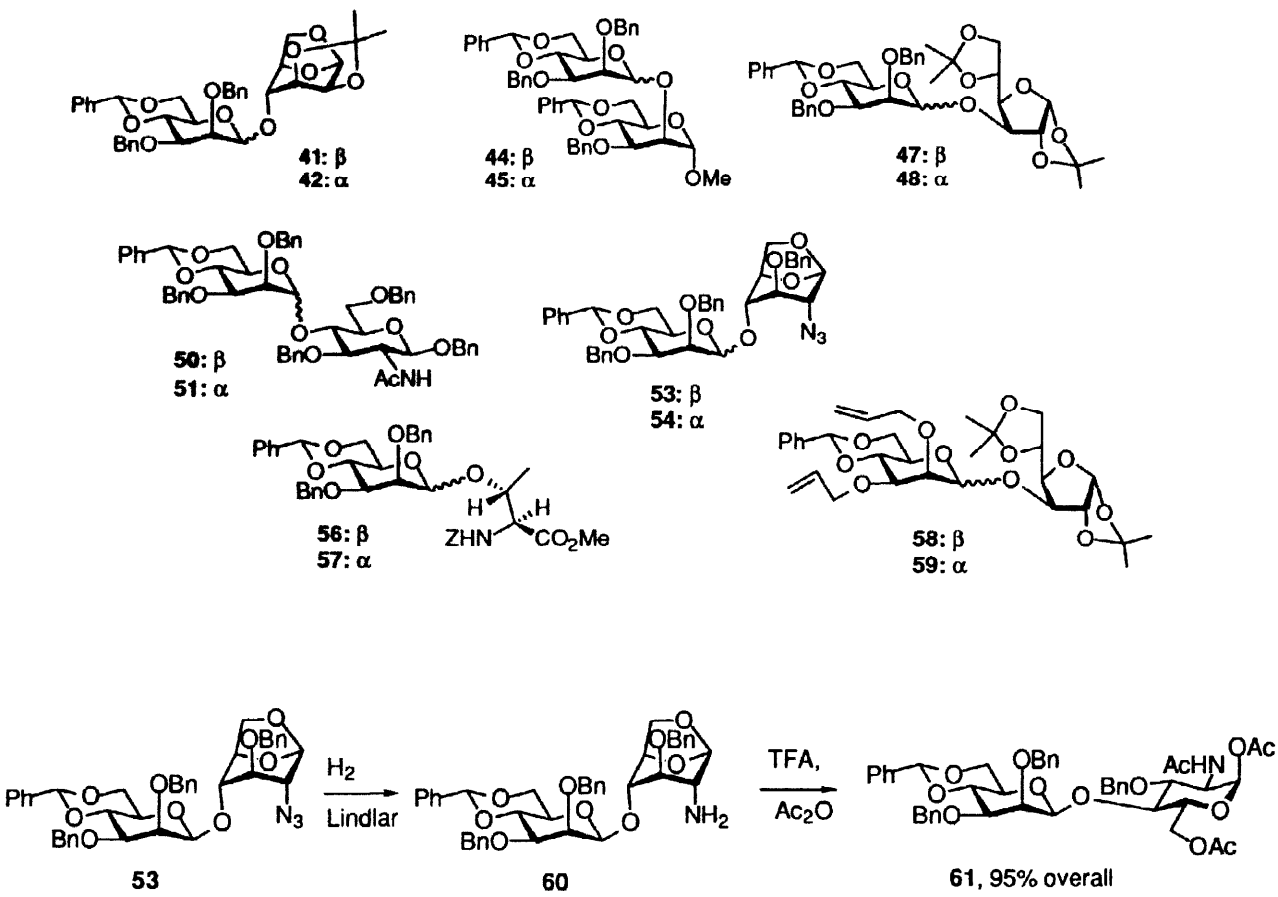
a) A: Protocol A: addition of ROH to premixed donor, Tf_2O, and DTBMP in ether/benzene; Protocol D: addition of ROH to premixed donor, Tf_2O, and DTBMP in CH_2Cl_2. b) Anomeric ratios were assigned by integration of ^{1}H-NMR spectra of crude reaction mixtures. c) Isolated after treatment of the reaction mixture with TBAF.



This series of experiments lends considerable weight to the mechanistic hypothesis of Scheme 2 but is not a proof. However, in a series of experiments reported separately[38] we have demonstrated by a combination of ^{1}H, ^{13}C, and ^{19}F-NMR spectroscopy that sulfoxide **36** is converted cleanly to the α-triflate **37** in CD_2Cl_2 within minutes at -78 °C. Moreover, this unstable triflate, which could also be accessed by exposure of bromide **38** to AgOTf in CD_2Cl_2 at -78 °C reacted instantaneously with methanol at -78 °C with good selectivity for formation of the methyl β-mannoside[38].

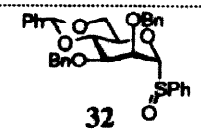
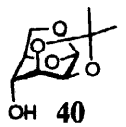
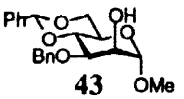
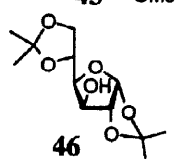
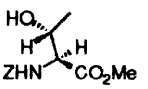
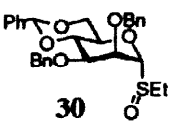
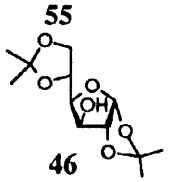
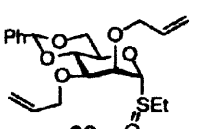
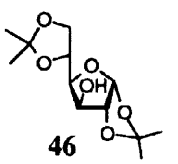
We next turned to coupling of a representative range of secondary alcohols with the 2,3-di-*O*-benzyl protected donors **30** and **32**, and with the 2,3-di-*O*-allyl protected analogue **39** by protocol D. As is evident from the results presented in Table 3, with one exception, the results were mostly excellent in terms of yield

and selectivity. We note from a comparison of entries 3 and 7 (Table 3) that the *S*-phenyl and *S*-ethyl sulfoxides may be used essentially interchangeably in this chemistry. This could be of future importance when it may be neccessary to work in different solvents to accomodate particular acceptors, as the two donors have different solubility patterns. We also note from comparison of entries 7 and 8 (Table 3) that the 2,3-di-*O*-allyl protected donor **39** is comparable with its 2,3-di-*O*-benzyl protected congenors: there is no tendency of the 2-*O*-allyl group to intercept the activated donor at any stage of the coupling process. The one example of poor yield and selectivity (Table 3, entry 4) involved the use of alcohol **49** as glycosyl acceptor. The 4-OH group of *N*-acetylglucosamine derivatives is a notoriously unreactive alcohol in glycosylation reactions and thus the result was not entirely unexpected. However, we do note that the low yield and selectivity is in part due to the insolubility of **49** in CH_2Cl_2 at low temperature which meant that coupling typically did not occur until the reaction mixture was allowed to warm up and the acceptor dissolve. We were largely able to circumvent this problem by adapting a method previously described by Paulsen[39]. Thus, the more reactive and soluble 1,6-anhydroglucosamine derivative **52** was found to couple with donor **32** in good yield and adequate selectivity (Table 3, entry 5). After isolation of the β-mannoside (**53**) by chromatography over silica gel, it was reduced to the corresponding amine (**60**) with hydrogen over Lindlar's catalyst. Finally, the 1,6-anhydro bridge was cleaved and the amine acylated by exposure to acetic anhydride and trifluoroacetic acid giving **61** in 95% overall yield (Scheme 3).



Scheme 3

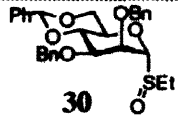
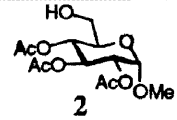
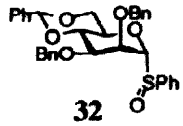
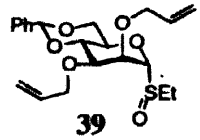
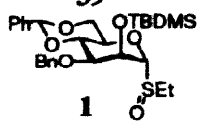
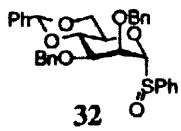
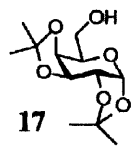
Table 3. Coupling of Secondary Acceptors to 30, 32, and 39 in Dichloromethane.

Entry	Donor	Acceptor	% Yield β-mannoside	% Yield α-mannoside	β:α Ratio[a]
1	 **32**	 **40**	(**41**) 93	(**42**) 5	18.6:1
2	**32**	 **43**	(**44**) 90	(**45**) 6	15.0:1
3	**32**	 **46**	(**47**) 94	(**48**) 5	18.8:1
4	**32**	 **49**	(**50**) 31	(**51**) 8	3.8:1[b]
5	**32**	 **52**	(**53**) 72	(**54**) 13	5.5:1
6	**32**	 **55**	(**56**) 94	(**57**) 3	31.3:1
7	 **30**	 **46**	(**47**) 91	(**48**) 7	13.0:1
8	 **39**	 **46**	(**58**) 90	(**59**) 7	12.9:1

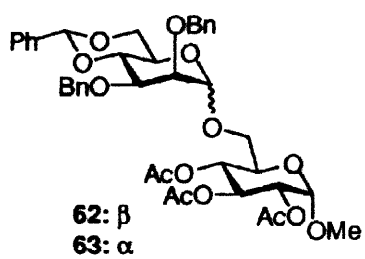
a) Anomeric ratios were assigned by integration of ^{1}H-NMR spectra of crude reaction mixtures. b) the reaction mixture was allowed to come to room temperature and stirred there for 24 h before workup.

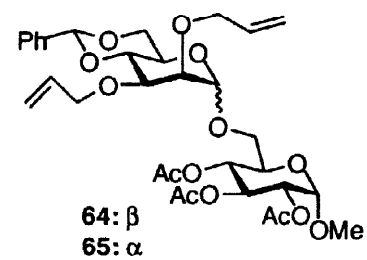
We also returned briefly to the mannosylation of primary acceptors, now using protocol D in CH_2Cl_2 as solvent. As is evident from Table 4, the full range of *O*-2 protecting groups investigated in the donor is compatible with coupling to the acceptor **2**. Excellent selectivities are even obtained with the original 2-*O*-TBDMS donor (**1**). However, we do draw attention to the relatively poor selectivity achieved on coupling to 1,2:3,4-di-*O*-isopropylidenegalactose (**17**) (Table 4, entry 6). This primary acceptor gives lower yields and selectivites than most of the secondary alcohols studied in Table 3. Indeed, the inadequacy of this alcohol as an acceptor in the β-mannosylation sequence was already evident in the early work in ether as solvent (Table 1, entries 15 - 18).

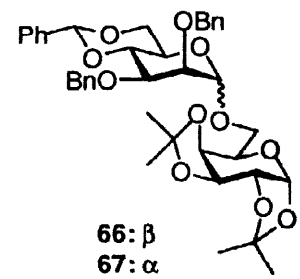
Table 4. Mannosylation of Primary Acceptors in Dichloromethane.

Entry	Donor	Acceptor	% Yield β-mannoside	% Yield α-mannoside	β:α Ratio[a]
1	 30	 2	(62) 95	(63) 0	>25:1
2	 32	2	(62) 95	(63) 0	>25:1
3	 39	2	(64) 91	(65) 4	22.8:1
4	 1	2	(3) 95	(4) 4	23.8:1
6	 32	 17	(66) 73	(67) 13	5.6:1

a) Anomeric ratios were assigned by integration of ^{1}H-NMR spectra of crude reaction mixtures.

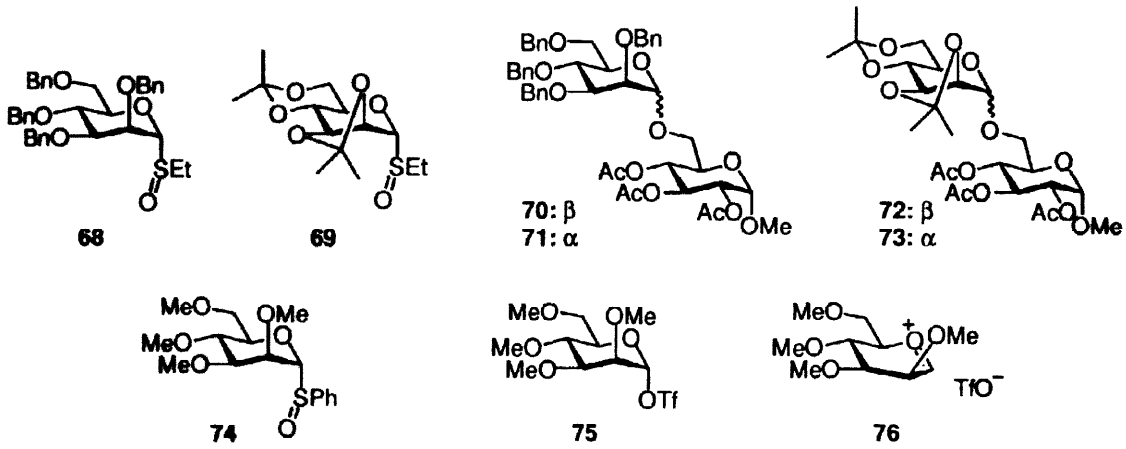






Through the aegis of sulfoxides **68** and **69** we have also briefly investigated the use of protecting systems other than the 4,6-benzylidene group employed in the majority of this work. Both the 2,3,4,6-tetra-*O*-benzyl and 2,3:4.6-bis-*O*-acetal protecting systems were employed with some success by previous workers in the field using the insoluble silver salt method to activate the glycosyl halides[5,6]. We were therefore disappointed to find, early in our program, that coupling of **68** to the primary acceptor **2** in ether according to protocol A gave only 16% of the β-mannoside **70**, together with 33% of the α-anomer **71**. This selectivity (β:α = 0.5:1) was far inferior to any couplings conducted with the 4,6-benzylidene protected donor **1** under the same conditions (Table 1) and, indeed, worse than the selectivity obtained by Wulff and Wichelhaus for formation of the same disaccahrides by the insoluble silver salt method[6]. The use of **68** was therefore not pursued further. We were similarly disappointed by the poor selectivity (1:1) obtained, despite the high combined yield (86%), for the formation of **72** and **73** on coupling of **69** with **2** under the optimal conditions of protocol D. Again, this selectivity was substantially worse than that obtained with a closely related donor by the insoluble silver salt method by Garegg[5]. Low temperature NMR studies with **74**, a simplified analogue of **68**, have shown that it is rapidly and cleanly converted to the α-triflate **75** on exposure to Tf_2O and DTBMP in

CD_2Cl_2 at -78 °C[38]. However, it was also demonstrated that triflate **75** is considerably less stable than the 4,6-benzylidene analogue **37** at -78 °C in CD_2Cl_2. We hypothesize that **37** is torsionally disarmed with respect to collapse to the ion pair, whereas **75** is in dynamic equilibrium with the (invisible on the NMR timescale) ion pair **76**, which results in α-mannoside formation. Thus, the importance of the 4,6-benzylidene protecting group in this β-mannosylation reaction is seen to be related to its ability to stabilize the intermediate triflates with respect to ion pair formation[38]. We have not conducted any mechanistic work with sulfoxide **69** but speculate that it fails for similar reasons. Either the axial methyl group in the 4,6-acetonide destabilizes the chair-chair system to such an extent that collapse of the intermediate triflate to the ion pair is facilitated, or ion pair formation relieves strain due to the fused 2,3-*O*-acetonide.

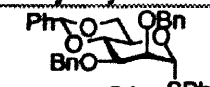
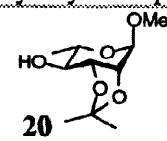
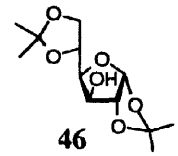
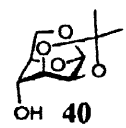
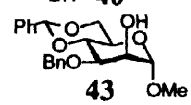
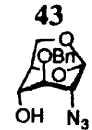
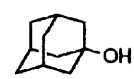
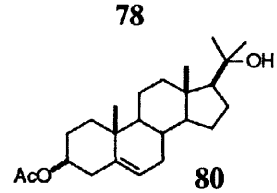
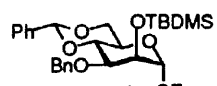
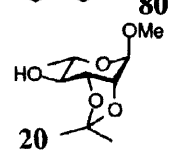
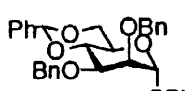
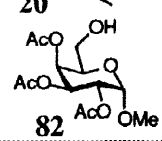


Our work on the mechanism of the sulfoxide/triflate interconversion also revealed to us the highly electrophilic nature of phenylsulfenyl triflate (PhSOTf)[38]. This substance is a necessary byproduct of the activation of the phenyl sulfoxides (**32**, **36**, **74**), however, ^{19}F-NMR experiments with **36** and **74** established that it is not present in CD_2Cl_2 solutions after treatment of the sulfoxides with Tf_2O even though formation of the glycosyl triflates (**37**, **75**) is complete. Thus, we came to the realization that PhSOTf is itself an extremely potent electrophile and serves to activate the sulfoxides, and transform them to the glycosyl triflates, as it is formed in the reaction mixture. This hypothesis was readily confirmed by the clean transformation of **36** to **37** on treatment with a stoichiometric amount of authentic PhSOTf[38]. The efficiency of the sulfoxide glycosylation method is such that the most problematic step is often the controlled oxidation of a thioglycoside to the requisite sulfoxide, which requires careful control of stoichiometry, and temperature, as well as continuous monitoring by TLC[36,37,40]. Indeed, this step promises to be problematic in any future development of solid phase glycosylation protocols involving resin-bound sulfoxide glycosyl donors. This impending problem and the evident, highly electrophilic nature of PhSOTf, prompted us to investigate the potential activation of simple thioglycosides by this reagent. In the event, it was readily demonstrated by low temperature NMR spectroscopy that the thioglycoside **35** was immediately and quantitatively converted to the triflate **37** on exposure to one equivalent of PhSOTf in the presence of DTBMP in CD_2Cl_2 at -78 °C. Thus, either sulfoxide **35**, thioglycoside **36**, or bromide **38** were shown to provide the same triflate, on the same timescale, on exposure to Tf_2O, PhSOTf, or AgOTf, respectively, in CD_2Cl_2 at -78 °C, always in the presence of DTBMP as base[35].

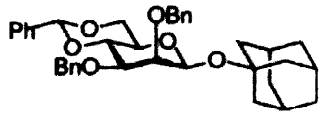
A series of preparative scale β-mannosylations with thioglycosides **31** and **77** were conducted with the results displayed in Table 5[35]. In these reactions, the unstable PhSOTf is first generated in CH_2Cl_2 solution at -78 °C by treatment of a mixture of DTBMP and phenylsulfenyl chloride with AgOTf, much as described by Whitesides and Martichonok[41,42]. The thioglycoside is then added followed, after a few minutes, by the acceptor (Protocol E). The complete operation is therefore conducted in one pot at -78 °C making this a very convenient procedure. The yields and selectivities in Table 5 require little further comment: with the secondary

alcohols as acceptors they are in every way comparable to those obtained by the sulfoxide method in CH_2Cl_2 (Table 3). We simply draw attention to entries 6 and 7, which we believe to be the first examples of selective formation of β-mannosides of tertiary alcohols, and to entry 9 in which the donor **31** is coupled to the primary galactosyl alcohol **82** in excellent yield and selectivity. The interest in last example derives from the contrast with mannosylations of the related galactose derivative **17** (Table 4, entry 6). As discussed above, **17** is a relatively poor acceptor in this chemistry, giving lower yields and selectivities. At the present time we do not have a satifactory explanation for the difference in reactivity of the two galactose derivates (**17** and **82**).

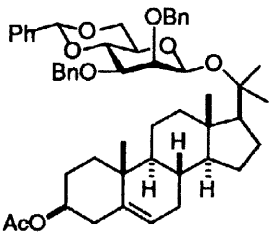
Table 5. β-Mannoside Formation from Thioglycosides with PhSOTf in Dichloromethane.

Entry	Glycosyl Donor	Glycosyl Acceptor	Product (% Yield)	β:α Ratio[a]
1	 **31**	 **20**	(**33**) 95	>25:1
2	**31**	 **46**	(**47**) 95	>25:1
3	**31**	 **40**	(**41**) 95	23:1
4	**31**	 **43**	(**44**) 97	18:1
5	**31**	 **52**	(**53**) 85	5.1:1
6	**31**	 **78**	(**79**) 94	>25:1
7	**31**	 **80**	(**81**) 90	>25:1
8	 **77**	 **20**	(**21**)[b] 80	10:1
9	 **31**	 **82**	(**83**) 82	>25:1

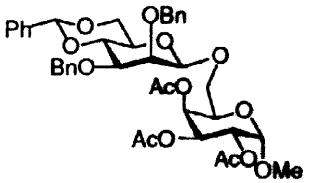
a) Anomeric ratios were assigned by integration of ^{1}H-NMR spectra of crude reaction mixtures. b) After treatment with TBAF



79



81



83

Table 6. Diagnostic NMR and Specific Rotation Data for Mannopyranosides

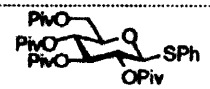
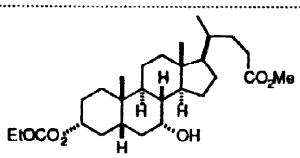
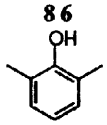
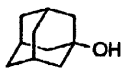
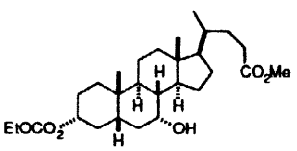
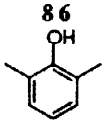
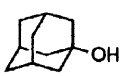
Cmpd	Config	δH-1	$^3J_{1,2}$	δH-5	δC-1	$[\alpha]_D$
3	β	4.26-4.36[a]	bs	3.25-3.34	102.5	+40
4	α	4.69	1.5	NR[b]	96.6	+69
6	β	4.26	bs	3.21-3.29	102.2	+0.3
7	α	4.78	1.7	NR[b]	101.7	+13
9	β	4.32	bs	3.23-3.32	102.5	+12.7
12	β	4.39	bs	3.24-3.32	102.1/101.5[c]	-43.3
13	α	4.68/4.72[c]	1.7	NR[b]	101.9	+21
15	β	4.30	bs	3.22-3.30	102.0	-34.1
16	α	4.58	1.6	NR[b]	102.2	+7.8
18	β	4.42	bs	3.25-3.34	102.5	-69.7
19	α	4.74	1.6	NR[b]	101.6	-21.8
21	β	4.84	bs	3.29-3.40	98.7	-21.1
22	α	4.94	1.2	NR[b]	100.6	+25
33	β	4.87	bs	3.27-3.38	100.0	-61.0
34	α	NR[b]	NR[b]	NR[b]	100.3	+37
41	β	4.68	bs	3.29-3.39	100.4	-48.8
42	α	4.91	1.5	NR[b]	99.1	+25.0
44	β	4.63	bs	3.28-3.37	99.4	-44.8
45	α	5.23	1.5	NR[b]	100.9	-0.9
47	β	4.56	bs	3.28-3.37	100.1	-38.6
48	α	5.22	1.4	NR[b]	99.8	+15.7
50	β	4.57	bs	3.08-3.19	101.7	-38.7
51	α	5.28	1.5	NR[b]	100.5	+2.7
53	β	4.76	bs	3.30-3.40	100.6	-29.2
54	α	4.71	1.4	NR[b]	100.4	+52.0
56	β	4.46	bs	3.18-3.28	99.7	-29.7
57	α	4.76	1.4	NR[b]	100.7	+45.6
58	β	4.57	bs	3.20-3.40	99.7	-43.5
59	α	5.16	1.5	NR	100.2	+20.1
62	β	4.48	0.6	3.26-3.35	102.4	+16.8
63	α	NR[b]	NR[b]	NR[b]	99.3	+92.8
64	β	4.46	bs	3.24-3.34	102.0	+36.2
65	α	NR[b]	NR[b]	NR[b]	99.5	+9.69
66	β	4.55	bs	3.26-3.36	102.8	-79.2
67	α	4.93	1.4	NR[b]	98.9	-5.3
70	β	4.38	bs	NR[b]	101.9	+22.7
71	α	NR[b]	NR[b]	NR[b]	98.1	+65.2
72	β	4.86	bs	3.21-3.30	98.9	+25.8
73	α	5.03	bs	NR[b]	97.8	+96.3
79	β	4.75	0.8	3.26-3,37	94.8	-19.9
81	β	4.66	bs	3.25-3.37	96.4	-65.0
83	β	4.45	bs	3.15-3.28	102.5	+16.7

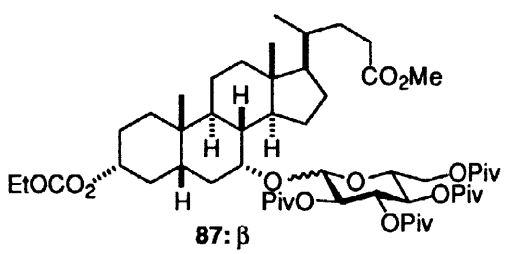
a) Part of an unresolved 2H multiplet. b) NR = not resolved. c) Resolved signals arising from the mixture of diastereomers in the aglycone.

The assignment of anomeric configuration in the mannopyranosides is not straightforward. Neither the chemical shifts of the anomeric protons, nor the $^3J_{H1-H2}$ scalar couplings are sufficiently differentiated between the α- and β-series to permit unambiguous assignment on the basis of ^{1}H-NMR spectroscopy alone (Table 6). In the β-series, the observance of nOe correlations between the axial anomeric hydrogen and those at *C*-3 and/or 5 are diagnostic. Also, extremely useful is the magnitude of the $^1J_{CH}$ coupling between *H*-1 and *C*-1 wherein a value of around 160 Hz signifies the β-configuration and 170 Hz the α-mannoside[43]. In the work described here, the stereochemistry of each new β-mannoside was confirmed by nOe experiments. However, as the work has progressed and we acquired a library of spectral data, we also noted that in the 4,6-benzylidene protected series the β-mannoside is immediately recognized by an isolated multiplet resonating at ~ δ 3.3-3.4 in the ^{1}H-NMR spectrum in $CDCl_3$ (Table 6). This signal, which is assigned to the β-mannoside *H*-5, is shifted downfield in the corresponding α-anomers when it typically appears at δ 3.6 - 3.9. With this in mind, and if NMR time is at a premium, a simple ^{1}H spectrum can be used to gauge the anomeric configuration until such a time as it can be confirmed by the more rigorous nOe and ^{13}C methods. In the same context, we also recall Hudson's classical isorotation rule[44-46], wherein a particular β-mannoside has less positive/more negative specific rotation than the corresponding α-anomer (Table 6), and which affords a rough and ready guide to anomeric configuration until more rigorous NMR work can be done, provided that both anomers are available.

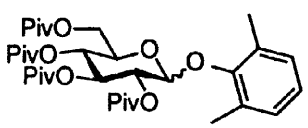
The new protocol (E) for the activation of thioglycosides with PhSOTf is not limited to the preparation of β-mannopyranosides. Table 7 sets out several examples of glucoside formation using a disarmed (**84**) and an armed (**85**) thioglucoside as donor[35]. The acceptors are chosen for ease of comparison of the new method with the sulfoxide protocol[36,37]. Of the six examples presented in Table 7, four require comment, otherwise the results are directly analogous to those reported previously for the sulfoxide method. With the highly hindered sterol **86**, thioglycoside **84** gave 61% of a pure β-glucoside (**87**) when the reaction was run in CH_2Cl_2/Et_2O (Table 7, entry 1). In either pure Et_2O or pure CH_2Cl_2 the yield in this last example was considerably lower owing to the low solubility of one or other of the two reaction partners in one of the two solvents. Coupling of the perpivaloyl thioglycoside **84** and 2,6-dimethylphenol (**89**) under the influence of PhSOTf gave 49% of the α- and 37% of the β-glycoside (Table 7, entry 2). This result differs somewhat from the analogous coupling achieved by the sulfoxide method when an 80% yield of a pure β-glucoside was reported. This difference must reflect minor variations in temperature and concentration and so changing influences of triflates, ion pairs, and neighboring group participation on the actual glycosylation subsequent to the initial formation of glucosyl triflates. Finally, we note that the tertiary alcohol **78** could be coupled to either an armed or disarmed[47] thioglucoside in excellent yield and complete β-selectivity (Table 7, entries 3 and 6). These results correspond to those described by Kahne for tertiary alcohols by the sulfoxide method[48] and presumably reflect the increased influence of 1,3-diaxial interactions in the formation of α-glycosides with tertiary alcohols. Self-evidently, given that both methods generate the same reactive glycosyl triflates, the sulfoxide/Tf_2O and thioglycoside/PhSOTf afford very similar results in most cases and may be seen as interchangeable. Nevertheless, both have advantages and disadvantages. The main strongpoint of the thioglycoside/PhSOTf method is the ability to proceed directly with the thioglycoside, without needing the extra oxidation step. Aside from the obvious advantage of removing a step from the reaction sequence, this should prove useful, as we have noted above, under conditions where control of the oxidation would be difficult. A further advantage of the thioglycoside/PhSOTf method lies in the fact that diphenyl disulfide is the main byproduct, as compared to the sulfoxide method in which PhSOSPh is generated *in situ* before undergoing disproportionation of to a mixture of the various higher oxidation states of diphenyl disulfide[38,49]. The main disadvantage of the thioglycoside/PhSOTf method is the need to generate PhSOTf *in situ* prior to the coupling, which in turn necessitates the preparation and distillation of PhSCl. The strongpoint of the sulfoxide method is that activation is achieved with commerical Tf_2O. When conducting mechanistic studies of the intermediate triflates on a small scale by low temperature NMR spectroscopy, the sulfoxide/Tf_2O method is preferable as the number of manipulations are kept to a minimum.

Table 7. Fomation of Hindered Glycosides from Thioglycosides with PhSOTf in Dichloromethane.

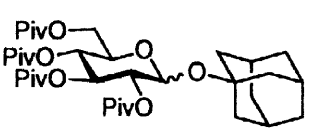
Entry	Glycosyl Donor	Glycosyl Acceptor	Solvent	β-glucoside (% Yield)	α-glucoside (% Yield)
1	 **84**	 **86**	1/1 CH_2Cl_2/Et_2O	(**87**) 61	(**88**) 0
2	**84**	 **89**	CH_2Cl_2	(**90**) 37	(**91**) 49
3	**84**	 **78**	CH_2Cl_2	(**92**) 84	(**93**) 0
4	 **85**	 **86**	Et_2O	(**94**) 0	(**95**) 85
5	**85**	 **89**	CH_2Cl_2	(**96**) 26	(**97**) 67
6	**85**	 **78**	CH_2Cl_2	(**98**) 93	(**99**) 0



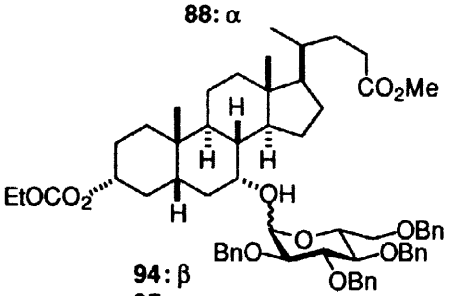
87: β
88: α



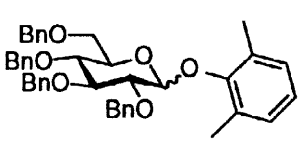
90: β
91: α



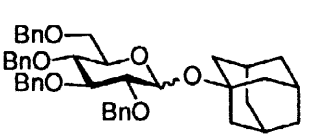
92: β
93: α



94: β
95: α



96: β
97: α



98

98: β
99: α

It is appropriate to note that methylsulfenyl triflate (MeSOTf) has previously been described as a reagent for the activation of thioglycosides[50,51], however it has not been widely adopted. Indeed, MeSOTf has been

found to be less satisfactory than PhSOTf for the activation of glycosyl xanthates[41]. A major difference between the work reported here and previous work on the activation of thioglycosides by sulfenyl triflates is the mode of operation. Earlier work has tended to involve the addition of the sulfenyl triflate to preformed mixtures of the thioglycoside and the acceptor, and is therefore akin to Scheme 2, protocol B. The key to the successful generation of glycosyl triflates and their very attractive chemistry, however, is the prior activation of the thioglycoside by PhSOTf in a suitable solvent at low temperature before addition of the acceptor. Benzeneselenenyl triflate (PhSeOTf) has also been recorded as a reagent for the activation of thioglycosides[52]. In our hands exposure of thioglycoside **35** to PhSeOTf in CD_2Cl_2 at –78 °C did not result in the formation of triflate **37** as determined by NMR spectroscopy. Rather an unidentified species was formed which returned the thioglycoside on exposure to MeOH at –78 °C: PhSeOTf is therefore less efficient than PhSOTf for the activation of thioglycosides at low temperature.

Finally, we stress that we are not the first to exploit the use of mannosyl sulfonates as glycosyl donors. This honor goes to Schuerch who typically prepared mannosyl toluenesulfonates from the corresponding glycosyl halides and silver toluenesulfonate[8,9]. Aside from the use of α-mannosyl sulfonates, the Schuerch chemistry was characterized by the use of a 2-*O*-sulfonyl protecting group, when β-mannosides were indeed obtained in good yield and selectivity. Evidently, the 2-*O*-sulfonyl esters are non-participating and, in more recent terminology[47], deactivating which permitted S_N2-like displacements in the absence of the 4,6-benzylidene protecting group and at higher temperatures. Unfortunately, possibly due to the inconvenient preparation and isolation of the intermediates sulfonate esters and the difficulties involved in removing sulfonyl ester protecting groups, Schuerch's method has not been widely applied. The distinct advantage of the chemistry described here is the ability to prepare the extremely reactive α-mannosyl triflates cleanly and quantitatively at low temperature *in situ* from stable glycosyl sulfoxides or thioglycosides.

EXPERIMENTAL PART

General Procedures. NMR experiments were conducted at 300 MHz for ^1H and ^{13}C, respectively, in $CDCl_3$ unless otherwise stated. Chemical shifts are downfield from tetramethylsilane. ^{19}F-NMR spectra were recorded at 282 MHz with chemical shifts downfield from trifluoroacetic acid. Specific rotations are for chloroform solutions. All solvents were dried and distilled by standard techniques. All reactions were conducted under inert atmospheres (N_2 or Ar). All extractions were dried over Na_2SO_4 and concentrated under vacuum at room temperature. Ether refers to diethyl ether. Microanalyses were conducted by Midwest Microlabs, Indianapolis. Glycosyl donors **1**[26], **35**[38], **77**[26], **84**[40], and **85**[53], and acceptors **2**[54], **5**[9], **8**[55], **14**[56], **20**[57], **40**[58], **43**[59], **49**[60], **52**[61], **55**[62], **80**[63], **82**[64], and **86**[65] were prepared by literature methods. Other glycosyl acceptors were either commercial or prepared as described in sequence below.

Protocol A. Synthesis of β-Mannopyranosides of Primary Alcohols from 1 in Ether. To a stirred solution of sulfoxide (**1**) (0.2 mmol) and DTBMP (82.1 mg, 0.4 mmol) in benzene-ether (1:7, 8.0 mL) at -78 °C was added Tf_2O (37.0 μL, 0.22 mmol) and, 5 min later, dropwise, the solution of the glycosyl acceptor (0.4 mmol) in ether (2 mL). The opaque reaction mixture was stirred at -78 °C for 1-2 h and then allowed to warm to 0 °C over 1-2 h and maintained there for a further 0.5 h before quenching with saturated aqueous $NaHCO_3$, washing with brine, drying, concentration and purification by chromatography on silica gel.

Protocol B. Synthesis of α-Mannopyranosides of Primary Alcohols from 1 in Ether. To a stirred solution of the sulfoxide (**1**) (0.2 mmol), DTBMP (41.1 mg, 0.2 mmol), and the glycosyl acceptor (0.4 mmol) in dry ether (10 mL) at -78 °C was added dropwise triflic anhydride (37.0 μL, 0.22 mmol). The turbid reaction mixture was stirred at this temperature for 1-2 h and then allowed to warm to 0 °C over 1-2 h and maintained there for a further 0.5 h before quenching with saturated aqueous $NaHCO_3$, washing with brine, drying, concentration and purification by chromatography on silica gel.

Protocol C. Synthesis of β-Mannopyranosides of Primary Alcohols from 1 in Ether. This protocol is analogous to Protocol A except that benzene as a cosolvent was replaced by 4 molar equiv (with respect to the sulfoxide) of 1,4-dimethoxybenzene.

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-[3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(*t*-butyldimethylsilyl)-β-D-mannopyranosyl]-(1→6)-α-D-glucopyranoside (3). $[\alpha]_D^{20}$ = +40.0° (c = 0.6); ^{1}H-NMR, δ: 0.13 (s, 3H), 0.16 (s, 3H), 1.25 (s, 9H), 2.01 (s, 3H), 2.04 (s, 3H), 2.07 (s, 3H), 3.25-3.34 (m, 1H), 3.40 (s, 3H), 3.43-3.55 (m, 2H), 3.84-4.10 (m, 3H), 4.09 (t, J = 9.4 Hz, 1H), 4.17 (d, J = 2.6 Hz, 1H), 4.26-4.32 (m, 2H), 4.72 (d, J = 12.4 Hz, 1H), 4.78 (d, J = 12.4 Hz, 1H), 4.85 (dd, J = 3.6, 9.8 Hz, 1H), 4.93 (d, J = 3.6 Hz, 1H), 5.05 (t, J = 9.8 Hz, 1H), 5.50 (t, J = 9.8 Hz, 1H), 5.60 (s, 1H), 7.24-7.41 (m, 8H), 7.48-7.52 (m, 2H); ^{13}C-NMR, δ: -4.9, -4.2, 18.5, 20.7, 25.9, 55.5. 67.6, 68.3, 68.6, 68.7, 68.8, 70.0, 70.8, 71.1, 72.14, 77.7, 78.7, 96.5, 101.4, 102.5, 126.0, 127.4, 127.7, 128.1, 128.1, 128.8, 137.5, 138.3, 169.7, 170.1; IR, υ: 2932, 1749, 1602 cm^{-1}. Anal. Calcd. for $C_{39}H_{54}O_{14}Si$: C, 60.45; H, 7.02. Found: C, 60.12; H, 7.02.

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-[3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(*t*-butyldimethylsilyl)-α-D-mannopyranosyl]-(1→6)-α-D-glucopyranoside (4). $[\alpha]_D^{20}$ = +69.7° (c = 1.4); ^{1}H-NMR, δ: 0.07 (s, 3H), 0.09 (s, 3H), 0.90 (s, 9H), 2.02 (s, 6H), 2.08 (s, 3H), 3.33 (s, 3H), 3.52 (dd, J = 2.2, 11.4 Hz, 1H), 3.66-3.86 (m, 4H), 3.86-3.96 (m, 1H), 4.04 (dd, J = 1.5, 2.9 Hz, 1H), 4.10 (t, J = 9.4 Hz, 1H), 4.19 (dd, J = 4.4, 9.8 Hz, 1H), 4.69 (d, J = 1.5 Hz, 1H), 4.70 (d, J = 12.0 Hz, 1H), 4.81 (d, J = 12.0 Hz, 1H), 4.85-4.92 (m, 2H), 5.06 (t, J = 9.8 Hz, 1H), 5.46 (t, J = 9.8 Hz, 1H), 5.60 (s, 1H), 7.24-7.39 (m, 8H), 7.47-7.51 (m 2H); ^{13}C-NMR, δ: -5.2, -4.5, 18.1, 20.6, 25.7, 55.2, 64.4, 65.0, 67.9, 68.8, 70.3, 70.7, 71.1, 72.9, 75.2, 79.0, 96.5, 101.5, 126.1, 127.3, 127.9, 128.0, 128.7, 137.7, 138.6, 169.4, 170.1; IR, υ: 1751 cm^{-1}. Anal. Calcd. for $C_{39}H_{54}O_{14}Si$: C, 60.45; H, 7.02. Found: C, 60.18; H, 6.97.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-[3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(*t*-butyldimethylsilyl)-β-D-mannopyranosyl]-(1→6)-α-D-mannopyranoside (6). $[\alpha]_D^{20}$ = +0.3° (c = 2.8); ^{1}H-NMR, δ: 0.05 (s, 3H), 0.09 (s, 3H), 0.89 (s, 9H), 3.21-3.29 (m, 1H), 3.29 (s, 1H), 3.46 (dd, *J* = 2.8, 9.5 Hz, 1H), 3.58-3.65 (m, 1H), 3.73-3.78 (m, 3H), 3.83-3.91 (m, 2H), 4.01 (d, J = 2.6 Hz, 1H), 4.07 (t, J = 9.5Hz, 1H), 4.24-4.30 (m, 2H), 4.56 (d, J = 11.3 Hz, 1H), 4.60 (s, 2H), 4.68 (d, J = 1.7Hz, 1H), 4.70 (d, J = 12.5 Hz, 1H), 4.71 (s, 2H), 4.76 (d, J = 12.5 Hz, 1H), 4.92 (d, J = 11.3 Hz, 1H), 5.60 (s, 1H), 7.24-7.39 (m, 23H), 7.49-7.53 (m, 2H); ^{13}C-NMR, δ: -5.1, -4.1, 18.5, 25.9, 54.7, 67.5, 68.8, 69.3, 71.2, 71.6, 71.9, 72.0, 72.7, 74.5, 74.9 (2), 77.6, 78.8, 80.2, 98.6, 101.4, 102.2, 126.1, 127.4, 127.6, 127.7, 127.9, 128.1, 128.2, 128.3, 128.7, 137.6, 138.2, 138.3, 138.5; IR, υ: 2930, 1455, 1363 cm^{-1}; MS (EI), m/z 918 (M), 862 (M+1-Bu^t), 861 (M-Bu^t), 828 (M+1-PhCH$_2$), 827 (M-PhCH$_2$); HRMS: Calcd. for $C_{54}H_{66}O_{11}Si$ (M): 918.4374. Found: 918.4395.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-[3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(*t*-butyldimethylsilyl)-α-D-mannopyranosyl]-(1→6)-α-D-mannopyranoside (7). $[\alpha]_D^{20}$ = +13.0° (c = 0.3); ^{1}H-NMR, δ: 0.06 (s, 3H), 0.07 (s, 3H), 0.90 (s, 9H), 3.23 (s, 3H), 3.57-3.90 (m, 8H), 4.05-4.22 (m, 4H), 4.52 (d, J = 11.0 Hz, 1H), 4.60 (s, 2H), 4.67-4.75 (m, 5H), 4.78 (d, J = 1.7 Hz, 1H), 4.90 (d, J = 11.0 Hz, 1H), 5.61 (s, 1H), 7.18-7.36 (m, 23H), 7.45-7.49 (m, 2H); ^{13}C-NMR, δ: 17.1, 25.8, 54.5, 64.3, 66.0, 69.0, 70.8, 71.2, 72.0, 72.3, 72.6, 74.3, 74.5, 75.0, 79.1, 80.3, 98.8, 101.4, 101.7, 127.2, 127.5, 127.5, 127.6, 127.6, 127.7, 127.7, 127.8, 127.8, 127.9, 128.0, 128.3, 128.6, 138.1, 138.3, 138.6 IR, υ: 2931, 1602, 1463 cm^{-1}; MS (EI), m/z 918 (M), 862 (M+1-Bu^t), 861 (M-Bu^t), 828 (M+1-PhCH$_2$), 827 (M-PhCH$_2$); HRMS: Calcd. for $C_{54}H_{66}O_{11}Si$ (M): 918.4374. Found: 918.4363.

Methyl 2-*N*-Acetylamino-2-deoxy-3,4-di-*O*-acetyl-6-*O*-[3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(*t*-butyldimethylsilyl)-β-D-mannopyranosyl]-(1→6)-α-D-glucopyranoside (9). $[\alpha]_D^{20}$ = +12.7° (c = 1.5); ^{1}H-NMR, δ: 0.10 (s, 3H), 0.12 (s, 3H), 0.91 (s, 9H), 1.93 (s, 3H), 1.99 (s,3H), 2.01 (s, 3H), 3.23-3.32 (m, 1H), 3.37 (s, 3H), 3.44 (dd, J = 6.2, 11.1 Hz, 1H), 3.50 (dd, J = 2.7, 9.4 Hz, 1H), 3.81-3.90 (m, 2H), 3.96 (dd, J = 1.7, 11.1 Hz, 1H), 4.08 (t, J = 9.4 Hz, 1H), 4.17 (d, J = 2.7 Hz, 1H), 4.25-4.43 (m, 3H), 4.68-4.79 (m, 3H), 5.04 (t, J = 9.9 Hz, 1H), 5.22 (t, J = 9.9 Hz, 1H), 5.60 (s, 1H),

5.68 (d, J = 9.5 Hz, 1H), 7.24-7.36 (m, 8H), 7.46-7.49 (m, 2H); ^{13}C-NMR, δ: -4.8, -4.1, 18.5, 20.7, 23.2, 25.9, 51.8, 55.5, 67.7, 68.5, 68.8, 68.8, 68.9, 71.1, 71.3, 72.2, 77.7, 78.8, 98.0, 101.5, 102.5, 126.1, 127.4, 127.8, 128.1, 128.2, 128.8, 137.6, 138.4, 169.5, 169.9, 171.4; IR, υ: 3052, 1745, 1422, 1265 cm^{-1}; MS (EI): m/z 773 (M), 772 (M-1), 742 (M-OMe), 716 (M-Bu^t); HRMS: Calcd. for $C_{39}H_{54}NO_{13}Si$ (M-H): 772.3365. Found: 772.3346.

(3,3-Dimethyl-2,4-dioxolanyl)methyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(*t*-butyldimethylsilyl)-β-D-mannopyranoside (12). A 1:1 diastereomeric mixture. $[\alpha]_D^{20}$ = -43.3° (c = 1.7); ^{1}H-NMR, δ: 0.06 (s, 3H), 0.07 (2s, 3H), 0.90 (s, 9H), 1.32 (s, 3H), 1.37 and 1.38 (2s, 3H), 3.24-3.32 (m, 1H), 3.46-3.62 (m, 2H), 3.67-3.92 (m, 3H), 4.00-4.14 (m, 3H), 4.19-4.30 (m, 2H), 4.39 (s, 1H), 4.69 (d, J = 12.5 Hz, 1H), 4.75 (d, J = 12.5 Hz, 1H), 5.59 (s, 1H), 7.24-7.37 (m, 8H), 7.46-7.50 (m, 2H); ^{13}C-NMR, δ: -4.7, -4.4, 18.5, 25.2, 25.24, 25.9, 26.75, 26.8, 66.6, 67.3, 67.5, 68.7, 69.7, 70.6, 71.1, 71.2, 72.2, 72.24, 74.2, 74.4, 77.5, 78.7, 101.4, 101.5, 102.1, 109.1, 109.3, 126.0, 127.4, 127.7, 127.8, 128.1, 128.2, 128.8, 137.6, 138.3; IR, υ: 2985, 1470, 1386, 1252, 1094 cm^{-1}. Anal. Calcd. for $C_{32}H_{46}O_8Si$: C, 65.50; H, 7.90. Found: C, 65.30; H, 7.90.

(3,3-Dimethyl-2,4-dioxolanyl)methyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(*t*-butyldimethylsilyl)-α-D-mannopyranoside (13). A 1:1 diastereomeric mixture. $[\alpha]_D^{20}$ = +2.1° (c = 0.8); ^{1}H-NMR, δ: 0.05 and 0.06 (2s, 3H), 0.08 (s, 3H), 0.90 (s, 9H), 1.37 (s, 3H), 1.40 and 1.41 (2s, 3H), 3.45-3.52 (m, 1H), 3.63-3.87 (m, 5H), 4.01-4.28 (m, 5H), 4.66 -4.73 (m, 2H), 4.81 and 4.82 (2d, J = 12.0 Hz, 1H), 5.62 (s, 1H), 7.25-7.39 (m, 8H), 7.47-7.50 (m, 2H); ^{13}C-NMR, δ: -5.1, -4.4, 18.2, 25.4, 25.8, 26.7, 64.5, 64.5, 66.5, 67.7, 68.4, 68.9, 71.1, 71.2, 72.97, 73.0, 74.3, 74.7, 75.6, 79.2, 101.4, 101.9, 109.5, 109.7, 126.1, 127.4, 127.7, 128.1, 128.8, 137.7, 138.7; IR, υ: 2985, 1475 cm^{-1}; MS (EI): m/z 586 (M), 572 (M+1-Me), 571 (M-Me), 530 (M+1-Bu^t), 529 (M-Bu^t); HRMS: Calcd. for $C_{32}H_{46}O_8Si$ (M): 586.2962. Found: 586.2953.

***N*-Benzyloxycarbonyl-*O*-[3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(*t*-butyldimethylsilyl)-β-D-mannopyranosyl]-L-serine Methyl Ester (15).** $[\alpha]_D^{20}$ = -34.1° (c = 4.7); ^{1}H-NMR, δ: 0.04 (s, 3H), 0.08 (s, 3H), 0.91 (s, 9H), 3.22-3.30 (m, 1H), 3.48 (dd, J = 2.7, 9.7 Hz, 1H), 3.76 (s, 3H), 3.81-3.91 (m, 2H), 4.03-4.09 (m, 2H), 4.20-4.31 (m, 3H), 4.47-4.53 (m, 1H), 4.71 (d, J = 12.4 Hz, 1H), 4.77 (d, J = 12.4 Hz, 1H), 5.11 (d, J = 12.3 Hz, 1H), 5.17 (d, J =12.3 Hz, 1H), 5.59-5.62 (m, 2H), 7.24-7.53 (m, 15H); ^{13}C-NMR, δ: -4.7, -4.6, 18.3, 25.8, 52.6, 54.2, 67.0, 67.5, 68.6, 69.3, 70.9, 72.2, 77.4, 77.5, 78.7, 101.4, 102.0, 126.0, 127.5, 127.7, 128.1, 128.2, 128.5, 128.8, 136.1, 137.5, 138.3, 155.8, 170.2; IR, υ: 3437, 2956, 2857, 1722 cm^{-1}; MS (EI): m/z 707 (M), 650 (M-Bu^t); HRMS. Calcd. for $C_{34}H_{40}NO_{10}Si$ (M-Bu^t): 650.2422. Found: 650.2413.

***N*-Benzyloxycarbonyl-*O*-[3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(*t*-butyldimethylsilyl)-α-D-mannopyranosyl]-L-serine Methyl Ester (16).** $[\alpha]_D^{20}$ = +7.8° (c = 0.5); ^{1}H-NMR, δ: 0.02 (s, 3H), 0.05 (s, 3H), 0.88 (s, 9H), 3.68-3.88 (m, 6H), 3.89-3.95 (m, 3H), 4.10 (t, J = 9.7 Hz, 1H), 4.22 (dd, J = 4.3, 9.7 Hz, 1H), 4.50-4.56 (m, 1H), 4.58 (d, J = 1.6 Hz, 1H), 4.66 (d, J = 11.9 Hz, 1H), 4.81 (d, J = 11.9 Hz, 1H), 5.08 (d, J = 12.0 Hz, 1H), 5.17 (d, J = 12.0 Hz, 1H), 5.57-5.62 (m, 2H), 7.23-7.49 (m, 15H); ^{13}C-NMR, δ: -5.3, -4.5, 18.1, 25.7, 52.6, 54.1, 64.8, 67.2, 68.0, 68.7, 71.0, 73.1, 75.5, 78.9, 101.4, 102.2, 126.0, 127.3, 127.8, 128.1, 128.2, 128.5, 128.7, 135.9, 137.5, 138.5, 155.8, 170.4 IR, υ: 3690, 2955, 1718, 1601, 1507, 1265 cm^{-1}.

6-*O*-[3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(*t*-butyldimethylsilyl)-β-D-mannopyranosyl]-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (18). $[\alpha]_D^{20}$ = -69.7° (c = 1.1); ^{1}H-NMR, δ: 0.13 (s, 6H), 0.92 (s, 9H), 1.32 (s, 3H), 1.33 (s, 3H), 1.45 (s, 3H), 1.51 (s,3H), 3.25-3.34 (m, 1H), 3.51 (dd, J = 3.2, 9.5 Hz, 1H), 3.64 (dd, J = 7.9, 11.4 Hz, 1H), 3.86 (t, J = 10.1 Hz,1H), 3.95-4.15 (m, 3H), 4.17-4.22 (m, 2H), 4.25-4.34 (m, 2H), 4.42 (s, 1H), 4.60 (dd, J = 3.0, 7.9 Hz, 1H), 4.74 (s, 2H), 5.56 (d, J = 5.4 Hz, 1H), 5.61 (s, 1H), 7.24-7.42 (m, 8H), 7.46-7.55 (m, 2H); ^{13}C-NMR, δ: -4.9, -3.7, 18.5, 24.3, 24.9, 26.0 (3), 67.4, 67.6, 68.9, 69.9, 70.2, 70.8, 71.0, 71.5, 72.0, 77.6, 78.8, 96.4, 101.5, 102.5, 108.5, 109.3, 126.1, 127.5, 127.8, 128.1, 128.2, 128.8, 137.7, 138.4; IR, υ: 2931, 1602, 1472,

1376, 1256, 1212, 1098, 1073, 1008 cm^{-1}; MS (EI): m/z 714 (M), 699 (M-Me), 657 (M-Bu^t); HRMS. Calcd. for $C_{37}H_{51}O_{11}Si$ (M-Me): 699.3201. Found: 699.3208.

6-*O*-[3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(*t*-butyldimethylsilyl)-α-D-mannopyranosyl]-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (19). $[\alpha]_D^{20}$ = -21.8° (c = 0.5); ^{1}H-NMR, δ: 0.05 (s, 3H),), 0.07 (s, 3H), 0.89 (s, 9H), 1.33 (s, 6H), 1.44 (s, 3H), 1.53 (s, 3H), 3.65-3.90 (m, 5H), 3.91-4.00 (m, 1H), 4.05-4.18 (m, 2H), 4.20-4.28 (m, 2H), 4.33 (dd, J = 2.5, 5.1 Hz, 1H), 4.62 (dd, J = 2.4, 7.9 Hz, 1H), 4.68 (d, J = 12.0 Hz, 1H), 4.74 (d, J = 1.6 Hz, 1H), 4.81 (d, J = 12.0 Hz, 1H), 5.53 (d, J = 5.0 Hz, 1H), 5.62 (s, 1H), 7.24-7.36 (m, 8H), 7.47-7.50 (m, 2H); ^{13}C-NMR, δ: -5.5, -4.4, 18.2, 24.6, 24.9, 25.8, 26.0, 26.1, 64.5, 65.5, 65.7, 69.0, 70.5, 70.7, 70.9, 71.2, 72.9, 75.8, 79.2, 96.3, 101.4, 101.6, 108.6, 109.7, 126.1, 127.3, 127.7, 128.1, 128.7, 137.7, 138.8; IR, υ: 2930, 1602, 1476 cm^{-1}; MS (EI): m/z 714 (M), 699 (M-Me), 657 (M-Bu^t). Anal. Calcd. for $C_{38}H_{54}O_{11}Si$: C, 63.84; H, 7.61. Found: C, 64.26; H, 7.70.

Methyl 4-*O*-(3-*O*-Benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnoside (21). The 2-*O*-silyl group was removed prior to isolation (TBAF) to facilitate separation of the anomers. $[\alpha]_D^{20}$ = -21.1° (c = 1.5); ^{1}H-NMR, δ: 1.30 (d, J = 5.6 Hz, 3H), 1.34 (s, 3H), 1.51 (s, 3H), 2.48 (bs, 1H), 3.29-3.40 (m, 5H), 3.62-3.70 (m, 2H), 3.90 (t, J = 10.3 Hz, 1H), 4.08-4.21 (m, 4H), 4.29 (dd, J = 4.9, 10.4 Hz, 1H), 4.76-4.90 (m, 3H), 5.02 (s, 1H), 5.61 (s, 1H), 7.24-7.44 (m, 8H),7.45-7.54 (m, 2H); ^{13}C-NMR, δ: 17.5, 26.3, 27.7, 54.7, 63.8, 66.9, 68.5, 69.9, 72.3, 76.0, 76.7, 78.1, 78.1, 78.4, 97.7, 98.7, 101.6, 109.3, 125.9, 127.8, 128.2, 128.4, 128.9, 137.3, 137.9; IR, υ: 3573, 2909, 1454, 1384, 1094 cm^{-1}; MS (EI): m/z 558 (M), 543 (M-Me), 527 (M-OMe), 526 (M-1-OMe); HRMS. Calcd. for $C_{30}H_{38}O_{10}$ (M): 558.2465. Found: 558.2461.

Methyl 4-*O*-(3-*O*-Benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl)-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnoside (22). The 2-*O*-silyl group was removed prior to isolation (TBAF) to facilitate separation of the anomers. $[\alpha]_D^{20}$ = +25.0° (c = 1.2); ^{1}H-NMR, δ: 1.25 (d, J = 5.6 Hz, 3H), 1.33 (s, 3H), 1.51 (s, 3H), 2.71(s, 1H), 3.34-3.42 (m, 4H), 3.61-3.67 (m, 1H), 3.79-3.93 (m, 2H), 4.05-4.16 (m, 5H), 4.26-4.31 (m, 1H), 4.73 (d, J = 11.9 Hz, 1H), 4.84 (s, 1H), 4.88 (d, J = 11.9 Hz, 1H), 4.94 (d, J = 1.2 Hz, 1H), 5.62 (s, 1H), 7.24-7.40 (m, 8H), 7.50-7.54 (m, 2H); ^{13}C-NMR, δ: 17.4, 26.3, 28.0, 54.8, 63.2, 64.6, 68.8, 69.9, 72.9, 75.4, 75.9, 76.7, 78.7, 80.6, 97.9, 100.6, 101.4, 109.1, 126.0, 127.7, 127.8, 128.1, 128.4, 128.8, 137.5, 137.9; IR, υ: 3573, 2936, 1454, 1384, 1095, 1046, 1028 cm^{-1}; MS (EI): m/z 558 (M), 543 (M-Me), 527 (M-OMe), 526 (M-1-OMe).

3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-(*t*-butyldimethylsilyl)-α-D-mannopyranose (23). (Major α-anomer). $[\alpha]_D^{20}$ = -3.6° (c = 2.4); ^{1}H-NMR, δ: 0.07 (s, 3H), 0.10 (s, 3H), 0.92 (s, 9H), 2.83 (bs, 1H), 3.83 (t, J = 10.1 Hz, 1H), 3.92 (dd, J = 3.0, 9.7 Hz, 1H), 3.96-4.07 (m, 1H), 4.09-4.19 (m, 2H), 4.23 (dd, J = 4.6, 10.1 Hz, 1H), 4.71 (d, J = 12.2 Hz, 1H), 4.83 (d, J = 12.2 Hz, 1H), 5.06 (bs, 1H), 6.17 (s, 1H), 7.23-7.40 (m, 8H), 7.49-7.53 (m, 2H); ^{13}C-NMR, δ: -5.1, -4.5, 18.1, 25.8, 64.4, 69.0, 71.3, 72.8, 75.1, 79.2, 96.4, 101.4, 126.0, 127.3, 127.7, 128.1, 128.7, 137.6, 138.6; IR, υ: 3052, 2986, 1423, 1265, 1100 cm^{-1}. Anal. Calcd. for $C_{26}H_{36}O_6Si$: C, 66.07; H, 7.68. Found: 65.85; H, 7.69.

Protocol D. General Synthesis of β-Mannopyranosides from Sulfoxide Donors in CH_2Cl_2. To a stirred solution of sulfoxide (0.2 mmol) and DTBMP (82.1 mg, 0.4 mmol) in CH_2Cl_2 (8.0 mL) at -78 °C was added Tf_2O (37.0 μL, 0.22 mmol) and, 5 min later, the solution of the glycosyl acceptor (0.4 mmol) in CH_2Cl_2 (2 mL) dropwise. The opaque reaction mixture was stirred at -78 °C for 1-2 h and then allowed to warm to 0 °C over 1-2 h and maintained there for a further 0.5 h before quenching with saturated aqueous $NaHCO_3$, washing with brine, drying, concentration and purification by chromatography on silica gel.

Ethyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*O*-trimethylsilyl-1-deoxy-1-thio-α-D-mannopyranoside *S*-Oxide (29). To a stirred solution of *S*-ethyl 3-*O*-benzyl-4,6-benzylidene-1-deoxy-1-thio-α-D-mannospyranoside[26] (104.3 mg, 0.259 mmol) and 2,6-lutidine (90.5 μL, 0.78 mmol) in CH_2Cl_2 (1 mL) was added TMSOTf (100 μL, 0.52 mmol) and the mixture was stirred at room temperature for 0.5 h before it was concentrated. The residue was dissolved in THF (1.5 mL) and water (0.1 mL) at 0 °C, and MMPP (64.0 mg,

0.130 mmol) was added. The mixture was stirred at this temperature for 1 h before dilution with water, extraction with CH_2Cl_2, washing with saturated aqueous $NaHCO_3$ and brine, and drying. Chromatography on silica gel (eluent: hexane:ethyl acetate = 5:1) provided **29** as a single, but unassigned isomer (109.3 mg, 86%). $[\alpha]_D^{20}$ = +7.6° (c = 3.1); ^{1}H-NMR, δ: 0.18 (s, 9H), 1.39 (t, J = 7.5 Hz, 3H), 2.61-2.77 (m, 1H), 2.90-3.04 (m, 1H), 3.63-3.72 (m, 1H), 3.81 (t, J = 10.0 Hz, 1H), 4.01 (dd, J = 3.1, 10.0 Hz, 1H), 4.19 (dd, J = 4.6, 10.0 Hz, 1H), 4.29 (t, J = 10.0 Hz, 1H), 4.45 (bs, 1H), 4.76 (d, J = 11.8 Hz, 1H), 4.78 (s, 1H), 4.85 (d, J = 11.8 Hz, 1H), 5.63 (s, 1H), 7.24-7.49 (m, 10H); ^{13}C-NMR, δ: 0.3, 5.7, 43.8, 67.2, 68.1, 70.2, 73.3, 75.5, 77.7, 95.2, 101.5, 125.9, 127.7, 127.9, 128.1, 128.2, 128.9, 137.1, 137.7.

Ethyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-deoxy-1-thio-α-D-mannopyranoside *S*-Oxide (30). *S*-Ethyl 4,6-*O*-benzylidene-1-deoxy-1-thio-α-D-mannopyranoside[66] (1.7 g, 5.44 mmol) in benzyl chloride (25 mL) was treated with NaH (60%, 1.0 g, 25.0 mmol) at 120 °C for 2 h. After cooling, the mixture was washed with water, 1 M HCl, saturated aqueous $NaHCO_3$ and concentrated *in vacuo*. The residue was dissolved in THF (32 mL) and water (2 mL), and MMPP (1.33 g, 2.72 mmol) was added. The mixture was stirred at this temperature for 1 h before dilution with water, extraction with CH_2Cl_2, washing with saturated aqueous $NaHCO_3$ and brine, and drying. After evaporation of the volatiles chromatography on silica gel (eluent: hexane:ethyl acetate = 5:1) provided **30** as a single, but unassigned isomer (2.21 g, 80%). mp: 110-113 °C. $[\alpha]_D^{20}$ = +10.4° (c = 0.5); ^{1}H-NMR, δ: 1.35 (t, J = 7.5 Hz, 3H), 2.55-2.70 (m, 1H), 2.84-2.96 (m, 1H), 3.66-3.84 (m, 2H), 4.11 (dd, J = 3.4, 10.0 Hz, 1H), 4.20 (dd, J = 4.1, 10.0 Hz, 1H), 4.34 (t, J = 10.0 Hz, 1H), 4.51 (dd, J = 1.3, 3.4 Hz, 1H), 4.61 (d, J = 1.3 Hz, 1H), 4.64-4.87 (m, 4H), 5.63 (s, 1H), 7.24-7.50 (m, 15H); ^{13}C-NMR, δ: 5.8, 43.9, 68.1, 70.0, 72.9, 73.1, 74.0, 76.0, 77.8, 92.6, 101.5, 125.9, 127.6, 127.9, 128.2, 128.3, 128.4, 129.0, 137.0, 137.4, 138.0; IR, υ: 1454, 1374, 1209 cm^{-1}. Anal. Calcd. for $C_{29}H_{32}O_6S$: C, 68.48; H, 6.34. Found: C, 68.14; H, 6.57.

Phenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-deoxy-1-thio-α-D-mannopyranoside (31). Phenyl 4,6-*O*-benzylidene-1-deoxy-1-thio-α-D-mannopyranoside[67] (2.0 g, 5.55 mmol) was dissolved in benzyl chloride (25 mL) and treated with NaH (60%, 1.0 g, 25 mmol) at 120 °C for 2 h. After cooling the mixture was diluted with CH_2Cl_2, washed with water, 1 M HCl, saturated aqueous NH_4Cl and brine, and dried. After evaporation of the volatiles chromatography on silica gel (eluent: hexane:ethyl acetate = 10:1) afforded **31** (3.0 g, 100%). $[\alpha]_D^{20}$ = +85.9° (c = 3.3); ^{1}H-NMR, δ: 3.85–4.07 (m, 3H), 4.18-4.38 (m, 3H), 4.66 (d, J = 12.2 Hz, 1H), 4.74 (s, 2H), 4.83 (d, J = 12.2 Hz, 1H), 5.51 (d, J = 0.9 Hz, 1H), 5.66 (s, 1H), 7.23-7.60 (m, 20H); ^{13}C-NMR, δ: 65.3, 68.4, 73.0, 76.1, 77.9, 79.0, 87.0, 101.4, 126.0, 127.6, 127.8, 128.0, 128.1, 128.3, 128.4, 128.7, 129.1, 131.5, 137.5, 137.6, 138.3. Anal. Calcd. for $C_{33}H_{32}O_5S.0.5H_2O$: C, 72.11; H, 6.05. Found: C, 72.40; H, 6.14.

Phenyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-deoxy-1-thio-α-D-mannopyranoside *S*-Oxide (32). To a stirred solution of **31** (3.0 g, 5.55 mmol) in CH_2Cl_2 (120 mL) at -78 °C was added MCPBA (60%, 1.4 g, 5.55 mmol) after which the mixture was warmed with stirring to -30 °C in 40 min before quenching with $NaHCO_3$, washing with brine, drying and concentration. Chromatography on silica gel (hexane:ethyl acetate = 10:1) provided **32** as a single, but unassigned isomer (2.50 g, 81%). mp: 136-139 °C. $[\alpha]_D^{20}$ = -52.7 (c = 1.0); ^{1}H-NMR, δ: 3.76 (t, J = 10.0 Hz, 1H), 4.05-4.17 (m, 1H), 4.22 (dd, J = 4.8, 10.0 Hz, 1H), 4.29-4.42 (m, 3H), 4.51 (bs, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.61 (d, J = 12.0 Hz, 1H), 4.67 (d, J = 12.0 Hz, 1H), 4.83 (d, J = 12.0 Hz, 1H), 5.64 (s, 1H), 7.21-7.55 (m, 15H); ^{13}C-NMR, δ: 68.1, 70.0, 72.7, 73.2, 73.4, 77.9, 97.5, 101.6, 124.3, 126.1, 127.6, 127.8, 127.9, 128.2, 128.3, 129.0, 129.4, 131.6, 137.2, 138.2, 141.4; IR, υ: 1454, 1373, 1314 cm^{-1}. Anal. Calcd. for $C_{33}H_{32}O_6S$: C, 71.20; H, 5.79. Found: C, 70.90; H, 5.92.

Methyl 4-*O*-(2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnoside (33). $[\alpha]_D^{20}$ = -61.0° (c = 2.6); ^{1}H-NMR, δ: 1.33 (s, 3H), 1.34 (d, J = 5.7 Hz, 3H), 1.50 (s, 3H), 3.27-3.38 (m, 1H), 3.40 (s, 3H), 3.60-3.72 (m, 3H), 3.91-4.00 (m, 2H), 4.06-4.15 (m, 2H), 4.21 (t, J = 9.6 Hz, 1H), 4.27 (dd, J = 4.9, 10.4 Hz, 1H), 4.60 (d, J = 12.6 Hz, 1H), 4.68 (d, J = 12.6 Hz, 1H), 4.82 (d, J = 12.2 Hz, 1H), 4.87 (s, 1H), 4.93 (d, J = 12.2 Hz, 1H), 5.00 (s, 1H), 5.63 (s,

1H), 7.24-7.55 (m, 15H); ^{13}C-NMR, δ: 17.6, 26.3, 27.7, 54.8, 64.1, 67.6, 68.5, 72.0, 74.8, 76.0, 76.2, 77.6, 77.9, 78.3, 78.6, 97.8, 100.0, 101.3, 109.3, 125.9, 127.3, 127.4, 128.1, 128.2, 128.3, 128.8, 137.5, 138.3, 138.5; IR, υ: 1451, 1386 cm^{-1}; MS (EI): m/z 648 (M), 633 (M-Me), 617 (M-OMe), 616 (M-1-OMe), 557 (M-PhCH$_2$); HRMS Calcd. For $C_{37}H_{44}O_{10}$ (M): 648.2934. Found: 648.2928.

Methyl 4-*O*-(2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl)-(1→4)-2,3-*O*-isopropylidene-α-L-rhamnoside (34). $[\alpha]_D^{20}$ = +37.0° (c = 1.4); ^{1}H-NMR, δ: 0.95 (d, J = 5.9 Hz, 3H), 1.31 (s, 3H), 1.50 (s, 3H), 3.20-3.30 (m, 1H), 3.33 (s, 3H), 3.45-3.59 (m, 1H), 3.75-3.96 (m, 3H), 3.96-4.12 (m, 3H), 4.20-4.30 (m, 2H), 4.64-4.79 (m, 3H), 4.79-4.91 (m, 3H), 5.65 (s, 1H), 7.20-7.41 (m, 13H), 7.48-7.60 (m, 2H); ^{13}C-NMR, δ: 16.9, 26.3, 28.0, 52.1, 54.7, 63.9, 64.5, 68.8, 73.2, 73.6, 75.4, 75.8, 76.3, 79.1, 80.3, 97.7, 100.3, 101.3, 109.1, 126.0, 127.4, 127.7, 128.1, 128.2, 128.3, 128.4, 128.7, 137.7, 137.8, 138.6. Anal. Calcd. for $C_{37}H_{44}O_{10}$: C, 68.50; H, 6.84; Found: C, 68.61; H, 6.89.

***S*-Ethyl 2,3-Di-*O*-allyl-4,6-*O*-benzylidene-1-deoxy-1-thio-α-D-mannopyranoside *S*-Oxide (39).** A mixture of *S*-ethyl 4,6-*O*-benzylidene-1-deoxy-1-thio-α-D-manno-pyranoside[66] (0.47 g, 1.50 mmol), NaH (60 %, 0.29 g, 7.5 mmol) and allyl bromide (0.65 mL, 7.5 mmol) in THF (7.0 mL) was heated to reflux for 5 h before it was concentrated, taken up with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ and concentrated again. The residue was then dissolved in THF (10 mL) and water (1 mL) at 0 °C, and MMPP (0.37 g, 0.75 mmol) was added portion wise until the substrate was consumed completely. The reaction mixture was concentrated, taken up with CH_2Cl_2, washed with water, saturated aqueous $NaHCO_3$ and brine. After evaporation of the volatiles, chromatography on silica gel (hexane:ethyl acetate = 2:1) afforded **39** as a single, but unassigned isomer (0.50 g, 81%). M.p. 59-62 °C; $[\alpha]_D^{20}$ = +52.0° (c = 1.3); ^{1}H-NMR, δ: 1.41 (t, J = 7.5 Hz, 3H), 2.65-2.78 (m, 1H), 2.93-3.06 (m, 1H), 3.65-3.82 (m, 2H), 4.02 (dd, J = 3.3, 10.1 Hz, 1H), 4.17-4.42 (m, 7H), 4.62 (s, 1H), 5.16-5.39 (m, 4H), 5.60 (s, 1H), 5.85-6.03 (m, 2H), 7.34-7.49 (m, 5H); ^{13}C-NMR, δ: 5.9, 44.0, 68.1, 69.9, 72.2, 72.9, 73.3, 75.4, 77.9, 92.8, 101.5, 117.2, 118.3, 125.9, 128.2, 129.0, 134.1, 134.3, 137.0; υ: 1457, 1380, 1217, 1129, 1100, 1046, 1024, 968, 923, 751, 699 cm^{-1}. Anal. Calcd. for $C_{21}H_{28}O_6S$: C, 61.74; H, 6.91; Found: C, 61.74; H, 6.96.

1,6-Anhydro-4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→4)-2,3-*O*-isopropylidene-β-D-mannopyranose (41). $[\alpha]_D^{20}$ = -48.8° (c = 6.4); ^{1}H-NMR, δ: 1.32 (s, 3H), 1.54 (s, 3H), 3.29-3.39 (m, 1H), 3.60 (dd, J = 3.1, 9.9 Hz, 1H), 3.76 (t, J = 6.6 Hz, 1H), 3.90-4.08 (m, 5H), 4.24 (t, J = 9.9 Hz, 1H), 4.30 (dd, J = 4.9, 10.4 Hz, 1H), 4.37 (bd, J = 6.2 Hz, 1H), 4.54 (bd, J = 6.2 Hz, 1H), 4.61 (d, J = 12.6 Hz, 1H), 4.68 (s, 1H), 4.70 (d, J = 12.6 Hz, 1H), 4.92 (d, J = 12.3 Hz, 1H), 4.98 (d, J = 12.3 Hz, 1 H), 5.38 (d, J = 2.8 Hz, 1 H), 5.63 (s, 1H), 7.24-7.53 (m, 15H); ^{13}C-NMR, δ: 25.6, 25.9, 64.2, 67.7, 68.3, 72.1, 72.4, 72.6, 74.9, 75.4, 75.7, 77.6, 78.4, 99.3, 100.4, 101.4, 109.8, 126.0, 127.5, 127.6, 127.7, 128.1, 128.2, 128.3, 128.7, 128.9, 137.3, 138.1 (2); IR, υ: 1378, 1151, 1091, 994, 916 cm^{-1}; MS (EI): m/z 632 (M), 617 (M-Me), 542 (M+1-PhCH$_2$), 541 (M-PhCH$_2$); HRMS Calcd. for $C_{36}H_{40}O_{10}$: 632.2621. Found: 632.2622.

1,6-Anhydro-4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl)-(1→4)-2,3-*O*-isopropylidene-β-D-mannopyranose (42). $[\alpha]_D^{20}$ = +25.0° (c = 0.5); ^{1}H-NMR, δ: 1.31 (s, 3H), 1.52 (s, 3H), 3.74 (t, J = 7.1 Hz, 1H), 3.84-4.05 (m, 8H), 4.20-4.32 (m, 2H), 4.59 (bd, J = 6.2 Hz, 1H), 4.68 (d, J = 12.1 Hz, 1H), 4.69 (d, J = 12.1 Hz, 1H), 4.90 (d, J = 12.1 Hz, 2H), 4.91 (d, J = 1.5 Hz, 1H), 5.33 (d, J = 2.9 Hz, 1H), 5.65 (s, 1H), 7.24-7.52 (m, 15H); ^{13}C-NMR, δ: 25.9, 64.5, 64.8, 68.5, 72.0, 73.3, 73.5, 73.9, 74.3, 74.6, 79.1, 99.0, 99.1, 101.4, 110.0, 125.9, 127.3, 127.4, 127.9, 128.1, 128.2, 128.4, 128.8, 137.4, 137.9, 138.6; IR, υ: 1370, 1124, 1096, 990, 924 cm^{-1}; MS (EI): m/z 632 (M), 617 (M-Me), 542 (M+1-PhCH$_2$), 541 (M-PhCH$_2$).

Methyl 3-*O*-Benzyl-2-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→2)-4,6-*O*-benzylidene-α-D-mannopyranoside (44). $[\alpha]_D^{20}$ = -44.8° (c = 3.9); ^{1}H-NMR, δ: 3.28-3.37 (m, 4H), 3.59 (dd, J = 3.2, 9.9 Hz, 1 H), 3.74-4.00 (m, 5H), 4.07-4.15 (m, 1H), 4.20-4.31 (m, 4H), 4.59-4.81 (m, 6H), 4.98 (d, J = 12.3 Hz, 1H), 5.07 (d, J = 12.3 Hz, 1H), 5.52 (s, 1H), 5.61 (s, 1H), 7.24-7.56 (m, 25H); ^{13}C-NMR, δ: 54.9, 64.0, 67.7, 68.5, 68.9, 71.3, 72.2, 74.0, 74.5, 75.1, 75.8, 77.5, 78.4, 78.6,

99.4, 100.8, 101.3, 101.6, 126.0, 126.1, 127.2, 127.5, 128.1, 128.2, 128.3, 128.6, 128.7, 137.5, 138.3, 138.4, 138.8; IR, υ: 1604 cm^{-1}; MS (EI): m/z 802 (M), 712 (M+1-$PhCH_2$), 711 (M-$PhCH_2$). HRMS Calcd. for $C_{41}H_{43}O_{11}$: 711.2805. Found: 711.2812 (M-$PhCH_2$).

Methyl 3-*O*-Benzyl-2-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl)-(1→2)-4,6-*O*-benzylidene-α-D-mannopyranoside (45). $[\alpha]_D^{20}$ = -0.9° (c= 0.4); ^{1}H-NMR, δ: 3.35 (s, 3H), 3.71-4.07 (m, 9H), 4.20-4.30 (m, 3H), 4.50 (d, J = 12.2 Hz, 1H), 4.56 (d, J = 12.2 Hz, 1H), 4.59-4.68 (m, 3H), 4.80 (d, J = 11.7 Hz, 1H), 4.86 (d, J = 12.1 Hz, 1H), 5.23 (d, J = 1.5 Hz, 1H), 5.62 (s, 1H), 5.65 (s, 1H), 7.24-7.54 (m, 25H); ^{13}C-NMR, δ: 54.8, 63.6, 64.6, 68.6, 68.7, 73.0, 73.4, 75.8, 75.9, 79.1, 79.2, 100.8, 100.9, 101.3, 101.4, 125.9, 126.0, 127.3, 127.5, 127.6, 127.7, 127.8, 128.2, 128.3, 128.8, 128.9, 137.5, 138.1, 138.3, 138.7; IR, υ: 1600, 1124, 1091, 1003, 966 cm^{-1}; MS (EI): m/z 803 (M+1), 802 (M), 801 (M-1), 711 (M-$PhCH_2$).

3-*O*-(2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (47). $[\alpha]_D^{20}$ = -38.6° (c = 2.9); ^{1}H-NMR, δ: 1.31 (s, 3H), 1.34 (s, 3H), 1.43 (s, 3H), 1.50 (s, 3H), 3.28-3.37 (m, 1H), 3.61 (dd, J = 3.0, 9.8 Hz, 1H), 3.87 (d, J = 3.0 Hz, 1H), 3.92 (t, J = 10.2 Hz, 1H), 4.02-4.15 (m, 2H), 4.22 (t, J = 9.8 Hz, 1H), 4.27-4.33 (m, 3H), 4.38-4.45 (m, 2H), 4.56 (bs, 1H), 4.63 (d, J = 12.5 Hz, 1H), 4.76 (d, J = 12.5 Hz, 1H), 4.82 (d, J = 11.9 Hz, 1H), 4.88 (d, J = 11.9 Hz, 1H), 5.63 (s, 1H), 5.89 (d, J = 3.8 Hz, 1H), 7.24-7.53 (m, 15H); ^{13}C-NMR, δ: 25.3, 26.2, 26.5, 26.7, 66.1, 67.7, 68.3, 72.5, 72.9, 74.8, 76.1, 77.9, 78.5, 80.4, 80.8, 82.7, 100.1, 101.3, 104.9, 108.6, 111.9, 125.9, 127.5, 127.6, 127.7, 128.1, 128.3, 128.4, 128.8, 137.4, 138.0, 138.2; IR, υ: 1451, 1377, 1090 cm^{-1}; MS (EI): m/z 690 (M), 676 (M+1-Me), 675 (M-Me), 600 (M+1-$PhCH_2$), 599 (M-$PhCH_2$); HRMS Calcd. for $C_{39}H_{46}O_{11}$: 690.3040. Found: 690.3047 (M).

3-*O*-(2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl)-(1→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (48). $[\alpha]_D^{20}$ = +15.7° (c = 1.1); ^{1}H-NMR, δ: 1.31 (s, 3H), 1.34 (s, 3H), 1.41 (s, 3H), 1.50 (s, 3H), 3.77-3.98 (m, 4H), 4.00-4.15 (m, 4H), 4.23-4.37 (m, 3H), 4.54 (d, J = 3.6 Hz, 1H), 4.60 (d, J = 12.1 Hz, 1H), 4.72 (d, J = 12.3 Hz, 1H), 4.77 (d, J = 12.3 Hz, 1H), 4.79 (d, J = 12.1 Hz, 1H), 5.22 (d, J = 1.4 Hz, 1H), 5.67 (s, 1H), 5.84 (d, J = 3.6 Hz, 1H), 7.24-7.55 (m, 15H); ^{13}C-NMR, δ: 25.5, 26.2, 26.7, 26.8, 65.0, 67.8, 68.7, 72.4, 73.0 (2), 75.6, 75.8, 78.9, 80.0, 81.3, 83.9, 99.8, 101.3, 105.2, 109.3, 112.1, 125.8, 127.4, 127.8, 127.9, 128.1, 128.2, 128.3, 128.8, 137.4, 137.7, 138.4; IR, υ: 1452, 1373, 1094, 1017 cm^{-1}; MS (EI): m/z 600 (M+1-$PhCH_2$), 599 (M-$PhCH_2$).

Benzyl 2-*N*-Acetylamino-2-deoxy-3,6-di-*O*-benzyl-4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→4)-β-D-glucopyranoside (50). $[\alpha]_D^{20}$ = -38.7° (c = 1.1); ^{1}H-NMR, δ: 1.73 (s, 3H), 3.08-3.19 (m, 1H), 3.45 (dd, J = 3.0, 9.8 Hz, 1H), 3.51-3.69 (m, 4H), 3.70-3.80 (m, 2H), 3.92 (t, J = 7.2 Hz, 1H), 4.02-4.18 (m, 3H), 4.35-4.65 (m, 6H), 4.72-4.98 (m, 6H), 5.54 (s, 1H), 5.76 (d, J = 8.0 Hz, 1H), 7.20-7.50 (m, 30H); ^{13}C-NMR, δ: 23.2, 54.9, 67.2, 68.5, 69.1, 70.7, 72.5, 73.4, 73.6, 75.0, 75.2, 77.9, 78.1, 78.6, 99.1, 101.3, 101.7, 126.0, 127.0, 127.4, 127.5, 127.7, 127.8, 127.9, 128.1, 128.3, 128.4, 128.8, 137.5, 137.8, 138.2, 138.4, 138.7, 170.1; MS (EI): m/z 921 (M), 829 (M+1-$PhCH_2$). Anal. Calcd for $C_{56}H_{59}O_{11}.1H_2O$: C, 71.54; H, 6.66. Found: C, 71.12; H, 6.19.

Benzyl 2-*N*-Acetylamino-2-deoxy-3,6-di-*O*-benzyl-4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl)-(1→4)-β-D-glucopyranoside (51). $[\alpha]_D^{20}$ = +2.67° (c = 0.3); ^{1}H-NMR, δ: 1.77 (s, 3H), 3.40-3.50 (m, 1H), 3.51-3.59 (m, 1H), 3.71-3.93 (m, 7H), 4.05-4.18 (m, 2H), 4.25 (t, J = 9.7 Hz, 1H), 4.37 (d, J = 12.1 Hz, 1H), 4.50-4.67 (m, 7H), 4.79-4.91 (m, 3H), 5.28 (d, J = 1.5 Hz, 1H), 5.40 (d, J = 7.9 Hz, 1H), 5.63 (s, 1H), 7.20-7.53 (m, 30H); ^{13}C-NMR, δ: 23.4, 30.9, 56.9, 65.1, 68.6, 69.1, 70.8, 73.0, 73.2, 73.3, 73.4, 74.3, 76.1, 76.2, 78.9, 80.7, 98.6, 100.5, 101.3, 126.0, 127.0, 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.5, 128.7, 137.3, 137.6, 137.9, 138.1, 138.6, 170.4.

1,6-Anhydro-2-azido-3-*O*-benzyl-4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→4)-2-deoxy-β-D-glucopyranose (53). $[\alpha]_D^{20}$ = -29.2° (c = 0.5); ^{1}H-NMR, δ: 3.30-3.40 (m, 2H), 3.63 (dd, J = 3.0, 9.9 Hz, 1H), 3.78-3.85 (m, 2H), 3.90-3.99 (m, 2H), 4.08 (d, J = 3.0 Hz,

1H), 4.15-4.31 (m, 3H), 4.58-4.71 (m, 5H), 4.76 (broad s, 1H), 4.92 (d, J = 12.1 Hz, 1H), 5.02 (d, J = 12.1 Hz, 1H), 5.56 (broad s, 1H), 5.65 (s, 1H), 7.22-7.56 (m, 20H); ^{13}C-NMR, δ: 59.1, 64.9, 67.8, 68.4, 71.9, 72.1. 72.4, 73.2, 75.0, 75.9, 77.5, 77.8, 78.3, 99.0, 100.6, 101.4, 126.0, 127.5, 127.9, 128.1, 128.2, 128.3, 128.4, 128.5, 128.7, 137.3, 137.4, 138.1, 138.4; MS (EI): m/z 679 (M-N_2), 617 (M+1-$PhCH_2$), 616 (M-$PhCH_2$), 589 (M+1-$PhCH_2$-N_2), 588 (M-$PhCH_2$-N_2); HRMS Calcd for $C_{33}H_{34}N_3O_9$ (M-$PhCH_2$): 616.2295; Found: 616.2270.

1,6-Anhydro-2-azido-3-*O*-benzyl-4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-manno-pyranosyl)-(1→4)-2-deoxy-β-D-glucopyranose (54). $[\alpha]_D^{20}$ = +52.0° (c = 0.6); ^{1}H-NMR, δ: 3.11 (br s, 1H), 3.36 (t, J = 1.4 Hz, 1H), 3.61 (br s, 1H), 3.76 (dd, J = 6.0, 7.3 Hz, 1H), 3.85-3.92 (m, 3H), 4.04 (dd, J = 3.3, 10.0 Hz, 1H), 4.11 (broad d, J = 7.3 Hz, 1H), 4.20-4.29 (m, 2H), 4.48 (d, J = 12.1 Hz, 1H), 4.55-4.65 (m, 4H), 4.71 (d, J = 1.4 Hz, 1H), 4.74-4.81 (m, 2H), 5.62 (br s, 1H), 5.64 (s, 1H), 7.24-7.52 (m, 20H); ^{13}C-NMR, δ: 58.6, 65.0, 65.1, 68.5, 72.0, 72.8, 73.1, 73.7, 75.1, 75.9, 76.1, 78.8, 98.6, 100.4, 101.4, 126.0, 127.4, 127.5, 127.8, 128.1, 128.2, 128.4, 128.6, 128.8, 136.8, 137.4, 137.8, 138.5; MS (EI): m/z 708 (M+1), 707 (M), 680 (M+1-N_2), 679 (M-N_2), 678 (M-1-N_2), 617 (M+1-$PhCH_2$), 616 (M-$PhCH_2$), 588 (M-$PhCH_2$-N_2); HRMS Calcd for $C_{40}H_{41}N_3O_9$ (M): 707.2843; Found: 707.2826.

***N*-Benzyloxycarbonyl-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-L-threonine Methyl Ester (56).** $[\alpha]_D^{20}$ = -29.7° (c = 5.8); ^{1}H-NMR, δ: 1.22 (d, J = 6.3 Hz, 3H), 3.18-3.28 (m, 1H), 3.56 (dd, J = 3.1, 9.9 Hz, 1 H), 3.73 (s, 3H), 3.80-3.90 (m, 2H), 4.15 (t, J = 9.9 Hz, 1H), 4.24 (dd, J = 4.9, 10.5 Hz, 1H), 4.37 (dd, J = 2.3, 9.3 Hz, 1H), 4.44-4.52 (m, 2H), 4.62 (d, J = 12.5 Hz, 1H), 4.72 (d, J = 12.5 Hz, 1H), 4.78 (d, J = 12.2 Hz, 1H), 4.87 (d, J = 12.2 Hz, 1 H), 5.15 (s, 2H), 5.55 (d, J = 9.2 Hz, 1H), 5.59 (s, 1H), 7.24-7.55 (m, 20H); ^{13}C-NMR, δ: 17.4, 52.5, 58.4, 67.1, 67.4, 68.4, 72.3, 74.1, 74.6, 76.2, 77.7, 78.4, 99.7, 101.3, 126.0, 127.5, 128.0, 128.1, 128.3, 128.5, 128.8, 136.2, 137.4, 138.2, 138.3, 156.7, 170.7; IR, υ: 1725 cm^{-1}; MS (EI): m/z 697 (M), 606 (M-$PhCH_2$), 562 (M-$PhCH_2OCO$); HRMS Calcd. for $C_{33}H_{36}NO_{10}$ (M-$PhCH_2$): 606.2313. Found: 606.2310.

***N*-Benzyloxycarbonyl-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl)-L-threonine Methyl Ester (57).** $[\alpha]_D^{20}$ = +45.6° (c = 0.2); ^{1}H-NMR, δ: 1.27 (d, J = 6.4 Hz, 3H), 3.56 (s, 3H), 3.59-3.62 (m, 1H), 3.78-3.90 (m, 3H), 4.17-4.39 (m, 4H), 4.62 (d, J = 12.1 Hz, 1H), 4.68 (d, J = 12.4 Hz, 1H), 4.75 (d, J = 12.4 Hz, 1H), 4.76 (d, J = 1.4 Hz, 1H), 4.82 (d, J = 12.1 Hz, 1H), 5.14 (s, 2H), 5.26 (d, J = 9.7 Hz, 1H), 5.63 (s, 1H), 7.24-7.52 (m, 20H); ^{13}C-NMR, δ: 18.4, 52.3, 58.4, 64.7, 67.3, 68.5, 73.2, 73.3, 75.9, 76.0, 76.2, 78.9, 100.7, 101.3, 125.9, 127.5, 127.7, 128.0, 128.1, 128.2, 128.3, 128.5, 128.7, 137.4, 137.8, 138.4, 156.4, 170.8; IR, υ: 1725, 1507, 1096, 1011 cm^{-1}; MS (EI): m/z 697 (M), 607 (M+1-$PhCH_2$), 606 (M-$PhCH_2$).

3-*O*-(2,3-Di-*O*-allyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (58). $[\alpha]_D^{20}$ = -43.5° (c = 2.6); ^{1}H-NMR, δ: 1.32 (s, 3H), 1.36 (s, 3H), 1.44 (s, 3H), 1.50 (s, 3H), 3.20-3.40 (m, 1H), 3.55 (dd, J = 3.0, 9.8 Hz, 1H), 3.81 (bd, J = 3.0 Hz, 1H), 3.89 (t, J = 10.3 Hz, 1H), 4.00-4.42 (m, 11H), 4.50 (d, J = 3.8 Hz, 1H), 4.57 (bs, 1H), 5.10-5.36 (m, 4H), 5.58 (s, 1H), 5.82-6.02 (m, 3H), 7.34-7.50 (m, 5H); ^{13}C-NMR, δ: 25.4, 26.2, 26.4, 26.7, 65.7, 67.6, 68.3, 71.8, 73.4, 74.3, 76.3, 77.9, 78.4, 80.2, 80.6, 82.7, 99.7, 101.3, 104.9, 108.3, 111.9, 116.8, 117.4, 125.9, 128.1, 128.8, 134.7, 135.1, 137.3; IR, υ: 1455, 1383, 1217 cm^{-1}; MS (EI): m/z 590 (M), 576 (M+1-Me), 575 (M-Me); HRMS Calcd. for $C_{31}H_{42}O_{11}$ (M): 590.2727. Found: 590.2730.

3-*O*-(2,3-Di-*O*-allyl-4,6-*O*-benzylidene-α-D-mannopyranosyl)-(1→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (59). $[\alpha]_D^{20}$ = +20.1° (c = 1.0); ^{1}H-NMR, δ: 1.32 (s, 3H), 1.35 (s, 3H), 1.41 (s, 3H), 1.50 (s, 3H), 3.75-4.39 (m, 16H), 4.56 (d, J = 3.6 Hz, 1H), 5.15-5.35 (m, 4H), 5.63 (s, 1H), 5.85-6.00 (m, 3H), 7.34-7.51 (m, 5H); ^{13}C-NMR, δ: 25.3, 26.2, 26.8 (2), 64.9, 67.8, 68.7, 72.2, 72.4, 72.7, 75.3, 75.8, 79.0, 80.0, 81.4, 84.0, 100.2, 101.3, 105.2, 109.4, 112.1, 116.5, 117.8, 125.8, 128.1, 128.8, 134.6, 134.8, 137.4; IR, υ: 1456, 1374 cm^{-1}; MS (EI): m/z 591 (M+1), 590 (M), 576 (M+1-Me), 575 (M-Me); HRMS Calcd. for $C_{31}H_{42}O_{11}$ (M): 590.2727. Found: 590.2806.

1,6-Di-*O*-acetyl-2-*N*-acetylamino-3-*O*-benzyl-4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→4)-2-deoxy-α-D-glucopyranose (61). A mixture of **53** (12.0 mg, 0.017 mmol) and Lindlar catalyst (100 mg) in ethyl acetate (4 mL) was stirred under H_2 for for 2 h at room temperature. Filtration and concentration gave the amine **60** (10.7 mg, 99%). ^{1}H-NMR, δ: 2.91 (bs, 1H), 3.25-3.36 (m, 1H), 3.59-3.68 (m, 2H), 3.75-3.82 (m, 2H), 3.88-4.02 (m, 2H), 4.15-4.30 (m, 4H), 4.50-4.99 (m, 7H), 5.44 (bs, 1H), 5.62 (s, 1H), 7.20-7.55 (m, 20H). Crude **60** (10.7 mg, 0.017 mmol) was dissolved in Ac_2O (0.5 mL) and stirred for 2 h before TFA (50 μL) was added. The reaction mixture was stirred for a further 5 h before it was concentrated. Chromatography on silica gel afforded **61** (13.1 mg, 95%). $[\alpha]_D^{20}$ = +1.3° (c = 0.5); ^{1}H-NMR, δ: 1.79 (s, 3H), 2.07 (s, 3H), 2.15 (s, 3H), 3.16-3.28 (m, 1H), 3.56-3.68 (m, 3H), 3.69-3.77 (m, 1H), 3.85 (t, J = 9.4 Hz, 1H), 3.94 (d, J = 2.7 Hz, 1H), 4.09-4.19 (m, 4H), 4.23-4.32 (m, 1H), 4.47 (br s, 1H), 4.60-4.70 (m, 2H), 4.80-4.85 (m, 2H), 4.92-4.99 (m, 2H), 5.03 (d, J = 8.4 Hz, 1H), 5.55 (s, 1H), 6.12 (d, J = 3.5 Hz, 1H), 7.23-7.48 (m, 20H); ^{13}C-NMR, δ: 20.8, 20.9, 23.1, 50.8, 52.1, 61.8, 64.7, 67.5, 68.3, 71.4, 72.8, 74.2, 75.2, 77.6, 78.3, 78.5, 90.7, 101.3, 101.9, 125.9, 127.4, 127.5, 127.6, 127.8, 128.1, 128.3, 128.8, 137.3, 138.2, 138.4, 138.5, 168.7, 169.9, 170.5; MS (EI): m/z 826 (M+1), 782 (M-MeCO), 766 (M-MeCOO), 735 (M-1-$PhCH_2$), 719 (M-1-$PhCH_2O$); HRMS Calcd for $C_{44}H_{48}NO_{11}$ (M): 766.3227; Found: 766.3158.

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→6)-α-D-glucopyranoside (62). $[\alpha]_D^{20}$ = +16.8° (c = 1.4); ^{1}H-NMR, δ: 2.02 (s, 3H), 2.03 (s, 3H), 2.08 (s, 3H), 3.26-3.35 (m, 1H), 3.37 (s, 3H), 3.50 (dd, J = 6.7, 10.8 Hz, 1H), 3.59 (dd, J = 3.1, 9.9 Hz, 1H), 3.92 (t, J = 10.3 Hz, 1H), 3.96-4.05 (m, 3H), 4.20 (t, J = 9.9 Hz, 1H), 4.30 (dd, J = 4.9, 10.3 Hz, 1H), 4.48 (d, J = 0.6 Hz, 1H), 4.57 (d, J = 12.5 Hz, 1H), 4.67 (d, J = 12.5 Hz, 1H), 4.83-5.02 (m, 5H), 5.50 (t, J = 10.1 Hz, 1H), 5.61 (s, 1H), 7.24-7.52 (m, 15H); ^{13}C-NMR, δ: 20.7 (3), 55.2, 67.5, 68.2, 68.4 (2), 68.9, 70.0, 70.8, 72.2, 75.0, 75.9, 77.6, 78.4, 96.4, 101.3, 102.4, 126.0, 127.5, 128.1, 128.2, 128.4, 128.8, 137.4, 138.2, 138.3, 169.8, 170.0, 170.1; IR, υ: 1748, 1452, 1369, 1258, 1040 cm^{-1}; MS (EI): m/z 750 (M), 660 (M+1-$PhCH_2$), 659 (M-$PhCH_2$); HRMS Calcd. For $C_{33}H_{39}O_{14}$ (M-$PhCH_2$): 659.2340. Found: 659.2264.

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl)-(1→6)-α-D-glucopyranoside (63). $[\alpha]_D^{20}$ = +92.2° (c = 0.6); ^{1}H-NMR, δ: 1.99 (s, 3H), 2.02 (s, 3H), 2.08 (s, 3H), 3.30 (s, 3H), 3.46 (dd, J = 2.2, 11.4 Hz, 1H), 3.67-3.76 (m, 3H), 3.79-3.96 (m, 4H), 4.16-4.27 (m, 2H), 4.65-4.89 (m, 6H), 5.01 (t, J = 9.9 Hz, 1H), 5.44 (t, J = 9.9 Hz, 1H), 5.62 (s, 1H), 7.24-7.52 (m, 15H); ^{13}C-NMR, δ: 20.7 (3), 55.2, 64.2, 65.2, 67.7, 68.7, 70.2, 70.7, 73.2, 73.5, 75.9, 76.2, 78.9, 96.5, 99.3, 101.4, 126.0, 127.4, 127.6, 128.0, 128.1, 128.2, 128.3, 128.7, 137.6, 138.0, 138.5, 169.4, 170.1 (2); IR, υ: 1748, 1456, 1369, 1096 cm^{-1}; MS (EI): m/z 751 (M+1), 750 (M), 749 (M-1), 660 (M+1-$PhCH_2$), 659 (M-$PhCH_2$).

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-(2,3-di-*O*-allyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→6)-α-D-glucopyranoside (64). $[\alpha]_D^{20}$ = +36.2° (c = 5.0); ^{1}H-NMR, δ: 2.00 (s, 3H), 2.02 (s, 3H), 2.06 (s, 3H), 3.24-3.34 (m, 1H), 3.39 (s, 3H), 3.43-3.55 (m, 2H), 3.83-4.39 (m, 10H), 4.46 (bs, 1H), 4.81-5.00 (m, 3H), 5.13-5.33 (m, 4H), 5.48 (t, J = 9.9 Hz, 1H), 5.55 (s, 1H), 5.82-6.04 (m, 2H), 7.30-7.49 (m, 5H); ^{13}C-NMR, δ: 20.6 (3), 55.0, 67.4, 68.1, 68.4, 68.5, 68.9, 70.0, 70.8, 71.7, 74.4, 75.7, 77.6, 78.4, 96.3, 101.3, 102.0, 116.7, 117.4, 125.9, 128.1, 128.7, 134.7, 135.4, 137.4, 169.8, 169.9, 170.1; IR, υ: 1750 cm^{-1}; MS (EI): m/z 650 (M), 609 (M-allyl); HRMS Calcd. for $C_{32}H_{42}O_{14}$ (M): 650.2574. Found: 650.2558.

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-(2,3-di-*O*-allyl-4,6-*O*-benzylidene-α-D-mannopyranosyl)-(1→6)-α-D-glucopyranoside (65). $[\alpha]_D^{20}$ = +96.9° (c = 0.5); ^{1}H-NMR, δ: 2.01 (s, 3H), 2.03 (s, 3H), 2.08 (s, 3H), 3.41 (s, 3H), 3.53 (dd, J = 2.2, 11.3 Hz, 1H), 3.70-3.87 (m, 5H), 3.91-3.99 (m, 1H), 4.07-4.38 (m, 6H), 4.83-4.96 (m, 3H), 5.08 (t, J = 9.5 Hz, 1H), 5.12-5.36 (m, 4H), 5.47 (t, J = 9.5 Hz, 1H), 5.58 (s, 1H), 5.85-6.01 (m, 2H), 7.33-7.51 (m, 5H); ^{13}C-NMR, δ: 20.6 (3), 55.3, 64.1, 65.3, 67.8, 68.6, 68.8, 70.2, 70.7, 72.2, 73.0, 75.6, 78.9, 96.6, 99.5, 101.5, 116.5, 117.7, 126.0, 128.1, 128.7, 134.7,

134.9, 169.4, 170.1 (2); IR, υ: 1753, 1371, 1225, 1038, 757 cm^{-1}; MS (EI): m/z 650 (M); HRMS Calcd. for $C_{32}H_{42}O_{14}$ (M): 650.2574. Found: 650.2537.

6-*O*-(2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (66). $[\alpha]_D^{20}$ = -79.2° (c = 3.3); ^{1}H-NMR, δ: 1.33 (s, 3H), 1.35 (s, 3H), 1.45 (s, 3H), 1.51 (s, 3H), 3.26-3.36 (m, 1H), 3,54 (dd, J = 3.0, 10.0 Hz, 1H), 3.64 (dd, J = 8.3, 10.7 Hz, 1H), 3.93 (t, J = 10.3 Hz, 1H), 4.03 (d, J = 3.0 Hz, 1H), 4.07-4.12 (m, 1H), 4.15-4.24 (m, 3H), 4.30 (dd, J = 4.9, 10.3 Hz, 1H), 4.35 (dd, J = 2.5, 5.0 Hz, 1H), 4.50-4.65 (m, 4H), 4.91 (d, J = 12.3 Hz, 1H), 5.03 (d, J = 12.3 Hz, 1H), 5.59 (d, J = 5.0 Hz, 1H), 5.62 (s, 1H), 7.19-7.54 (m, 15H); ^{13}C-NMR, δ: 24.3, 25.0, 25.9, 26.0, 67.5, 67.9, 68.5, 70.0, 70.4, 70.7, 71.5, 72.0, 74.5, 74.7, 78.4, 96.3, 101.3, 102.8, 108.7, 109.5, 126.0, 127.4, 128.1, 128.2, 128.7, 137.5, 138.1, 138.2; IR, υ: 1600, 1498, 1456, 1378 cm^{-1}; MS (EI): m/z 690 (M), 676 (M+1-Me), 675 (M-Me), 600 (M+1-$PhCH_2$), 599 (M-$PhCH_2$); HRMS Calcd. for $C_{39}H_{46}O_{11}$ (M): 690.3040. Found: 690.3043.

6-*O*-(2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranosyl)-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (67). $[\alpha]_D^{20}$ = -5.3° (c = 1.3); ^{1}H-NMR, δ: 1.34 (s, 6H), 1.44 (s, 3H), 1.52 (s, 3H), 3.65-3.93 (m, 5H), 3.95-4.00 (m, 2H), 4.15-4.29 (m, 3H), 4.33 (dd, J = 2.4, 5.0 Hz, 1H), 4.59-4.65 (m, 2H), 4.72-4.84 (m, 3H), 4.93 (d, J = 1.4 Hz, 1H), 5.53 (d, J = 5.0 Hz, 1H), 5.64 (s, 1H), 7.24-7.53 (m, 15H); ^{13}C-NMR, δ: 24.5, 24.8, 25.9, 26.0, 64.3, 65.3, 65.7, 68.7, 70.5, 70.6, 70.8, 73.0, 73.3, 76.2, 76.3, 79.0, 96.3, 98.9, 101.3, 108.5, 109.3, 126.0, 127.3, 127.4, 127.6, 127.9, 128.1, 128.2, 128.3, 128.7, 137.6, 138.0, 138.6; IR, υ: 1600, 1498, 1447, 1373, 1100 cm^{-1}; MS (EI): m/z 600 (M+1-$PhCH_2$), 599 (M-$PhCH_2$).

***S*-Ethyl 2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-thio-α-D-mannopyranoside *S*-Oxide (68).** To a stirred solution of *S*-ethyl 2,3,4,6-tetra-*O*-acetyl-1-deoxy-1-thio-α-D-mannopyranoside[66] (4.4 g, 11.2 mmol) in MeOH (200 mL) was added sodium (50 mg). The mixture was stirred overnight , concentrated, taken up with benzyl chloride (50 mL) and heated with sodium hydride (60%, 3.6 g, 89.6 mmol) at 120 °C for 6 h. It was then diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ and brine, dried and concentrated. Chromatography on silica gel (eluent: hexane/ethyl acetate = 25/1→5/1) gave 5.45 g of *S*-ethyl 2,3,4,6-tetra-*O*-benzyl-1-deoxy-1-thio-α-D-mannopyranoside (83%). This (2.15 g, 3.68 mmol) was treated with MMPP (80%, 1.14 g, 1.84 mmol) in THF (25 mL) and water (4 mL) at 0 °C for 2 h. Subsequent concentration, extraction with CH_2Cl_2, washing with saturated aqueous $NaHCO_3$ and brine, drying, concentration and column chromatography on silica gel (eluent: hexane/ethyl acetate = 1/1) gave 1.99 g of **68** as a single, but unassigned isomer (90%). $[\alpha]_D^{20}$ = +21.2° (c = 1.3); ^{1}H-NMR, δ: 1.37 (t, J = 7.4 Hz, 3H), 2.65-2.80 (m, 1H), 2.92-3.06 (m, 1H), 3.65-3.77 (m, 3H), 4.01-4.10 (m, 2H), 4.49-4.80 (m, 9H), 4.92 (d, J = 10.8 Hz, 1H), 7.17-7.44 (m, 20H); ^{13}C-NMR, δ: 5.9, 43.6, 69.1, 71.8, 72.0, 72.7, 73.4, 73.6, 75.1, 77.6, 79.5, 91.1, 127.6, 127.7 (2), 127.9, 128.1, 128.3, 128.4, 137.7, 137.9; IR υ: 3033, 2871, 1602, 1496, 1455, 1110, 1044, 1027 cm^{-1}. Anal. Calcd for $C_{36}H_{40}O_6S.0.5H_2O$: C, 70.91; H, 6.78. Found: C, 70.55; H, 6.62.

***S*-Ethyl 1,2:3,4-Di-*O*-isopropylidene-1-deoxy-1-thio-α-D-mannopyranoside *S*-Oxide (69).** *S*-Ethyl 1-deoxy-1-thio-α-D-mannopyranoside[66] (1.43 g, 6.37 mmol) and *p*-toluenesulphonic acid monohydrate (150 mg) were dissolved in acetone dimethyl acetal (20 mL) and stirred for 7 h before washing with $NaHCO_3$ and brine, drying, and concentration. The residue was then dissolved in THF (40 mL) and water (6 mL) at 0 °C, and MMPP (1.58 g, 3.18 mmol) was added portion wise until the substrate was consumed completely. The mixture was concentrated, taken up with CH_2Cl_2, washed with water, saturated aqueous $NaHCO_3$ and brine. After evaporation of the volatiles chromatography on silica gel (hexane:ethyl acetate = 2:1) afforded **69** as a single, but unassigned isomer (1.67 g, 82%). m.p. 109-111 °C; $[\alpha]_D^{20}$ = +19.8° (c = 0.5); ^{1}H-NMR, δ: 1.37-1.43 (m, 9H), 1.51 (s, 3H), 1.57 (s, 3H), 2.67-2.82 (m, 1H), 2.91-3.06 (m, 1H), 3.40-3.50 (m, 1H), 3.69 (t, J = 10.8 Hz, 1H), 3.77-3.90 (m, 2H), 4.26 (dd, J = 5.8, 8.1 Hz, 1H), 4.82-4.86 (m, 2H); ^{13}C-NMR, δ: 5.8, 18.6, 25.9, 28.0, 28.7, 43.6, 61.4, 67.3, 70.9, 71.7, 74.3, 90.0, 99.7, 109.6; Anal. Calcd. for $C_{14}H_{24}O_6S$: C, 52.48; H, 7.55; Found: C, 52.36; H, 7.60.

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-mannopyranosyl)-(1→6)-α-D-glucopyranoside (70)[6]. $[\alpha]_D^{20}$ = +22.7° (c = 1.6); ^{1}H-NMR, δ: 1.97 (s, 3H), 2.01 (s, 3H), 2.08 (s, 3H), 3.36 (s, 3H), 3.41-3.52 (m, 3H), 3.69-3.80 (m, 2H), 3.87 (t, J = 9.5 Hz, 1H), 3.97-4.13 (m, 3H), 4.38 (s, 1H), 4.41-4.63 (m, 5H), 4.82-5.00 (m, 6H), 5.49 (t, J = 10.0Hz, 1H), 7.14-7.47 (m, 20H); ^{13}C-NMR, δ: 20.6, 29.6, 55.1, 68.3, 69.0, 69.5, 70.1, 70.7, 71.3, 73.4, 73.8, 74.0, 74.6, 75.0, 75.8, 82.1, 96.4, 101.9, 127.5, 127.8, 127.9, 128.1, 128.2, 138.0, 138.2, 138.6, 169.8, 169.9, 170.1; IR υ: 2936, 1749, 1368, 1229, 1048 cm^{-1}; MS (EI): m/z 751 (M-PhCH$_2$); HRMS Calcd for $C_{40}H_{47}O_{14}$ (M-PhCH$_2$): 751.2966; Found: 751.3012.

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-α-D-glucopyranoside (71)[6]. $[\alpha]_D^{20}$ = +65.2° (c = 3.9); ^{1}H-NMR, δ: 1.95 (s, 3H), 2.01 (s, 3H), 2.08 (s, 3H), 3.30 (s, 3H), 3.51 (dd, J = 2.3, 11.5 Hz, 1H), 3.66-3.76 (m, 5H), 3.83-3.96 (m, 3H), 4.49-4.90 (m, 11H), 5.01 (t, J = 9.8 Hz, 1H), 5.43 (t, J = 9.8 Hz, 1H), 7.16-7.38 (m, 20H); ^{13}C-NMR, δ: 20.6, 29.6, 55.2, 65.0, 67.8, 68.8, 69.2, 70.3, 70.7, 71.9, 72.3, 72.6, 73.3, 74.7, 74.8, 79.7, 96.4, 98.1, 127.4, 127.5, 127.6, 127.7, 128.2, 138.2, 138.4, 138.5, 169.4, 170.1; IR υ: 2937, 1751, 1455, 1369, 1228, 1044 cm^{-1}; MS (EI): m/z 842 (M), 751 (M-PhCH$_2$).

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-(1,2:3,4-di-*O*-isopropylidene-β-D-mannopyranosyl)-(1→6)-α-D-glucopyranoside (72). $[\alpha]_D^{20}$ = +25.8° (c = 0.8); ^{1}H-NMR, δ: 1.36 (s, 3H), 1.43 (s, 3H), 1.53 (s, 3H), 1.57 (s, 3H), 2.00 (s, 3H), 2.02 (s, 3H), 2.07 (s, 3H), 3.21-3.30 (m, 1H), 3.41 (s, 3H), 3.62 (dd, J = 6.6, 11.6 Hz, 1H), 3.77 (t, J = 10.3 Hz, 1H), 3.90-4.19 (m, 5H), 4.28 (dd, J = 2.6, 6.1 Hz, 1H), 4.82-4.88 (m, 2H), 4.90-5.01 (m, 2H), 5.48 (t, J = 9.3 Hz, 1H); ^{13}C-NMR, δ: 18.8, 20.6 (3), 25.8, 27.4, 28.7, 55.2, 62.5, 65.9, 67.6, 68.6, 69.1, 70.0, 70.8, 71.8, 74.1, 76.1, 96.3, 98.9, 99.6, 111.0, 169.7, 170.0, 170.1; MS (EI): m/z 563 (M+1), 562 (M), 547 (M-Me). Anal. Calcd for $C_{25}H_{38}O_{14}.1.5H_2O$: C, 50.92; H, 7.00. Found; C, 50.58; H, 6.48.

Methyl 2,3,4-tri-*O*-acetyl-6-*O*-(1,2:3,4-di-*O*-isopropylidene-α-D-mannopyranosyl)-(1→6)-α-D-glucopyranoside (73). $[\alpha]_D^{20}$ = +96.3° (c = 3.0); ^{1}H-NMR, δ: 1.36 (s, 3H), 1.41 (s, 3H), 1.50 (s, 3H), 1.52 (s, 3H), 2.00 (s, 3H), 2.03 (s, 3H), 2.07 (s, 3H), 3.40 (s, 3H), 3.42-3.58 (m, 2H), 3.66-3.84 (m, 4H), 3.90-3.97 (m, 1H), 4.10-4.21 (m, 2H), 4.84-4.95 (m, 2H), 5.03 (s, 1H), 5.10 (t, J = 10.0 Hz, 1H), 5.46 (t, J = 10.0 Hz, 1H); ^{13}C-NMR, δ: 18.7, 20.5, 20.6 (2), 26.1, 28.1, 28.9, 55.4, 61.4, 61.7, 65.1, 67.7, 68.7, 70.2, 70.7, 72.4, 74.7, 75.7, 96.7, 97.8, 99.6, 109.4, 169.4, 170.0 (2); MS (FAB): m/z 505 (M+1-MeCOMe).

Reaction of 35 with PhSOTf and DTBMP at -78 °C. ^{1}H and ^{19}F-NMR Verification of Formation of Triflate 37: To AgOTf (34.9 mg, 0.142 mmol) in a 5 mm NMR tube at -78 °C was added a cold solution of PhSCl (7.9 mg, 0.057 mmol) in CD_2Cl_2 (0.5 mL) and the tube shaken vigorously at this temperature for 5 min. ^{19}F-NMR spectroscopy indicated the formation of PhSOTf (δ_F: -3.17). Then a cold solution of the thioglycoside **35** (11.0 mg, 0.028 mmol) and DTBMP (11.6 mg, 0.057 mmol) in CD_2Cl_2 (0.5 mL) was added at the same temperature. ^{1}H- and ^{19}F-NMR spectroscopy indicated the immediate formation of the glycosyl triflate **37** (anomeric δ_H: 6.20; δ_F: -0.13; Lit[38]. δ_H: 6.20; δ_F: -0.04).

Protocol E. General Glycoside Synthesis from Thioglycosides in CH_2Cl_2. To a stirred solution of AgOTf (83 mg, 0.324 mmol) in the chosen solvent (1.5 mL) at -78 °C is added a solution of PhSCl (39 mg, 0.27 mmol) in the same solvent (1.5 mL). After stirring for 5 min at -78 °C, a solution of the thioglycoside (0.11 mmol) and DTBMP (67 mg, 0.33 mmol) in the same solvent is added dropwise. After stirring for a further 5 min at that temperature the glycosyl acceptor (0.22 mmol) is added dropwise in the same solvent (1.5 mL). The reaction mixture is then allowed to warm to -20 °C over 40 min before quenching with sat. aqueous $NaHCO_3$, and filtration through Celite™. The filtrate is washed with brine, dried (Na_2SO_4), concentrated under vacuum, and the disaccharides isolated by chromatography on silica gel.

1-Adamantanyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranoside (79). $[\alpha]_D^{20}$ = -19.9° (c = 0.7); ^{1}H-NMR, δ: 1.55-1.72 (m, 6H), 1.72-1.91 (m, 6H), 2.11-2.21 (m, 3H), 3.26-3.37 (m, 1H), 3.59 (dd, J = 3.0, 9.9 Hz, 1H), 3.78 (bd, J = 3.0 Hz, 1H), 3.93 (t, J = 10.3 Hz, 1H), 4.15-4.30 (m,

2H), 4.58 (d, J = 12.5 Hz, 1H), 4.68 (d, J = 12.5 Hz, 1H), 4.75 (d, J = 0.8 Hz, 1H), 4.94 (d, J = 12.5 Hz, 1H), 5.03 (d, J = 12.5 Hz, 1H), 5.61 (s, 1H), 7.24-7.53 (m, 15H); ^{13}C-NMR, δ: 30.5, 36.1, 42.3, 67.2, 68.8, 72.2, 74.5, 75.1, 76.8, 78.3, 78.5, 94.8, 101.3, 126.0, 127.4, 128.0, 128.1, 128.2, 128.8, 137.7, 138.4, 138.5; MS (EI): m/z 583 (M+1), 582 (M^+); 581 (M-1); 491 (M- $PhCH_2$). HRMS Calcd. for $C_{30}H_{35}O_6$: 491.2434. Found: 491.2460 (M- $PhCH_2$).

3β-Acetoxy-20-(2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyloxyl)-20-methyl-5-pregnene (81). $[\alpha]_D^{20}$ = -65.0° (c = 4.2); ^{1}H-NMR, δ: 0.75-2.49 (m, 35H), 3.25-3.37 (m, 1H), 3.63 (dd, J = 3.0, 9.8 Hz, 1H), 3.82 (bd, J = 3.0 Hz, 1H), 3.95 (t, J = 10.3 Hz, 1H), 4.17-4.28 (m, 2H), 4.55-4.69 (m, 1H), 4.59 (d, J = 12.5 Hz, 1H), 4.66 (s, 1H), 4.71 (d, J = 12.5 Hz, 1H), 4.87 (d, J = 11.9 Hz, 1H), 4.98 (d, J = 11.9 Hz, 1H), 5.37-5.44 (m, 1H), 5.61 (s, 1H), 7.20-7.54 (m, 15H); ^{13}C-NMR, δ: 13.9, 19.2, 20.8, 21.4, 23.0, 23.8, 24.6, 27.7, 28.8, 31.2, 31.7, 36.5, 36.7, 38.0, 40.1, 42.5, 49.7, 56.7, 60.5, 67.3, 68.7, 72.2, 73.7, 75.0, 78.0, 78.6, 80.5, 96.4, 101.3, 122.5, 126.0, 127.4, 128.0, 128.1, 128.2, 128.3, 128.7, 137.6, 138.4, 138.7, 139.6, 170.4; MS (EI): m/z 805 (M+1), 804 (M^+). Anal. Calcd for $C_{51}H_{64}O_8.2H_2O$: C, 72.83; H, 8.15. Found: C, 72.41; H, 7.75.

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→6)-α-D-galactopyranoside (83). $[\alpha]_D^{20}$ = +16.7 (c = 3.4); ^{1}H-NMR, δ: 1.95 (s, 3H), 2.07 (s, 3H), 2.10 (s, 3H), 3.15-3.28 (m, 1H), 3.41 (s, 3H), 3.50 (dd, J = 3.0, 10.0 Hz, 1H), 3.90 (t, J = 10.4 Hz, 1H), 4.00 (bd, J = 3.0 Hz, 1H), 4.03-4.10 (m, 1H), 4.11-4.29 (m, 4H), 4.40 (dd, J = 4.3, 11.6 Hz, 1H), 4.45 (br s, 1H), 4.60 (d, J = 12.4 Hz, 1H), 4.69 (d, J = 12.4 Hz, 1H), 4.88 (d, J = 12.1 Hz, 1H), 4.97-5.05 (m, 2H), 5.24 (dd, J = 3.4, 10.8 Hz, 1H), 5.34 (dd, J = 3.4, 10.8 Hz, 1H), 5.61 (s, 1H), 7.20-7.59 (m, 15H); ^{13}C-NMR, δ: 20.7, 20.8 (2), 63.6, 67.6, 67.7, 68.3, 68.4, 69.8, 72.1, 74.0, 74.7, 75.6, 78.2, 97.0, 101.3, 102.4, 125.9, 127.5, 128.1, 128.2, 128.5, 128.8, 137.4, 138.1, 138.2, 169.7, 170.2, 170.5; MS (EI): m/z 751 (M+1), 750 (M), 749 (M-1), 719 (M-OMe), 718 (M-1-OMe), 708 (M+1-COMe), 707 (M-COMe), 691 (M-OOCMe), 660 (M+1-$PhCH_2$), 659 (M-$PhCH_2$); HRMS Calcd for $C_{33}H_{39}O_{14}$ (M-$PhCH_2$): 659.2340; Found: 659.2331.

Methyl 3-*O*-(Ethoxycarbonyl)-7α-(2,3,4,6-tetra-*O*-pivaloyl-β-D-glucopyranosyloxyl)-chenodeoxycholate (87)[36]. $[\alpha]_D^{20}$ = +12.2° (c = 5.4); ^{1}H-NMR, δ: 0.61 (s, 3H), 0.80-2.48 (m, 71H), 3.60-3.78 (m, 4H), 3.93 (dd, J = 5.5, 12.3 Hz, 1H), 3.98-4.07 (m, 1H), 4.10-4.28 (m, 3H), 4.32-4.49 (m, 1H), 4.71 (d, J = 7.6 Hz, 1H), 5.01 (dd, J = 7.6, 9.6 Hz, 1H), 5.10 (t, J = 9.6 Hz, 1H), 5.32 (t, J = 9.6 Hz, 1H); ^{13}C-NMR, δ: 11.5, 14.1, 18.2, 20.5, 22.5, 23.3, 26.7, 26.9, 27.0, 27.1, 27.2, 27.9, 30.9, 31.1, 33.1, 34.0, 34.9, 35.0, 35.3, 38.6, 38.7, 39.5, 40.7, 42.3, 49.4, 51.3, 55.6, 61.7, 63.3, 68.4, 70.3, 71.6, 72.4, 77.6, 95.3, 154.9, 174.6, 176.5, 176.7, 176.8, 178.0; MS (EI): m/z 978 (M+1), 977 (M), 945 (M-1-OMe), 876 (M-Bu^tCOO), 875 (M-1-Bu^t).

2,6-Dimethylphenyl 2,3,4,6-Tetra-*O*-pivaloyl-β-D-glucopyranoside (90)[36]. $[\alpha]_D^{20}$ = +3.7° (c = 1.7); ^{1}H-NMR, δ: 1.09 (s, 9H), 1.13 (s, 9H), 1.14 (s, 9H), 1.21 (s, 9H), 2.27 (s, 6H), 3.58 (ddd, J = 2.1, 5.2, 10.0 Hz, 1H), 5.98 (dd, J = 5.2, 12.2 Hz, 1H), 4.06 (dd, J = 2.1, 12.2 Hz, 1H), 4.96 (d, J = 7.8 Hz, 1H), 5.19 (t, J = 9.4 Hz, 1H), 5.35-5.41 (m, 2H), 6.90-7.00 (m, 3H); ^{13}C-NMR, δ: 16.9, 26.8, 26.9, 27.1, 27.2, 38.7, 38.8, 61.4, 68.0, 71.7, 72.6, 100.7, 124.7, 128.7, 131.4, 151.9, 176.3, 176.5, 177.2, 177.9; MS (EI): m/z 620 (M), 619 (M-1), 605 (M-Me).

2,6-Dimethylphenyl 2,3,4,6-Tetra-*O*-pivaloyl-α-D-glucopyranoside (91). $[\alpha]_D^{20}$ = +20.8° (c = 1.7); ^{1}H-NMR, δ: 1.13 (s, 9H), 1.14 (s, 9H), 1.16 (s, 9H), 1.29 (s, 9H), 2.28 (bs, 3H), 2.32 (bs, 3H), 3.45 (dd, J = 4.2 Hz, 1H), 4.00-4.15 (m, 3H), 4.89 (t, J = 8.8 Hz, 1H), 5.08 (d, J = 5.8 Hz, 1H), 5.13 (dd, J = 4.2, 8.8 Hz, 1H); ^{13}C-NMR, δ: 17.4, 17.5, 25.5, 26.7, 27.0, 38.5, 38.6, 38.7, 39.8, 62.4, 65.9, 69.8, 73.2, 78.5, 97.4, 124.7, 128.7, 128.9, 129.3, 150.0, 176.6, 176.7, 177.8; MS (EI): m/z 619 (M-1), 605 (M-Me), 564 (M+1-Bu^t), 563 (M-Bu^t). Anal. Calcd for $C_{34}H_{52}O_{10}.0.5H_2O$: C, 64.84; H, 8.48. Found: C, 65.05; 8.46.

1-Adamantanyl 2,3,4,6-Tetra-*O*-pivaloyl-β-D-glucopyranoside (92). Mp = 215-217 °C; $[\alpha]_D^{20}$ = +3.8 (c = 3.2); ^{1}H-NMR, δ: 1.09 (s, 9 H), 1.14 (2s, 18H), 1.20 (s, 9H), 1.50-1.88 (m, 12H), 2.06-2.18 (m,

3H), 3.67-3.76 (m, 1H), 3.91 (dd, J = 7.6, 12.0 Hz, 1H), 4.20 (dd, J = 1.6, 12.0 Hz, 1H), 4.84 (d, J = 8.0 Hz, 1H), 4.94-5.02 (m, 2H), 5.32 (t, J = 9.4 Hz, 1H); ^{13}C-NMR, δ: 26.9, 27.0, 27.2, 30.5, 36.0, 38.7, 42.5, 62.7, 68.6, 71.2, 71.9, 72.5, 75.5, 94.0, 176.2, 176.6, 177.1, 178.0; MS (EI): m/z 635 (M-Me), 594 (M+1-Bu^t), 593 (M-Bu^t), 549 (M-Bu^{t}COO). Anal. Calcd for $C_{36}H_{58}O_{10}$: C, 66.44; H, 8.98. Found: C, 66.52; 9.05.

Methyl 3-*O*-(Ethoxycarbonyl)-7α-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyloxyl)chenodeoxycholate (95)[36]. $[\alpha]_D^{20}$ = +33.2° (c = 3.9); ^{1}H-NMR, δ: 0.56 (s, 3H), 0.65-2.34 (m, 34H), 2.50 (bq, J = 11.9 Hz, 1H), 3.55 (dd, J = 3.4, 9.9 Hz, 1H), 3.60-3.70 (m, 5H), 3.71-3.89 (m, 3H), 3.91-4.06 (m, 3H), 4.38-4.55 (m, 3H), 4.62 (d, J = 12.0 Hz, 1H), 4.68-4.87 (m, 4H), 4.95 (d, J = 10.8 Hz, 1H), 5.09 (d, J = 3.5 Hz, 1H), 7.10-7.40 (m, 20H); ^{13}C-NMR, δ: 11.6, 14.1 18.2, 20.3, 22.5, 24.9, 26.5, 28.0, 30.8, 31.1, 32.1, 32.4, 34.9, 35.1, 35.2, 38.6, 40.2, 41.4, 42.5, 48.7, 51.4, 54.8, 63.2, 68.3, 71.2, 72.8, 73.4, 74.5, 75.7, 76.2, 77.8, 80.5, 82.0, 97.5, 126.8, 127.3, 127.5, 127.8, 128.0, 128.1, 128.2, 137.9, 138.6, 138.8, 154.7, 174.6; MS (EI): m/z 1000 (M), 910 (M+1-PhCH$_2$), 909 (M-PhCH$_2$), 895 (M+1-Me-PhCH$_2$).

2,6-Dimethylphenyl 2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranoside (96). Mp = 140-141 °C (lit.[68] 140-141 °C); $[\alpha]_D^{20}$ = +21.5° (c = 1.7) (lit. +25[68]; +39.7[69]); ^{1}H-NMR, δ: 2.39 (s, 6H), 3.26-3.35 (m, 1H), 3.60-3.80 (m, 5H), 4.46 (d, J = 12.1 Hz, 1H), 4.54 (d, J = 12.1 Hz, 1H), 4.62 (d, J = 11.0 Hz, 1H), 4.77-4.90 (m, 4H), 5.00 (d, J = 11.0 Hz, 1H), 5.16 (d, J = 11.0 Hz, 1H), 7.10-7.45 (m, 20 H); ^{13}C-NMR, δ: 17.1, 68.8, 73.4, 74.9, 75.3, 75.6, 77.7, 82.7, 84.7, 104.1, 124.5, 127.5, 127.9, 128.1, 128.3, 128.7, 138.1, 138.2, 138.6.

2,6-Dimethylphenyl 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranoside (97). $[\alpha]_D^{20}$ = +36.7° (c = 4.2) (lit. +46[68]; +48.2[69]); ^{1}H-NMR, δ: 2.36 (s, 6H), 3,65-3.74 (m, 2H), 3.77-3.88 (m, 2H), 4.23-4.34 (m, 2H), 4.44-4.74 (m, 5H), 4.92 (2d, J = 11.1 Hz, 2H), 5.30 (d, J = 3.3 Hz, 1H), 7.20-7.45 (m, 20 H); ^{13}C-NMR, δ: 17.7, 68.4, 71.6, 73.4, 73.8, 75.1, 75.6, 77.6, 80.7, 81.6, 99.5, 123.4, 127.6, 127.8, 128.0, 128.2, 128.3, 129.2, 130.0, 135.6, 137.7, 137.8, 138.2, 138.6.

1-Adamantanyl 2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranoside (98). Mp = 125-127 °C; $[\alpha]_D^{20}$ = +14.1 (c = 6.1); ^{1}H-NMR, δ: 1.60-2.30 (m, 15H), 3.40-3.81 (m, 6H), 4.58 (d, J = 11.0 Hz, 1H), 4.59 (d, J = 12.2 Hz, 1H), 4.64 (d, J = 12.2 Hz, 1H), 4.74 (d, J = 7.8 Hz, 1H), 4.76 (d, J = 11.0 Hz, 1H), 4.82 (d, J = 11.0 Hz, 1H), 4.87 (d, J = 11.0 Hz, 1H), 4.96 (d, J = 11.0 Hz, 1H), 5.06 (d, J = 11.0 Hz, 1H), 7.20-7.48 (m, 20H); ^{13}C-NMR, δ: 30.6, 36.2, 42.7, 69.4, 73.3, 74.5, 74.9, 75.3, 75.7, 78.2, 82.3, 85.1, 96.2, 127.4, 127.5, 127.7, 127.8, 127.9, 128.2, 128.3, 138.1, 138.4, 138.5, 138.6; MS (EI): m/z 675 (M+1), 674 (M), 673 (M-1), 583 (M+1-PhCH$_2$), 582 (M-PhCH$_2$), 581 (M-1-PhCH$_2$). Anal. Calcd for $C_{44}H_{50}O_6$: C, 78.31; H, 7.47. Found: C, 78.43; H, 7.53.

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