# Tuning glycoside reactivity: New tool for efficient oligosaccharide synthesis

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**The concise preparation of complex oligosaccharides remains a significant challenge for synthetic organic chemistry. The tuning of donor reactivity during coupling reactions, such that we may avoid the lengthy protecting-group manipulations of classical carbohydrate synthesis, affords a strategy for the rapid assembly of large sugar systems. Competition reactions have been used to quantify the influence of protecting groups, monosaccharide type, and anomeric leaving groups on the reactivity of various glycosyl donors.**

## Introduction

An enduring area of research in both chemistry and biology is that of carbohydrates. In recent years, advances in analytical methods have shown that, as well as being renewable stores of energy and skeletal components,[1] carbohydrates play an extensive role in biochemical processes.[2] The structural diversity of sugar oligomers leads to their involvement in many key inter- and intra-molecular events.[3] The glycans of glycoconjugates are essential for biological recognition, whilst cells, bacteria, viruses and toxins all use cell-surface carbohydrates as points of attachment.[4] Such important discoveries have reinvigorated research interest in oligosaccharides, focusing on both their synthesis and function.

The concise preparation of complex oligosaccharides remains a significant challenge for synthetic organic chemistry. The combined demands of regio- and stereo-selectivity in glycoside bond forming processes leads to extended synthetic schemes and extensive protecting group manipulations. In particular, in classical approaches to oligosaccharides the unmasking of hydroxy (acceptor) or anomeric (donor) functionality is often required between coupling protocols, increasing the linearity and decreasing the efficiency of carbohydrate assembly. A coupling strategy that avoids such protecting group manipulations thus offers significant advantages for convergent glycoside synthesis. The foundations for such synthetic routes were laid when Paulsen noted a significant influence of the protecting groups situated on a glycosyl halide on the rate of hydrolysis of the anomeric position.[5] For example, benzoyl protected glycosyl halides were hydrolysed significantly slower than were glycosyl donors protected with benzyl groups. Such an effect arises from the fact that the electron withdrawing benzoyl groups destabilise the presumed cationic transition state leading to glycoside formation. Such ideas were further advanced when Fraser-Reid observed similar effects in the glycosidation of *O*-pentenyl glycosides.[6] The key observation was that if two glycosyl donors of different reactivity were mixed and only one equivalent of promoter added, only the most reactive glycosyl donor in the system was activated and glycosylated. Such a reaction profile arises because activation of the glycosyl donor by reaction with the promoter is reversible and rapid compared with the subsequent steps leading to glycoside formation.† The inherent reactivity of the glycosyl donors is thus revealed in the final product distribution. If the acceptor functionality is located in the less reactive component, selective glycosidation can occur leading to a specific disaccharide. Similar effects were noted by van Boom in the reaction of thioglycosides.[7] In this early work, reactions were generally confined to the formation of disaccharides, usually involving the coupling of highly reactive perbenzylated glycosyl donors with, for example, systems containing large numbers of deactivating benzoyl protecting groups.


Dispiroketal or 'dispoke' protected methyl mannoside

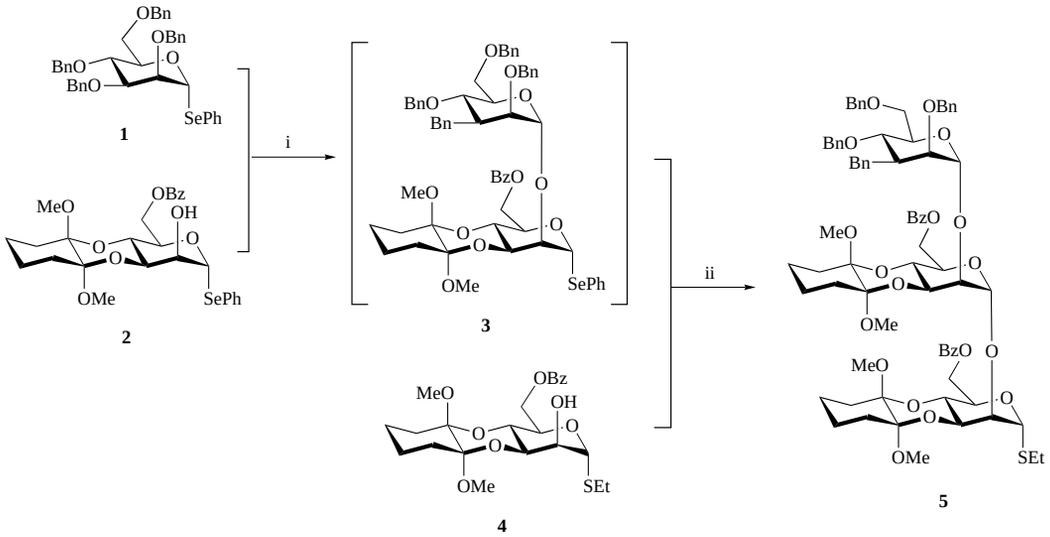
Cyclohexane-1,2-diacetal or 'CDA' protected methyl mannoside

**Fig. 1** Illustration of the dispoke and CDA protecting groups

With our discovery of the dispiroketal and later the cyclohexane-1,2-diacetal (CDA) protecting group (Fig. 1) we were able to extend these concepts to develop a strategy for the rapid assembly of much larger systems.[8,9] The key feature in this work was the observation that the reactivity of glycosyl donors protected with the octahydro-2,2′-bi-2*H*-pyran-2,2′-diyl (dispoke) or CDA systems had a reactivity tuning effect between that of the fully benzylated and fully benzoylated system. This advance immediately led to the opportunity for preparing tri- and tetra-saccharides *without the need for protecting-group manipulations.*[10] The general strategy is illustrated in Scheme 1 by the preparation of a trisaccharide **5**[10b] from monomers **1**, **2** and **4** *via* disaccharide **3** (Scheme 1).

This approach to oligosaccharide assembly by the use of designed, chemoselective glycosidation sequences requires a change in the perception of the reactivity of glycosyl donor systems; rather than the systems being grouped simply into reactive or unreactive, the reactivity of glycosyl donors must be regarded as a continuum. Many factors affect the reactivity of a system; the protecting groups, the anomeric leaving group and the nature and stereochemistry of the monosaccharide skeleton. Even remote positions can have a profound influence on the outcome of tandem sequences; for example, in the preparation of a high mannose nonasaccharide the change of the protecting group on the 6-position of one component proved critical for the assembly of this large saccharide.[10b] The challenge in the design of rapid syntheses of complex oligosaccharides using such glycosidation sequences thus becomes based on the ability of the chemist to *tune* the reactivity of all the coupling components such that each of the coupling reactions is

† Reaction with promoter may in fact not be reversible. Transfer of the promoting agent may instead occur directly between activated and unactivated donor systems in a bimolecular reaction. The effect is however the same as if the promotion reaction were reversible.

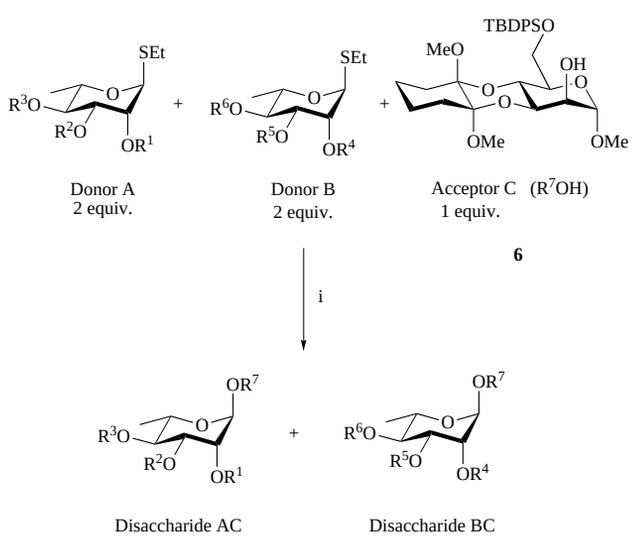



**Scheme 1** *Reagents and conditions:* i, NIS, cat. TfOH, 4 Å molecular sieves, 1,2-dichloroethane (DCE)–diethyl ether, 10 min; ii, NIS, cat. TfOH, 4 Å molecular sieves, DCE–diethyl ether, 1 h (67%)

highly chemoselective. Such tuning of reactivity must also be performed such that the designed monosaccharide building blocks can be synthesised rapidly and without endless protecting group manipulations. With experience we have acquired a level of semi-quantitative information about the tuning effects of various parameters on glycoside reactivity, and such knowledge has enabled the efficient synthesis of several large oligosaccharide targets to be achieved. However, as we became focused on increasingly complex oligosaccharides the need for more precise data on the reactivity of glycosyl donors became even more apparent. In order to achieve such an aim the reactivity of the donors must be better quantified. In practice such a task rapidly assumes immense proportions as the number of variables in protecting groups, anomeric leaving groups and monosaccharide cores becomes so large that to explicitly define the reactivity of every glycosyl donor is clearly impossible. We were, however, intrigued by the possibility that such a mammoth task may not be necessary. If the effect of a certain protecting group at a certain position on the monosaccharide skeleton was always the same, regardless of the other protecting groups on the rest of the molecule, it would be possible to generate a matrix of reactivity coefficients that would allow the precise prediction of the reactivity of any glycosyl donor. Not only would such a tool aid the confident design of glycosylation sequences but, by tuning the reactivity of all the components to maximise the number of couplings that can be achieved between the most reactive and least reactive systems, it would also enable ever larger oligosaccharides to be prepared without protecting group manipulations. For such a predictive tool to be useful a particular protecting group at a particular position must always influence the transition state leading to glycosylation by the same amount of energy. If such a correlation can be determined, a highly useful method for oligosaccharide assembly could be developed.

## Results and discussion

In order to establish whether the assembly of such a matrix was possible it was decided to investigate the reactivity of thiorhamnoside glycosyl donors protected with just benzyl and benzoyl groups. By synthesising and evaluating the reactivity of donors with *all possible* combinations of benzyl and benzoyl protecting groups around the rhamnoside core it would be possible to determine both the influence of the benzoyl groups at each position of the monosaccharide, and the consistency of their deactivation of anomeric reactivity. We were particularly keen to evaluate the reactivity of these systems under conditions that closely resembled selective glycosidation reactions rather than glycoside hydrolysis. The steric demands of water as a glycosyl acceptor are clearly completely different to those of a monosaccharide. This could result in significantly different mechanisms operating during such hydrolyses as compared with glycosidation processes. It was therefore decided to evaluate the reactivity of glycosyl donors through a series of competition reactions. In these experiments two glycosyl donors are mixed and compete for a standard acceptor alcohol, in this case the CDA protected mannoside **6** (Scheme 2). Each donor is




**Scheme 2** *Reagents and conditions:* i, NIS, cat. TfOH, 4 Å molecular sieves, DCE–diethyl ether

present in excess so that as the reaction progresses the availability of each remains high. The reaction is complete when all the acceptor has reacted, which equates to consumption of 25% of the available donors, ensuring that the acceptor is the controlling factor. As in standard coupling reactions the product ratio thus reflects the inherent reactivity of the two glycoside donors.

The ratio of products can be readily determined by analysis of the 500 MHz $^1$H NMR spectrum of the mixture of products. The methoxy groups of the CDA group and at the anomeric centre in the products are particularly useful in such a determination; they act as excellent markers in the NMR spectrum and are usually sufficiently resolved to allow accurate determination of product ratios. The choice of rhamnose for

**Table 1** Product ratios for competition reactions in the thiorhamnoside series

| Entry | Donor A | | Donor B | | Quotient AC/BC | |
|---|---|---|---|---|---|---|
| 1 | TriBn | **7** | 3-Bz | **9** | 3.1[a] | **16/18** |
| 2 | TriBn | **7** | 4-Bz | **10** | 8.9 ± 1.0[a,b] | **16/19** |
| 3 | TriBn | **7** | 2-Bz | **8** | 26.6 ± 9.5[a,b] | **16/17** |
| 4 | 2,4-DiBz | **12** | TriBz | **14** | 2.5 | **21/23** |
| 5 | 2,3-DiBz | **11** | TriBz | **14** | 13.0 ± 2.8[b] | **20/23** |
| 6 | 3,4-DiBz | **13** | TriBz | **14** | 24.2 ± 2.1[b] | **22/23** |
| 7 | 3-Bz | **9** | 4-Bz | **10** | 2.5 | **18/19** |
| 8 | 3-Bz | **9** | 3,4-DiBz | **13** | 5.1 | **18/22** |
| 9 | 4-Bz | **10** | 3,4-DiBz | **13** | 2.1 | **19/22** |
| 10 | 4-Bz | **10** | 3,4-CDA | **15** | 2.6 | **19/24** |
| 11 | 4-Bz | **10** | 2-Bz | **8** | 3.9 | **19/17** |
| 12 | 3,4-DiBz | **13** | 3,4-CDA | **15** | 1.7 | **22/24** |
| 13 | 3,4-DiBz | **13** | 2-Bz | **8** | 2.1 | **22/17** |
| 14 | 3,4-DiBz | **13** | 2,3-DiBz | **11** | 2.8 | **22/20** |
| 15 | 3,4-DiBz | **13** | 2,4-DiBz | **12** | 27.3 ± 9.4[b] | **22/21** |
| 16 | 3,4-CDA | **15** | 2-Bz | **8** | 1.7 | **24/17** |
| 17 | 2-Bz | **8** | 2,3-DiBz | **11** | 1.6 | **17/20** |
| 18 | 2,3-DiBz | **11** | 2,4-DiBz | **12** | 5.3 ± 0.5[b] | **20/21** |

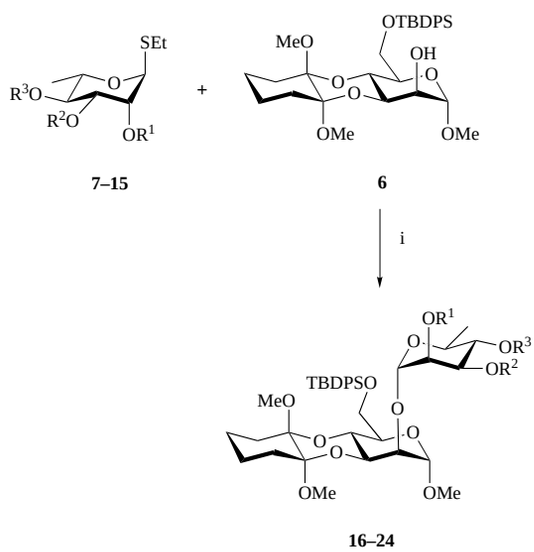
[a] Ratios are equal to DFs. [b] Large product quotients have inherently large errors in measurement.

our model system greatly simplifies this initial trial study as the glycosylations are highly alpha selective and hence only two products are formed in the competition reaction. Furthermore, as rhamnose only has three hydroxy groups there are only eight combinations of benzyl and benzoyl protected systems that can be prepared, as compared with sixteen for a monosaccharide such as mannose.

Benzylation of ethyl 1-thio-α-L-rhamnopyranoside gave a statistical mixture of all possible benzylation products which could be separated by column chromatography and benzoylated to provide all eight required glycosyl donors. The acceptor **6** for the glycosylation reactions was prepared using standard CDA methodology.[9b] All the target disaccharides were prepared and characterised independently by the *N*-iodosuccinimide (NIS), catalytic triflic acid (TfOH)-mediated glycosylation protocol of van Boom (Scheme 3).[11]

The competition reactions were performed between donors of similar reactivity to ensure measurable ratios in the NMR spectra and the results are shown in Table 1 and Fig. 2. Competition of tribenzyl protected rhamnoside **7** with the monobenzoates **8**–**10** showed the profound effect of the benzoate group. For example, benzoate protection at the 2-position caused the donor to be 26 times less reactive than the perbenzylated system. This implies that the transition state leading to glycosylation is approximately 8 kJ $mol^{-1}$ higher in energy when the benzyl group is replaced by the benzoate. As expected, the benzoate has most influence when it is closest to the anomeric position; however, both the 3- and 4-benzoate protected systems do show significant deactivation compared with the tribenzyl system. Interestingly, the 4-benzoate was noticeably more deactivating than the corresponding 3-benzoate, an effect that is not easily rationalised. Such an observation may indicate that, when remote from the neighbouring 2-position, proximity of an electron withdrawing group to the ring oxygen becomes more important than proximity to the anomeric centre in destabilising glycosylation transition states.

Significantly, when the dibenzoates **11**–**13** were competed with the tribenzoate donor **14**, similar ratios were observed to the above reactions, *i.e.* a change of a 2-*O*-benzyl group to a 2-*O*-benzoate causes the same amount of deactivation of the glycosyl donor *irrespective* of the other protecting groups on the molecule. Therefore, in principle, starting from the reactivities of the monobenzoate systems **8**–**10** it should be possible to predict the reactivities of all the other glycosyl donors and hence the ratios for competition reactions between any pair of donors. To test this hypothesis competition reactions were performed




**Scheme 3** *Reagents and conditions:* i, NIS, cat. TfOH, 4 Å molecular sieves, DCE–diethyl ether

| Donor | $R^1$ | $R^2$ | $R^3$ | Disacc. |
|---|---|---|---|---|
| **7** | Bn | Bn | Bn | **16** |
| **8** | Bz | Bn | Bn | **17** |
| **9** | Bn | Bz | Bn | **18** |
| **10** | Bn | Bn | Bz | **19** |
| **11** | Bz | Bz | Bn | **20** |
| **12** | Bz | Bn | Bz | **21** |
| **13** | Bn | Bz | Bz | **22** |
| **14** | Bz | Bz | Bz | **23** |
| **15** | Bn | CDA | | **24** |

between all donors which would give a measurable ratio of products.

In order to convert the data from these competition reactions into a more usable form, a 'deactivation factor' (DF) was defined for a given protecting group as the reduction of the rate of glycosylation by the presence of that group with respect to the fully benzylated compound. The DF of the fully benzylated compound is defined as 1. In the simplest case the deactivation factor is the ratio in the competition reaction between the fully benzylated compound and a donor having one non-benzyl protecting group. The deactivation factor is a

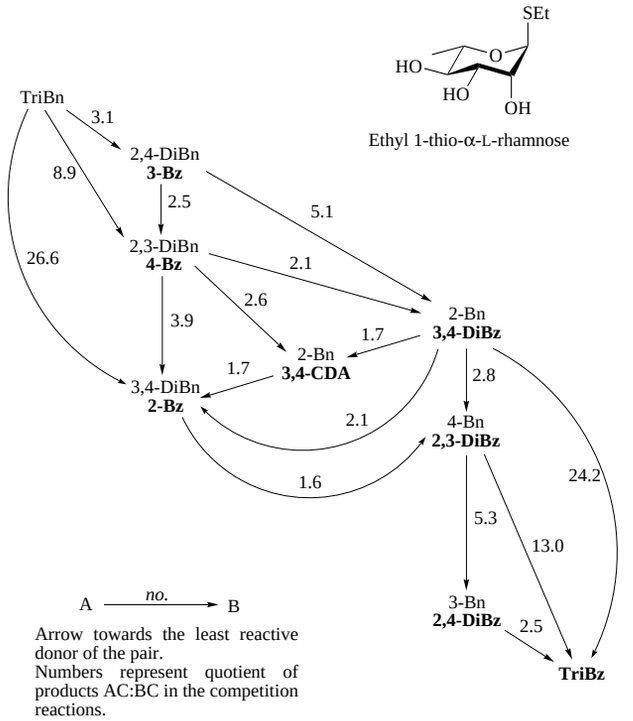



**Fig. 2** Flowchart demonstrating the deactivation of thiorhamnoside donors by various protecting group combinations

measure of the increase in the activation energy of the glycosylation reaction when a benzyl group is replaced with another substituent, with DF = $e^{\Delta\Delta G^{\ddagger}/RT}$. Larger values of DF indicate a more deactivating influence of the protecting group.‡ Hence from our initial data on the reactivity of the monobenzoylated systems the DF of the benzoate group at each position is 2-*O*-Bz = 26.6, 3-*O*-Bz = 3.1, 4-*O*-Bz = 8.9.

In order to predict the reactivity of any glycosyl donor the DFs of each protecting group on the monosaccharide are just multiplied together (the equivalent of adding the $\Delta\Delta G^{\ddagger}$). It can be readily seen that using the results from the competition reactions shown in Table 1 (entries 1–3) the outcome of the reactions in the rest of the series are predicted with a high level of accuracy from our initial data on the reactivity of the monosubstituted systems. For example, the 3,4-di-*O*-benzoyl-2-*O*-benzyl glycosyl donor **13** is predicted to have a total deactivation of 3.1 × 8.9 × 1 = 27.6 whilst a 2,3-di-*O*-benzoyl-4-*O*-benzyl donor **11** is predicted to have a total deactivation of 87.5. The competition reaction between them should therefore give a quotient of 87.5/27.6 = 3.1 (Table 1, entry 14) which is close to the observed value of 2.8, demonstrating the predictive ability of this technique.

Using all the data collected it is possible to use averaging to calculate more accurate DFs for the three positions of rhamnose, the results of which are shown in Table 2. It is notable that these averages do not significantly deviate from the factors calculated from the initial studies of the monobenzoylated systems.

These results imply that from a relatively limited amount of data the reactivity of a wide variety of glycoside donors can be predicted. Competition reactions to calculate the deactivation factor for the CDA protecting group were also performed. The results clearly demonstrated that protection of the 3- and 4-positions of rhamnose with a CDA group produces a greater deactivation effect than when these two positions are protected with Bz groups. This effect may be explained by considering that the annulated CDA group resists the flattening of the sugar ring that is required during oxonium ion formation, although

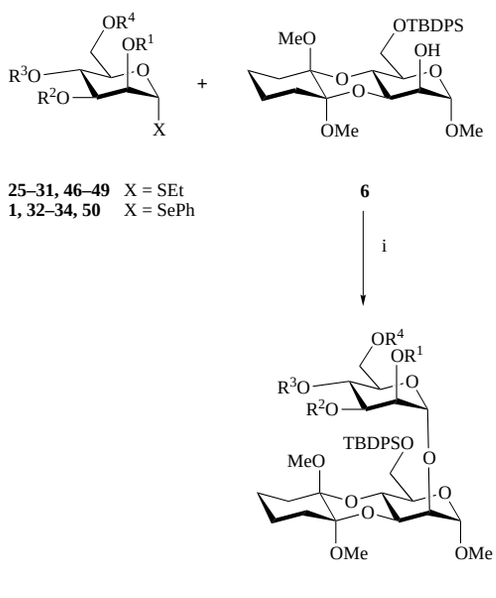
‡ *i.e.* $\Delta\Delta G$ is positive.

**Table 2** Standardised deactivation factors for non-Bn protecting groups on thiorhamnose

| Entry | Position of non-Bn group | DF |
|---|---|---|
| 1 | 3-Bz | 2.3 |
| 2 | 4-Bz | 9.0 |
| 3 | 3,4-CDA | 27.0 |
| 4 | 2-Bz | 36.5 |

Fraser-Reid has suggested that the deactivation of dispoke protected glycosyl donors may be due to solvation effects.[12]

Encouraged by these results we studied next the reactivity of the mannoside glycosyl donors. The important questions in this case were whether the deactivation factors for the 2-, 3- and 4-positions of a mannoside donor would be the same as those in rhamnose and what was the influence of the protecting groups at the 6-position. Accordingly, the monobenzoylated thiomannoside donors were prepared and the disaccharides synthesised for characterisation (Scheme 4). The results of the subsequent




**Scheme 4** i, NIS, cat. TfOH, 4 Å molecular sieves, DCE–diethyl ether

| Donor | $R^1$ | $R^2$ | $R^3$ | $R^4$ | Disacc. |
|---|---|---|---|---|---|
| **25** | Bz | Bn | Bn | Bn | **35** |
| **26** | Bn | Bz | Bn | Bn | **36** |
| **27** | Bn | Bn | Bz | Bn | **37** |
| **28** | Bn | Bn | Bn | Bz | **38** |
| **29** | Bn | CDA | | Bn | **39** |
| **30** | Bn | dispoke | | Bn | **40** |
| **31** | Bn | BDA | | Bn | **41** |
| **46** | Bn | Bn | Bn | Bn | **42** |
| **47** | Bn | Bn | Bn | 4-MeOBz | **43** |
| **48** | Bn | Bn | Bn | 4-MeBz | **44** |
| **49** | Bn | Bn | Bn | 4-$NO_2$Bz | **45** |
| **1** | Bn | Bn | Bn | Bn | **42** |
| **32** | Bn | Bn | Bn | 4-MeOBz | **43** |
| **33** | Bn | Bn | Bn | 4-MeBz | **44** |
| **34** | Bn | Bn | Bn | 4-$NO_2$Bz | **45** |
| **50** | Bn | Bn | Bn | Bz | **38** |

competition reactions are shown in Table 3 and Fig. 3. From these data it was possible to calculate the DFs for each position (Table 4). It can be seen directly that these differ from those observed in the rhamnose series, although the order of importance 2 > 4 > 3 remains the same. The protecting group at the 6-*O*-position shows a dramatic effect with a DF of approximately 10 for the 6-*O*-benzoyl group. Again, this is indicating that

**Table 3** Product ratios for competition reactions in the thiomannoside series

| Entry | Donor A | | Donor B | | Quotient AC/BC | |
|---|---|---|---|---|---|---|
| 1 | TetraBn | **46** | 3-Bz | **26** | 1.1[a] | **42/36** |
| 2 | TetraBn | **46** | 4-Bz | **27** | 4.6 ± 0.5[a,b] | **42/37** |
| 3 | TetraBn | **46** | 6-Bz | **28** | 10.2[a] | **42/38** |
| 4 | TetraBn | **46** | 2-Bz | **25** | >30[a] | **42/35** |
| 5 | 3-Bz | **26** | 4-Bz | **27** | 4.5 | **36/37** |
| 6 | 3-Bz | **26** | 6-Bz | **28** | 7.2 | **36/38** |
| 7 | 3-Bz | **26** | 2-Bz | **25** | 32.6 ± 3.0[b] | **36/35** |
| 8 | 4-Bz | **27** | 6-Bz | **28** | 1.7 | **37/38** |
| 9 | 4-Bz | **27** | 2-Bz | **25** | 5.4 | **37/35** |
| 10 | 6-Bz | **28** | 3,4-CDA | **29** | 1.7 | **38/39** |
| 11 | 6-Bz | **28** | 2-Bz | **25** | 3.2 | **38/35** |
| 12 | 3,4-CDA | **29** | 3,4-dispoke | **30** | 1.1 | **39/40** |
| 13 | 3,4-CDA | **29** | 3,4-BDA | **31** | 1.2 | **39/41** |
| 14 | 3,4-CDA | **29** | 2-Bz | **25** | 2.4 | **39/35** |

[a] Ratios are equal to DFs. [b] Large product quotients have inherently large errors in measurement.

**Table 4** Standardised DFs for non-Bn protecting groups on thiomannose

| Entry | Position of non-Bn group | DF |
|---|---|---|
| 1 | 3-Bz | 1.1 |
| 2 | 4-Bz | 5.0 |
| 3 | 6-Bz | 8.2 |
| 4 | 3,4-CDA | 13.9 |
| 5 | 3,4-dispoke | 14.9 |
| 6 | 3,4-BDA | 16.5 |
| 7 | 2-Bz | 33.6 |

proximity of the electron withdrawing group to the ring oxygen is an important feature. The difference in DF values between rhamnose and mannose indicates that the effects of a protecting group would have to be calculated independently for each monosaccharide skeleton, although we anticipate that the DF values will remain constant within each monosaccharide system. The variation of deactivations between rhamnose and mannose probably indicates that the transition states are not directly comparable between the two systems. The effect of the CDA group was again evaluated in this system. As with the rhamnose system the CDA group was more deactivating than donors protected with benzoate groups at these positions. We also compared the reactivity of CDA protected systems with dispoke and butane diacetal (BDA) protected glycosyl donors.[13,14] The reactivity differences between these systems are small; however, indications are that deactivating effects are in the order BDA > dispoke > CDA.

In order to enable prediction of the outcome of reactions between mannose and rhamnose systems we also performed competition reactions between these two sugars. The results show that mannose systems are 2.6 times less reactive than rhamnosides.

In order to be able to fine tune the reactivity of glycoside donors for a given synthetic plan the effect of substituents on the ring of a 6-*O*-benzoate group were also investigated. Competition experiments between glycosyl donors protected at the 6-*O*-position with benzoate and substituted benzoate groups produced the quotients shown in Table 5 which imply the DF values shown. Substitution with electron withdrawing substituents and electron donating groups had the expected effect. As can be seen such substitutions offer another area for control of the reactivity of donor systems, whilst synthetic schemes remain essentially unchanged.

The final task was to evaluate the influence of changing the anomeric leaving group to a phenylseleno system, both on the reactivity of glycosyl donor and on the values of the DFs, as compared with those calculated for thioglycoside systems. As can be seen in Table 6 the effect of a benzoyl group at the 6-position of selenoglycosides produces a much smaller DF than in the thioglycoside series. Also, variation of the protecting group on the 6-position produces smaller changes in the reactivity of the glycosyl donor as compared with the thioglycoside series. Again this is probably due to changes in the transition states between the selenoglycoside and thioglycoside reactions.

The calculation of the relative reactivity of seleno- and thio-glycosides using our competition reaction system is much harder as the same disaccharide is produced by activation of both glycoside donors. A competition reaction was performed between the fully benzylated selenomannoside **1** and 3-*O*-benzoylated thiomannoside **26**, and gave a product ratio of 23.9 : 1 (**42** : **36**). By comparison of this ratio with the data from Table 3, entry 1, the effect of the seleno leaving group can be separated from the change in the protecting group. These results imply that selenoglycosides are some 21.7 times more reactive than their sulfur counterparts.

## Conclusions

In order to advance the design and understanding of glycoside assembly using chemoselective glycosylation sequences we have broadly quantified the influence of protecting groups, monosaccharide type and anomeric leaving group on the reactivity of various glycosyl donors. This research has demonstrated, importantly, that for a given monosaccharide skeleton and anomeric leaving group, the influence of a protecting group is constant *regardless of the other protecting groups around the monosaccharide ring.* This enables the reactivity of glycoside systems to be predicted from a relatively small set of initial data. For rhamnose systems, electron withdrawing groups decrease the rate of reaction most when placed at the 2-position, with the 4-position being the next most important. For mannose the influence of the positions is in the order 2 > 6 > 4 > 3. From these results it is clear that, excepting the neighbouring 2-position, proximity of electron withdrawing groups to the ring oxygen is more important than their distance from the anomeric position.

The quantitative influence of protecting groups on the reactivity of a glycosyl donor does however change between monosaccharide types and when the anomeric leaving group is changed. This probably reflects changes in the character of the transition state leading to glycosidation when these parameters are altered.

The data revealed by this research enable the prediction of the reactivity of rhamnoside and mannoside glycosyl donors with SEt or SePh at the anomeric position and any combination of benzyl, benzoate or CDA protecting groups. Fine tuning of the reactivity can be achieved by employing phenyl ring substituted benzoate groups. These data could be rapidly expanded to provide information for other carbohydrate systems. Alternatively, this research provides excellent data for the generation

**Table 5** Competition reactions of substituted 6-*O*-benzoylthiomannosides

| Entry | Donor A | | Donor B | | Quotient AC/BC | | DF |
|---|---|---|---|---|---|---|---|
| 1 | 6-Bz | **28** | 6-(4-$MeOC_6H_4CO$) | **47** | 0.8 | **38/43** | 6.6 |
| 2 | 6-Bz | **28** | 6-(4-$MeC_6H_4CO$) | **48** | 0.8 | **38/44** | 6.6 |
| 3 | | | 6-Bz | **28** | 1 | | 8.2 |
| 4 | 6-Bz | **28** | 4-$NO_2C_6H_4CO$ | **49** | 2.3 | **38/45** | 18.9 |

**Table 6** Competition reactions of substituted 6-*O*-benzoylselenomannosides

| Entry | Donor A | | Donor B | | DF (quotient AC/BC) | |
|---|---|---|---|---|---|---|
| 1 | TetraBn | **1** | 6-(4-$MeOC_6H_4CO$) | **32** | 1.5 | **42/43** |
| 2 | TetraBn | **1** | 6-(4-$MeC_6H_4CO$) | **33** | 2.0 | **42/44** |
| 3 | TetraBn | **1** | 6-Bz | **50** | 2.4 | **42/38** |
| 4 | TetraBn | **1** | 4-$NO_2C_6H_4CO$ | **34** | 3.8 | **42/45** |

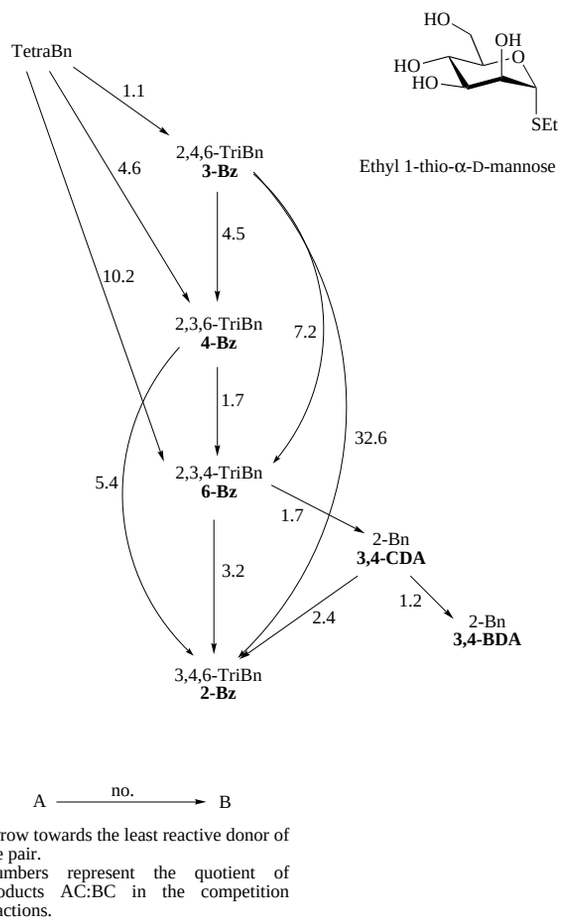



**Fig. 3** Flowchart demonstrating the deactivation of thiomannoside donors by various protecting group combinations

and evaluation of computer modelling protocols for the prediction of glycoside reactivity. The development of such tools should enable the rapid and effective design of syntheses of complex oligosaccharides and hence pave the way to the understanding of the mode of action of these key bio-molecules.

## Experimental

### General procedures

IR spectra were obtained on a Perkin-Elmer 1620FT spectrophotometer as thin films or Nujol mulls. $^1$H NMR spectra were recorded on a Bruker DRX-600 or a Bruker DRX-500 machine for solutions in deuteriochloroform using the residual $CHCl_3$ as reference ($\delta$ 7.26) unless otherwise stated. Integrals are always in agreement with the assigned number of protons. Coupling constants $J$ are quoted in Hz. $^{13}$C NMR spectra were recorded on a Bruker DRX-600 (150.03 MHz) or a Bruker AM-400 (100.12 MHz) machine and chemical shifts are quoted relative to the middle peak of $CDCl_3$ ($\delta_C$ 77). Low and high resolution mass spectra were recorded under electron impact (EI) or fast atom bombardment (FAB) conditions using a Kratos MS 890 spectrometer. Microanalyses were performed in the University of Cambridge microanalysis laboratory. Light petroleum refers to that fraction with distillation range 40–60 °C. When appropriate, reactions were carried out under argon in oven dried glassware. Reagents were either dried by standard procedures or used as purchased. Flash chromatography was carried out using Merck-Kieselgel 60 (0.040–0.063 mm) under pressure. TLC was visualised with UV light (254 nm) and acidified ammonium molybdate(IV). Optical rotations were measured using a Optical activity AA-1000 polarimeter. $[\alpha]_D$ Values are given in $10^{-1}$ deg cm$^2$ g$^{-1}$. Where the two protons of a $CH_2$ group can be assigned separately they are termed $H^a$ and $H^b$ in order of appearance. Where more than one benzyl group is present they are given a capital subscript, *i.e.* $CH_2Ph_A$, so that the $CH_2$ protons, and carbon where possible, can be associated. 'Ph' is used in NMR assignments to mean any benzene ring, whether substituted or not.

### General procedure for glycosylation reactions

A mixture of the glycoside donor (1.0 equiv.), acceptor **6** (1.33 equiv.) and molecular sieves (4 Å) in DCE–diethyl ether (1:1; ~1 ml per 0.1 mmol) was stirred at room temp. for 2 h. NIS (1.3 equiv.) was dissolved in DCE–diethyl ether (2:1; ~0.9 ml per 0.1 mmol) and 5–10 μl of a mixture of 30 μl TfOH in 1 ml of diethyl ether were added. The freshly prepared NIS–TfOH solution was added to the reaction mixture. After consumption of glycoside donor the reaction mixture was diluted with diethyl ether (10 ml), washed successively with saturated aq. sodium thiosulfate (10 ml) and saturated aq. sodium hydrogen carbonate (10 ml), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed on silica gel (diethyl ether–hexane mixtures) to give a glycosylation product.

### Preparation of disaccharides from rhamnoside donors

**Preparation of methyl 2-*O*-(2,3,4-tri-*O*-benzyl-α-L-rhamnopyranosyl)-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 16.** Compound **7** (34.5 mg, 0.072 mmol) was used to prepare *title compound* **16** (56.0 mg, 79%) *via* the general procedure described above. The rhamnopyranoside starting material was consumed within 20 min; $\nu_{max}$(film)/cm$^{-1}$ 2932 (C–H), 1496 (aromatic C–C), 1455, 1428 and 1362 (C–H), 1173, 1103 and 1063 (ether C–O, cyclic C–C, Si–O), 883 (Si–O), 823 (Si–C) and 738, 699 (aromatic C–H); $\delta_H$(500 MHz; $CDCl_3$) 1.03 [9H, s, $C(CH_3)_3$], 1.26 (3H, d, $J$ 6.2, 6′-$H_3$), 1.34–1.72 [8H, m, 4 × $CH_2$(CDA)], 3.06 [3H, s, $OCH_3$(CDA)], 3.22 [3H, s, $OCH_3$-(CDA)], 3.33 (3H, s, 1-$OCH_3$), 3.64 (1H, t, $J$ 9.5, 4′-H), 3.75–3.78 (1H, m, 5-H), 3.88–3.94 (4H, m, 2-H, 2 × 6-H and 2′-H), 3.96 (1H, dd, $J_{2',3'}$ 2.9, $J_{3',4'}$ 9.4, 3′-H), 4.14 (1H, dd, $J_{2,3}$ 2.9, $J_{3,4}$

10.6, 3-H), 4.23 (1H, t, *J* 10.3, 4-H), 4.34–4.37 (1H, m, 5′-H), 4.52 (1H, s, 1-H), 4.57 (1H, d, *J* 11.7, OC$H_a$$H_b$$Ph_A$), 4.61 (1H, d, *J* 11.7, OCH$_a$$H_b$$Ph_A$), 4.66 (1H, d, *J* 11.7, OC$H_a$$H_b$$Ph_B$), 4.72 (1H, d, *J* 12.3, OC$H_a$$H_b$$Ph_C$), 4.80 (1H, s, 1′-H), 4.82 (1H, d, *J* 12.3, OCH$_a$$H_b$$Ph_C$), 4.94 (1H, d, *J* 11.7, OCH$_a$$H_b$$Ph_B$) and 7.16–7.77 (25H, m, 5 × Ph); $\delta_C$(100 MHz; $CDCl_3$) 17.9 (6′-C), 19.4 [*C*$(CH_3)_3$], 21.3 [$CH_2$(CDA)], 21.4 [$CH_2$(CDA)], 26.8 [C(*C*$H_3)_3$], 27.0 [2 × $CH_2$(CDA)], 46.8 [$OCH_3$(CDA)], 46.9 [$OCH_3$(CDA)], 54.5 (1-$OCH_3$), 62.3 (6-C), 63.8 (4-C), 67.8 (5′-C), 67.8 (3-C), 72.2 (5-C), 72.2 (O*C*$H_2Ph_A$), 73.0 (O*C*$H_2Ph_C$), 73.7 (O*C*$H_2Ph_B$), 73.9 (2-C), 75.5 (2′-C), 79.9 (3′-C), 80.3 (4′-C), 97.1 (1′-C), 98.3 [C(CDA)], 98.6 [C(CDA)], 99.2 (CH, 1-C), 127.1–129.9 (23CH, 5 × Ph), 133.4 (C, SiPh), 134.2 (C, SiPh), 135.7 (CH, Ph), 136.1 (CH, Ph), 138.6 (C, $OCH_2$*Ph*), 138.7 (C, $OCH_2$*Ph*) and 139.5 (C, $OCH_2$*Ph*); *m*/*z* (FAB) 1011 (100%, $MNa^+$), 987 (14, $M^+ - H$) and 957 (86, $[M - OCH_3]^+$) (Found: $MNa^+$, 1011.4733. $C_{58}H_{72}NaO_{12}Si$ requires *M*Na, 1011.4691).

**Preparation of methyl 2-*O*-(2-*O*-benzoyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 17.** Compound **8** (35.5 mg, 0.072 mmol) was used to prepare *title compound* **17** (54.9 mg, 76%) *via* the general procedure as described above. The rhamnopyranoside starting material was consumed within 20 min; $\nu_{max}$(film)/$cm^{-1}$ 3068 and 3009 (aromatic C–H), 2933, 2859 and 2831 (C–H), 1723 (C=O), 1601, 1587 and 1496 (aromatic C–C), 1452, 1428, 1390, 1361 and 1342 (C–H), 1268 (Si–C), 1174, 1106 and 1069 (ether C–O, cyclic C–C), 1044 (Si–O), 883 (Si–O), 823 (Si–O) and 755 and 702 (aromatic C–H); $\delta_H$(500 MHz; $CDCl_3$) 1.09 [9H, s, C$(CH_3)_3$], 1.30 (3H, d, *J* 6.2, 6′-$H_3$), 1.20–1.83 [8H, m, 4 × $CH_2$-(CDA)], 3.06 [3H, s, $OCH_3$(CDA)], 3.24 [3H, s, $OCH_3$(CDA)], 3.36 (3H, s, 1-$OCH_3$), 3.58 (1H, t, *J* 9.5, 4′-H), 3.81–3.83 (1H, m, 5-H), 3.91–3.96 (3H, m, 2-H and 2 × 6-H), 4.12 (1H, dd, $J_{2',3'}$ 3.2, $J_{3',4'}$ 9.4, 3′-H), 4.19 (1H, dd, $J_{2,3}$ 2.8, $J_{3,4}$ 10.7, 3-H), 4.27 (1H, t, *J* 10.3, 4-H), 4.46 (1H, d, *J* 11.4, OC$H_a$$H_b$$Ph_A$), 4.50–4.56 (1H, m, 5′-H), 4.66 (1H, d, *J* 11.7, OC$H_a$$H_b$$Ph_B$), 4.72 (1H, d, *J* 11.4, OCH$_a$$H_b$$Ph_A$), 4.74 (1H, s, 1-H), 4.91 (1H, d, *J* 11.7, OCH$_a$$H_b$$Ph_B$), 4.97 (1H, d, *J* 1.4, 1′-H), 5.66 (1H, dd, $J_{1',2'}$ 2.0, $J_{2',3'}$ 2.9, 2′-H), 7.12–8.10 (25H, m, 5 × Ph); $\delta_C$(100 MHz; $CDCl_3$) 18.1 (6′-C), 19.4 [*C*$(CH_3)_3$], 21.4 [$CH_2$(CDA)], 21.5 [$CH_2$(CDA)], 26.8 [C(*C*$H_3)_3$], 27.0 [$CH_2$(CDA)], 27.1 [$CH_2$(CDA)], 46.8 [$OCH_3$(CDA)], 46.9 [$OCH_3$(CDA)], 54.5 (1-$OCH_3$), 62.4 (6-C), 63.9 (4-C), 67.5 (5′-C), 67.9 (3-C), 69.9 (2′-C), 71.4 (O*C*$H_2Ph_A$), 72.3 (5-C), 73.6 (O*C*$H_2Ph_B$), 75.3 (2-C), 7.77 (3′-C), 79.7 (4′-C), 97.2 (1′-C), 98.3 [C(CDA)], 98.7 [C(CDA)], 99.5 (1-C), 127.2–130.0 (22CH, 5 × Ph), 130.1 [C, OC(O)*Ph*], 133.2 (CH, Ph), 133.4 (C, SiPh), 134.1 (C, SiPh), 135.6 (CH, Ph), 136.0 (CH, Ph), 138.2 (C, $OCH_2$*Ph*), 139.3 (C, $OCH_2$*Ph*) and 166.0 [O*C*(O)Ph]; *m*/*z* (FAB) 1025 (100%, $MNa^+$) and 971 (75, $[M - OCH_3]^+$) (Found: $MNa^+$, 1025.4477. $C_{58}H_{70}NaO_{13}Si$ requires *M*Na, 1025.4483).

**Preparation of methyl 2-*O*-(3-*O*-benzoyl-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 18.** Compound **9** (35.5 mg, 0.072 mmol) was used to prepare *title compound* **18** (38.7 mg, 54%) *via* the general procedure described above. The rhamnopyranoside starting material was consumed within 20 min; $\nu_{max}$(film)/$cm^{-1}$ 3068 and 3009 (aromatic C–H), 2933, 2859 and 2831 (C–H), 1725 (C=O), 1605, 1587 and 1496 (aromatic C–C), 1452, 1428, 1390, 1361 and 1342 (C–H), 1268 (Si–C), 1174, 1106 and 1070 (ether C–O, cyclic C–C), 1044 (Si–O), 883 (Si–O), 823 (Si–C) and 755 and 702 (aromatic C–H); $\delta_H$(500 MHz; $CDCl_3$) 1.05 [9H, s, C$(CH_3)_3$], 1.31 (3H, d, *J* 6.2, 6′-$H_3$), 1.18–1.83 [8H, m, 4 × $CH_2$-(CDA)], 3.17 [3H, s, $OCH_3$(CDA)], 3.23 [3H, s, $OCH_3$(CDA)], 3.36 (3H, s, 1-$OCH_3$), 3.80–3.84 (2H, m, 5- and 4′-H), 3.93–3.94 (1H, m, 2-H), 3.95 (2H, d, $J_{5,6}$ 3.7, 2 × 6-H), 4.06 (1H, dd, $J_{1',2'}$ 1.9, $J_{2',3'}$ 3.0, 2′-H), 4.16 (1H, dd, $J_{2,3}$ 2.9, $J_{3,4}$ 10.6, 3-H), 4.28 (1H, t, *J* 10.3, 4-H), 4.50–4.56 (1H, m, 5′-H), 4.57 (1H, s, 1-H), 4.62 (1H, d, *J* 12.0, OC$H_a$$H_b$$Ph_A$), 4.67 (2H, d, *J* 12.0, OCH$_a$-$H_b$$Ph_A$ and OC$H_a$$H_b$$Ph_B$), 4.74 (1H, d, *J* 12.0, OCH$_a$$H_b$$Ph_B$), 4.84 (1H, d, $J_{1',2'}$ 1.4, 1′-H), 5.65 (1H, dd, $J_{2',3'}$ 3.3, $J_{3',4'}$ 9.4, 3′-H) and 7.16–8.06 (25H, m, 5 × Ph); $\delta_C$(100 MHz; $CDCl_3$) 17.9 (6′-C), 19.4 [*C*$(CH_3)_3$], 21.3 [$CH_2$(CDA)], 21.4 [$CH_2$-(CDA)], 26.8 [C(*C*$H_3)_3$], 27.0 [2 × $CH_2$(CDA)], 46.8 [$OCH_3$-(CDA)], 46.9 [$OCH_3$(CDA)], 54.5 (1-$OCH_3$), 62.6 (6-C), 64.1 (4-C), 67.3 (5′-C), 67.9 (3-C), 72.6 (5-C), 72.8 (O*C*$H_2Ph_B$), 73.3 (3-C), 73.5 (O*C*$H_2Ph_A$), 73.9 (2-C), 77.4 (2′-C), 78.9 (4′-C), 97.0 (1-C), 98.2 [C(CDA)], 98.6 [C(CDA)], 99.1 (1′-C), 127.3–129.8 (22CH, 5 × Ph), 130.4 [C, OC(O)*Ph*], 132.9 (CH, Ph), 133.7 (C, SiPh), 134.2 (C, SiPh), 135.6 (CH, Ph), 136.0 (CH, Ph), 138.1 (C, $OCH_2$*Ph*), 138.7 (C, $OCH_2$*Ph*) and 165.4 [O*C*(O)Ph]; *m*/*z* (FAB) 1002 (56%, $M^+$), 988 (42, $[MH - CH_3]^+$), 972 (71, $[MH - OCH_3]^+$), 940 (19, $[M - 2OCH_3]^+$), 241 {18, $[SiPh_2$-$C(CH_3)_3 + 2H]^+$}, 213 (16), 197 (45, $[OSiPh_2 - H]^+$), 181 (100, $[SiPh_2 - H]^+$) and 163 {27, $[HSiPhC(CH_3)_3]^+$} (Found: $MNa^+$, 1025.4466).

**Preparation of methyl 2-*O*-(4-*O*-benzoyl-2,3-di-*O*-benzyl-α-L-rhamnopyranosyl)-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 19.** Compound **10** (35.5 mg, 0.072 mmol) was used to prepare *title compound* **19** as a clear oil (17.0 mg, 25%) *via* the general procedure described above. The rhamnopyranoside starting material was consumed within 20 min; $\nu_{max}$(film)/$cm^{-1}$ 2931 and 2857 (C–H), 1727 (C=O), 1588 and 1488 (aromatic C–C), 1453, 1428 and 1342 (C–H), 1174, 1103 and 1068 (ether C–O, cyclic C–C), 1040 (Si–O), 881 (Si–O), 823 (Si–C) and 754 and 702 (aromatic C–H); $\delta_H$(500 MHz; $CDCl_3$) 1.03 [9H, s, C$(CH_3)_3$], 1.17–1.18 (3H, d, *J* 6.2, 6′-$H_3$), 1.26–1.80 [8H, m, 4 × $CH_2$(CDA)], 3.03 [3H, s, $OCH_3$(CDA)], 3.22 [3H, s, $OCH_3$-(CDA)], 3.35 (3H, s, 1-$OCH_3$), 3.80 (1H, dt, $J_{4,5}$ 9.6 $J_{5,6}$ 3.4, 5-H), 3.91–3.93 (4H, m, 2- and 2′-H and 6-$H_2$), 4.02 (1H, dd, $J_{2',3'}$ 2.8, $J_{3',4'}$ 9.7, 3′-H), 4.15 (1H, dd, $J_{2,3}$ 2.7, $J_{3,4}$ 10.6, 3-H), 4.20 (1H, t, *J* 10.2, 4-H), 4.37 (1H, d, *J* 12.4, OC$H_a$$H_b$$Ph_A$), 4.55 (1H, d, *J* 12.4, OCH$_a$$H_b$$Ph_A$), 4.56 (1H, s, 1-H), 4.58–4.63 (1H, m, 5′-H), 4.75 (1H, d, *J* 12.7, OC$H_a$$H_b$$Ph_B$), 4.88 (1H, d, *J* 12.7, OCH$_a$$H_b$$Ph_B$), 4.89 (1H, s, 1′-H), 5.47 (1H, t, *J* 9.8, 4′-H) and 6.99–8.03 (25H, m, 5 × Ph); $\delta_C$(100 MHz) 17.4 (6′-C), 19.3 [*C*$(CH_3)_3$], 21.3 [$CH_2$(CDA)], 21.5 [$CH_2$(CDA)], 26.8 [C(*C*$H_3)_3$], 26.9 [$CH_2$(CDA)], 27.1 [$CH_2$(CDA)], 46.7 [$OCH_3$(CDA)], 46.9 [$OCH_3$(CDA)], 54.5 (1-$OCH_3$), 62.4 (6-C), 63.9 (3-C), 66.6 (4-C), 67.8 (5-C), 71.7 (O*C*$H_2Ph_A$), 72.2 (5′-C), 73.0 (O*C*$H_2Ph_B$) 73.8 (2-C), 73.8 (4′-C), 74.4 (2′-C), 77.3 (3′-C), 97.1 (1′-C), 98.3 [C(CDA)], 98.4 [C(CDA)], 99.2 (1-C), 127.3–129.7 (22CH, 5 × Ph), 130.5 [C, OC(O)*Ph*], 132.8 (CH, Ph), 133.3 (C, SiPh), 134.1 (C, SiPh), 135.6 (CH, Ph), 136.0 (CH, Ph), 138.1 (C, $OCH_2$Ph), 138.4 (C, $OCH_2$Ph) and 165.6 [O*C*(O)Ph]; *m*/*z* (FAB) 1025 (100%, $MNa^+$) and 971 (42, $[M - OCH_3]^+$) (Found: $MNa^+$, 1025.4518).

**Preparation of methyl 2-*O*-(2,3-di-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 20.** Compound **11** (36.5 mg, 0.072 mmol) was used to prepare title compound **20** (46.0 mg, 63%) *via* the general procedure described above. The rhamnopyranoside starting material was consumed within 30 min; $\nu_{max}$(film)/$cm^{-1}$ 3069 (aromatic C–H), 2934 and 2859 (C–H), 1730 (C=O), 1602 and 1586 (aromatic C–C), 1451 and 1428 (C–H), 1273 (Si–C), 1174, 1104 and 1069 (ether C–O, cyclic C–C, Si–O), 884 (Si–O), 823 (Si–C) and 756 and 710 (aromatic C–H); $\delta_H$(500 MHz; $CDCl_3$) 1.07 [9H, s, C$(CH_3)_3$], 1.35 (3H, d, $J_{5',6'}$ 6.2, 6′-$H_3$), 1.27–1.82 [8H, m, 4 × $CH_2$(CDA)], 3.20 [3H, s, $OCH_3$(CDA)], 3.25 [3H, s, $OCH_3$(CDA)], 3.37 (3H, s, 1-$OCH_3$), 3.83–3.87 (2H, m, 5- and 4′-H), 3.94–4.01 (3H, m, 2-H and 6-$H_2$), 4.20 (1H, dd, $J_{2,3}$ 2.7, $J_{3,4}$ 10.6, 3-H), 4.33 (1H, t, *J* 10.3, 4-H), 4.70 (2H, s, O$CH_2$Ph), 4.70–4.75 (1H, m, 5′-H), 4.75 (1H, s, 1-H), 5.01 (1H, s, 1′-H), 5.62 (1H, s, 2′-H), 5.88 (1H, dd, $J_{2',3'}$ 3.3, $J_{3',4'}$ 9.8, 3′-H) and 7.17–8.07 (25H, m, 5 × Ph); $\delta_C$(100 MHz; $CDCl_3$) 18.0 (6′-C), 19.4 [*C*$(CH_3)_3$], 21.4 [2 × $CH_2$(CDA)], 26.9 [C(*C*$H_3)_3$], 27.0 [$CH_2$(CDA)], 27.1 [$CH_2$(CDA)], 46.8

[$OCH_3$(CDA)], 46.9 [$OCH_3$(CDA)], 54.5 (1-$OCH_3$), 62.5 (6-C), 64.1 (4-C), 67.2 (5′-C), 68.0 (3-C), 71.0 (3′-C), 72.0 (2′-C), 72.4 (O*C*$H_2$Ph), 72.6 (5-C), 74.9 (2-C), 78.5 (4′-C), 96.5 (1′-C), 98.3 [C(CDA)], 98.7 [C(CDA)], 99.2 (1-C), 127.4–129.9 [21CH, 5 × Ph and C, OC(O)*Ph*], 130.1 [C, OC(O)*Ph*], 132.8 (CH, Ph), 133.3 (CH, Ph), 133.6 (C, SiPh), 134.2 (C, SiPh), 135.6 (CH, Ph), 136.0 (CH, Ph), 138.4 (C, $OCH_2$Ph), 164.9 [O*C*(O)Ph] and 165.7 [O*C*(O)Ph]; *m*/*z* (FAB) 1040 (48%, $MH^+$ + Na), 1016 (5, $M^+$), 986 (61, $[M - 2CH_3]^+$), 960 (48, $[MH - C(CH_3)_3]^+$), 909 {10, $[M - (C(O)Ph + 2H)]^+$}, 197 (52, $[OSiPh_2 - H]^+$), 183 (16, $[SiPh_2 + H]^+$), 163 {26, $[SiPhC(CH_3)_3 + H]^+$} and 135 (100) (Found: $MH^+$ + Na, 1040.4354. $C_{58}H_{69}NaO_{14}Si$ requires *M*H + Na, 1040.4354).

**Preparation of methyl 2-*O*-(3-*O*-benzyl-2,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 21.** Compound **12** (36.5 mg, 0.072 mmol) was used to prepare title compound **21** (54.2 mg, 74%) *via* the general procedure described above. After 1 h, the rhamnopyranoside starting material had not been fully consumed and extra TfOH solution (5 μl) was added. After a further 0.5 h the reaction mixture was worked up to give *compound* **21**; $\nu_{max}$(film)/$cm^{-1}$ 3011 (aromatic C–H), 2934 and 2858 (C–H), 1726 (C=O), 1602, 1585 and 1492 (aromatic C–C), 1452, 1428, 1391, 1355 and 1323 (C–H), 1256 (Si–C), 1174, 1106 and 1070 (ether C–O, cyclic C–C, Si–O), 883 (Si–O), 823 (Si–C) and 755 and 703 (aromatic C–H); $\delta_H$(500 MHz; $CDCl_3$) 1.09 [9H, s, $C(CH_3)_3$], 1.22 (3H, d, *J* 5.9, 6′-$H_3$), 1.15–1.75 [8H, m, 4 × $CH_2$(CDA)], 2.97 [3H, s, $OCH_3$(CDA)], 3.23 [3H, s, $OCH_3$(CDA)], 3.39 (3H, s, 1-$OCH_3$), 3.86–3.98 (4H, m, 2-, 5-H and 6-$H_2$), 4.13 (1H, dd, $J_{2',3'}$ 3.1, $J_{3',4'}$ 9.6, 3′-H), 4.14–4.20 (2H, m, 3- and 4-H), 4.40 (1H, d, *J* 12.5, OC$H_a$$H_b$Ph), 4.63 (1H, d, *J* 12.5, OC$H_a$$H_b$Ph), 4.72–4.76 (2H, m, 1- and 5′-H), 5.06 (1H, s, 1′-H), 5.42 (1H, t, *J* 9.8, 4′-H), 5.68 (1H, s, 2′-H) and 6.86–8.15 (25H, m, 5 × Ph); $\delta_C$(100 MHz; $CDCl_3$) 17.6 (6′-C), 19.4 [*C*$(CH_3)_3$], 21.3 [$CH_2$(CDA)], 21.6 [$CH_2$(CDA)], 26.8 [C(*C*$H_3$)$_3$], 7.0 [$CH_2$(CDA)], 27.2 [$CH_2$(CDA)], 46.7 [$OCH_3$(CDA)], 47.0 [$OCH_3$(CDA)], 54.6 (1-$OCH_3$), 62.7 (6-C), 64.2 (4-C), 65.9 (5′-C), 66.4 (3-C), 67.9 (2′-C), 69.3 (O*C*$H_2$Ph), 70.8 (5-C), 72.4 (4′-C), 73.4 (3′-C), 74.4 (2-C), 96.8 (1′-C), 98.3 [C(CDA)], 98.5 [C(CDA)], 99.4 (1-C), 127.3–130.3 [21CH, 5 × Ph and 2 × C, 2 × C(O)*Ph*], 133.0 (CH, Ph), 133.3 (CH, Ph), 133.4 (C, SiPh), 134.0 (C, SiPh), 135.7 (CH, Ph), 136.0 (CH, Ph), 137.8 (C, $OCH_2$*Ph*), 165.7 [O*C*(O)Ph] and 166.1 [O*C*(O)Ph]; *m*/*z* (FAB) 1040 (68%, $[MH + Na]^+$), 1017 (5, $MH^+$), 986 (68, $[MH - OCH_3]^+$), 960 (34, $[MH - C(CH_3)_3]^+$), 241 (18, $[SiPh_2C(CH_3)_3 + 2H]^+$), 197 (50, $[OSiPh_2 - H]^+$), 183 (16, $[HSiPh_2]^+$), 163 {24, $[HSiPhC(CH_3)_3]^+$} and 135 (100) (Found: $MH^+$ + Na, 1040.4358).

**Preparation of methyl 2-*O*-(2-*O*-benzyl-3,4-di-*O*-benzoyl-α-L-rhamnopyranosyl)-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 22.** Compound **13** (36.5 mg, 0.072 mmol) was used to prepare compound **22** (33.9 mg, 46%) *via* the general procedure. After 1 h, some of the rhamnopyranoside starting material still remained and an extra portion of TfOH solution (5 μl) was added. After a further 0.5 h the reaction mixture was worked up; $\nu_{max}$(film)/$cm^{-1}$ 3069 (aromatic C–H), 2833, 2859 and 2832 (C–H), 1729 (C=O), 1602, 1586 and 1492 (aromatic C–C), 1452, 1428, 1391 and 1357 (C–H), 1277 (Si–C), 1104 and 1070 (ether C–O, cyclic C–C), 1041 (Si–O), 883 (Si–O), 823 (Si–C) and 755 and 708 (aromatic C–H); $\delta_H$(500 MHz; $CDCl_3$) 1.05 [9H, s, $C(CH_3)_3$], 1.22 (3H, d, *J* 6.8, 6′-$H_3$), 1.20–1.87 [8H, m, 4 × $CH_2$(CDA)], 3.24 [3H, s, $OCH_3$(CDA)], 3.28 [3H, s, $OCH_3$(CDA)], 3.37 (3H, s, 1-$OCH_3$), 3.82–3.85 (1H, m, 5-H), 3.94–4.00 (3H, m, 2-H and 6-$H_2$), 4.10 (1H, dd, $J_{1',2'}$ 1.7, $J_{2',3'}$ 2.8, 2′-H), 4.18 (1H, dd, $J_{2,3}$ 2.8, $J_{3,4}$ 10.6, 3-H), 4.37 (1H, t, *J* 10.4, 4-H), 4.60 (1H, s, 1-H), 4.66 (1H, d, *J* 12.2, OC$H_a$$H_b$Ph), 4.74 (1H, d, *J* 12.2, OC$H_a$$H_b$Ph), 4.80–4.86 (1H, m, 5′-H), 4.92 (1H, s, 1′-H), 5.62 (1H, t, *J* 9.9, 4′-H), 5.74 (1H, dd, $J_{2',3'}$ 3.2, $J_{3',4'}$ 10.0, 3′-H) and 7.21–8.01 (25H, m, 5 × Ph); $\delta_C$(100 MHz; $CDCl_3$) 17.4 (6′-C), 19.4 [*C*$(CH_3)_3$], 21.4 [$CH_2$(CDA)], 21.6 [$CH_2$(CDA)], 26.8 [C(*C*$H_3$)$_3$], 27.0 [$CH_2$(CDA)], 27.1 [$CH_2$(CDA)], 46.9 [$OCH_3$(CDA)], 47.0 [$OCH_3$(CDA)], 54.5 (1-$OCH_3$), 62.5 (6-C), 64.1 (4-C), 66.3 (5′-C), 68.1 (3-C), 72.2 (3′-C), 72.5 (4′-C), 72.7 (5-C), 73.5 (O*C*$H_2$Ph), 73.8 (2-C), 76.4 (2′-C), 96.8 (1′-C), 98.3 [C(CDA)], 98.5 [C(CDA)], 99.1 (1-C), 127.5–129.9 (21CH, 5 × Ph), 130.0 [2C, 2OC(O)*Ph*], 132.9 (CH, Ph), 133.0 (CH, Ph), 133.6 (C, SiPh), 134.2 (C, SiPh), 135.6 (CH, Ph), 136.0 (CH, Ph), 137.9 (C, $OCH_2$*Ph*), 165.4 [O*C*(O)Ph] and 165.7 [O*C*(O)Ph]; *m*/*z* (FAB) 1039 (100%, $MNa^+$) and 985 (100, $[M - OCH_3]^+$) (Found: $MNa^+$, 1039.4255. $C_{58}H_{68}NaO_{14}Si$ requires *M*Na, 1039.4276).

**Preparation of methyl 2-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 23.** Compound **14** (37.5 mg, 0.072 mmol) was used to prepare title compound **23** (49.9 mg, 67%) *via* the general procedure described above. Three extra portions of TfOH solution (5 μl) were added after 0.5, 1.5 and 3.5 h. After a further 0.5 h the reaction mixture was worked up to give *title compound* **23**; $\nu_{max}$(film)/$cm^{-1}$ 3070 (aromatic C–H), 2934, 2858 and 2832 (C–H), 1731 (C=O), 1601, 1585 and 1491 (aromatic C–C), 1452, 1451, 1428 and 1391 (C–H), 1264 (Si–C), 1174, 1104 and 1070 (ether C–O, cyclic C–C), 1040 (Si–O), 883 (Si–O), 823 (Si–C) and 757 and 709 (aromatic C–H); $\delta_H$(500 MHz; $CDCl_3$) 1.08 [9H, s, $C(CH_3)_3$], 1.28 (3H, d, *J* 6.2, 6′-$H_3$), 1.13–1.88 [8H, m 4 × $CH_2$(CDA)], 3.26 [3H, s, $OCH_3$(CDA)], 3.34 [3H, s, $OCH_3$-(CDA)], 3.38 (3H, s, 1-$OCH_3$), 3.86–3.88 (1H, m, 5-H), 3.97 (1H, dd, $J_{5,6a}$ 1.7, $J_{6a,6b}$ 11.2, 6-$H_a$), 4.00–4.03 (2H, m, 2-H and 6-$H_b$), 4.22 (1H, dd, $J_{2,3}$ 2.7, $J_{3,4}$ 10.7, 3-H), 4.44 (1H, t, *J* 10.4, 4-H), 4.78 (1H, s, 1-H), 4.99 (1H, dq, $J_{4',5'}$ 9.9, $J_{5',6'}$ 6.2, 5′-H), 5.13 (1H, s, 1′-H), 5.63 (1H, t, *J* 9.9, 4′-H), 5.67 (1H, dd, $J_{1',2'}$ 1.8, $J_{2',3'}$ 3.1, 2′-H), 5.97 (1H, dd, $J_{2',3'}$ 3.3, $J_{3',4'}$ 9.9, 3′-H) and 7.24–8.15 (25H, m, 5 × Ph); $\delta_C$(100 MHz; $CDCl_3$) 17.5 (6′-C), 19.4 [*C*$(CH_3)_3$], 21.4 [$CH_2$(CDA)], 21.6 [$CH_2$(CDA)], 26.8 [C(*C*$H_3$)$_3$], 27.0 [$CH_2$(CDA)], 27.2 [$CH_2$(CDA)], 47.0 [2 × $OCH_3$(CDA)], 54.6 (1-$OCH_3$), 62.4 (6-C), 64.1 (4-C), 66.3 (5′-C), 68.2 (3-C), 69.8 (3′-C), 71.5 (2′-C), 72.5 (4′-C), 72.7 (5-C), 74.9 (2-C), 96.3 (1′-C), 98.3 [C(CDA)], 98.5 [C(CDA)], 99.3 (1-C), 127.5–129.8 [20CH, 4Ph and 3C, 3OC(O)*Ph*], 132.9 (CH, Ph), 133.2 (CH, Ph), 133.5 (C, SiPh), 133.5 (CH, Ph), 134.2 (C, SiPh), 135.6 (CH, Ph), 136.1 (CH, Ph), 165.0 [O*C*(O)Ph], 165.8 [O*C*(O)Ph], 167.7 [O*C*(O)Ph]; *m*/*z* (FAB) 1054 (82%, $MH^+$ + Na), 1000 (100, $[MH - OCH_3]^+$), 974 {96, $[MH - C(CH_3)_3]^+$}, 968 {36, $[M - (2OCH_3)]^+$}, 954 (13, $[MH - Ph]^+$), 942 (13, {$M - [C(CH_3)_3 + OCH_3]$}$^+$), 241 {19, $[SiPh_2C(CH_3)_3 + 2H]^+$}, 183 (16, $[SiPh_2H]^+$) and 163 {26 $[HSiPhC(CH_3)_3]^+$} (Found: $MH^+$ + Na, 1054.4053. $C_{58}H_{67}$-$NaO_{15}Si$ requires *M*H + Na, 1054.4146).

**Preparation of methyl 2-*O*-{2-*O*-benzyl-3,4-*O*-[(1‴*S*,2‴*S*)-1‴,2‴-dimethoxycyclohexane-1‴,2‴-diyl]-α-L-rhamnopyranosyl}-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 24.** Compound **15** (32.6 mg, 0.074 mmol) was used to prepare compound **24** (50 mg, 70%) *via* the general procedure described above. After 1 h, some rhamnopyranoside starting material remained and additional TfOH solution (5 μl) was added. Three further additions of TfOH solution (5 μl) were made at intervals of 1 h and the reaction mixture was stirred overnight. Four further additions of TfOH solution (10 μl) were made at hourly intervals on the following day before work-up according to the general procedure to give *title compound* **24**; $\nu_{max}$(film)/$cm^{-1}$ 3007 (aromatic C–H), 2936, 2859 and 2830 (C–H), 1589 (aromatic C–C), 1462, 1428, 1391, 1358 and 1342 (C–H), 1265 (Si–C), 1175, 1131, 1102 and 1063 (ether C–O, cyclic C–C, Si–O), 884 (Si–O), 823 (Si–C) and 756 and 702 (aromatic C–H); $\delta_H$(500 MHz; $CDCl_3$) 1.02 [9H, s, $C(CH_3)_3$], 1.20 (3H, d, $J_{5',6'}$ 6.1, 6′-$H_3$), 1.31–1.43 [4H, m, 2 × $CH_2$-(CDA)], 1.46–1.54 [4H, m, 2 × $CH_2$(CDA)], 1.67–1.84 [8H, m, 4 × $CH_2$(CDA)], 3.11 [3H, s, $OCH_3$(CDA)], 3.14 [3H, s, $OCH_3$-

(CDA)], 3.20 [3H, s, $OCH_3$(CDA)], 3.31 [3H, s, $OCH_3$(CDA)], 3.32 (3H, s, 1-$OCH_3$), 3.75–3.78 (2H, m, 5- and 2′-H), 3.86–3.92 (3H, m, 2-H and 6-$H_2$), 3.96 (1H, t, *J* 10.1, 4′-H), 4.13 (1H, dd, $J_{2,3}$ 3.0, $J_{3,4}$ 10.6, 3-H), 4.18–4.28 (3H, m, 4-, 3′- and 5′-H), 4.53 (1H, s, 1-H), 4.65 (1H, d, *J* 11.9, $OCH_aH_bPh$), 4.76 (1H, s, 1′-H), 5.00 (1H, d, *J* 11.9, $OCH_aH_bPh$), 7.25–7.47 (11H, m, Ph) and 7.70–7.72 (4H, m, Ph); $\delta_C$(100 MHz; $CDCl_3$) 16.6 (6′-C), 19.4 [$C(CH_3)_3$], 21.3 [$CH_2$(CDA)], 21.5 [2 × $CH_2$(CDA)], 26.9 [$C(CH_3)_3$], 26.8 [$CH_2$(CDA)], 26.9 [$CH_2$(CDA)], 27.0 [$CH_2$-(CDA)], 27.1 [$CH_2$(CDA)], 27.2 [$CH_2$(CDA)], 46.5 [2 × $OCH_3$-(CDA)], 46.8 [2 × $OCH_3$(CDA)], 54.5 (1-$OCH_3$), 62.4 (6-C), 64.0 (CH), 67.6 (CH), 67.7 (CH), 69.4 (CH), 69.7 (CH), 72.0 (CH), 73.0 (CH), 73.3 ($OCH_2Ph$), 76.9 (CH), 97.9 (1′-C), 98.2 [C(CDA)], 98.3 [C(CDA)], 98.4 [C(CDA)], 98.7 [C(CDA)], 98.8 (1-C), 127.5–129.5 (13CH, 3 × Ph), 133.4 (C, SiPh), 134.2 (C, SiPh), 135.6 (CH, Ph), 136.0 (CH, Ph) and 139.0 (C, $OCH_2Ph$); *m/z* (FAB) 971 (17%, $MNa^+$), 918 (28, $[MH - OCH_3]^+$), 886 (13, $[M - 2OCH_3]^+$), 569.2 (5, $\{M - [OSiPh_2C(CH_3)_3 + 4OCH_3]\}^+$), 523.3 (51, $\{M - [OSiC(CH_3)_3Ph_2 + 2OCH_3 + OCH_2Ph + H]\}^+$), 491 (11, $\{M - [OSiPh_2C(CH_3)_3 + 3OCH_3 + OCH_2Ph + 2H]\}^+$), 255 {22, $[OSiPh_2C(CH_3)_3]^+$}, 197 (37, $[OSiPh_2 - H]^+$), 141 {100, $[(CH_2)_4(COCH_3)_2 - H]^+$} (Found: $MNa^+$, 971.4543. $C_{52}H_{72}NaO_{14}Si$ requires *M*Na, 971.4589).

### Preparation of disaccharides from thiomannoside donors

**Preparation of methyl 2-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 35.** Compound **25** (42 mg, 0.070 mmol) was used to prepare title compound **35** (39.7 mg, 51%) *via* the general procedure as described above. After 5.5 h, some of the mannopyranoside starting material remained and extra TfOH solution (10 μl) was added. Three further additions of TfOH solution (10 μl) were made after 23, 29 and 32 h. After a total reaction time of 48 h the reaction was worked up to give *compound* **35**; $\nu_{max}$(film)/$cm^{-1}$ 3067 and 3009 (aromatic C–H), 2931 and 2858 (C–H), 1727 (C=O), 1602, 1587 and 1496 (aromatic C–C), 1452, 1428, 1390 and 1361 (C–H), 1268 (Si–C), 1173, 1111, 1071 and 1040 (ether C–O, cyclic C–C, Si–O), 883 (Si–O), 823 (Si–C) and 754 and 700 (aromatic C–H); $\delta_H$(500 MHz; $CDCl_3$) 1.05 [9H, s, $C(CH_3)_3$], 1.22–1.86 [8H, m, 4 × $CH_2$(CDA)], 3.16 [3H, s, $OCH_3$(CDA)], 3.20 [3H, s, $OCH_3$(CDA)], 3.32 (3H, s, 1-$OCH_3$), 3.80–3.84 (2H, m, 5-H and 6′-$H_b$), 3.90–3.96 (3H, m, 6-$H_2$ and 6′-$H_a$), 4.00 (1H, s, 2-H), 4.03 (1H, dd, $J_{4',5'}$ 9.8, $J_{5',6'}$ 2.1, 5′-H), 4.08 (1H, dd, $J_{4',5'}$ 9.8, $J_{3',4'}$ 9.0, 4′-H), 4.18–4.21 (2H, m, 3- and 3′-H), 4.32 (1H, t, *J* 10.3, 4-H), 4.50 (1H, d, *J* 10.7, $OCH_aH_bPh_A$), 4.52 (1H, d, *J* 10.1, $OCH_aH_bPh_B$), 4.57 (1H, d, *J* 11.9, $OCH_aH_bPh_C$), 4.77 (1H, d, *J* 11.9, $OCH_aH_bPh_C$), 4.78 (1H, s, 1-H), 4.86 (1H, d, *J* 10.1, $OCH_aH_bPh_B$), 4.87 (1H, d, *J* 10.7, $OCH_aH_bPh_A$), 5.39 (1H, d, $J_{1',2'}$ 2.4, 1′-H), 5.90 (1H, t, *J* 2.4, 2′-H), 7.18–7.41 (23H, m, Ph), 7.53 (1H, t, *J* 7.4, Ph), 7.73–7.77 (4H, m, Ph) and 8.08 (2H, d, *J* 7.3, Ph); $\delta_C$(100 MHz; $CDCl_3$) 19.4 [$C(CH_3)_3$], 21.4 [2 × $CH_2$(CDA)], 26.8 [$C(CH_3)_3$], 27.0 [$CH_2$(CDA)], 29.7 [$CH_2$(CDA)], 46.9 [$OCH_3$(CDA)], 47.0 [$OCH_3$(CDA)], 54.4 (1-$OCH_3$), 62.3 (6-C), 64.1 (4-C), 68.7 (2′-C), 69.3 (6′-C), 69.4 (3- or 3′-C), 71.6 ($OCH_2Ph_A$), 72.0 (5- and 5′-C), 73.5 ($OCH_2Ph_C$), 74.4 (4′-C), 75.3 ($OCH_2Ph_B$), 76.1 (2-C), 78.9 (3′- or 3-C), 98.5 [C(CDA)], 98.9 [C(CDA)], 99.4 (1′-C), 100.4 (1-C), 127.5–128.4 (24 CH, Ph), 129.5 (2CH, Ph), 130.0 (CH, Ph), 130.3 [C, OC(O)*Ph*], 132.9 (CH, Ph), 133.4 (C, SiPh), 134.1 (C, SiPh), 135.6 (CH, Ph), 136.0 (CH, Ph), 138.2 (C, $OCH_2Ph$), 138.5 (C, $OCH_2Ph$), 138.6 (C, $OCH_2Ph$) and 165.2 [O*C*(O)Ph]; *m/z* (FAB) 1132 (49%, $MNa^+$), 1078 (61, $[M - OCH_3]^+$), 1002 (70, $\{M - [C(O)Ph + 2H]\}^+$), 911 (7, $\{M - [2OCH_3 + C(CH_3)_3 + Ph + 2H]\}^+$), 537 {67, $[C_6H_7O_5 + 3CH_2Ph + C(O)Ph]^+$}, 429 (14, $[C_6H_7O_5 + 3CH_2Ph - 3H]^+$) and 339 (43, $[C_6H_7O_5 + 2CH_2Ph - 2H]^+$) (Found: $MNa^+$, 1131.4957. $C_{65}H_{76}NaO_{14}Si$ requires *M*Na, 1131.4902).

**Preparation of methyl 2-*O*-(3-*O*-benzoyl-2,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 36.** Compound **26** (64 mg, 0.106 mmol) was used to prepare *title compound* **36** (119 mg, 67%) *via* the general procedure described above. The mannopyranoside starting material was consumed within 24 h; $[\alpha]_D^{26}$ +26.4 (*c* 1.0, $CDCl_3$) (Found: C, 70.10; H, 6.86. $C_{65}H_{76}O_{14}Si$ requires C, 70.37; H, 6.91%); $\nu_{max}$(film)/$cm^{-1}$ 3067 and 3010 (aromatic C–H), 2933, 2859 and 2832 (C–H), 1725 (C=O), 1602, 1586 and 1496 (aromatic C–C), 1453, 1428, 1390 and 1357 (C–H), 1271 (Si–C stretch), 1173, 1109 and 1036 (ether C–O, cyclic C–C, Si–O), 883 (Si–O), 823 (Si–C) and 755 and 701 (aromatic C–H); $\delta_H$(500 MHz; $CDCl_3$) 1.05 [9H, s, $C(CH_3)_3$], 1.27–1.37 [2H, m, $CH_2$-(CDA)], 1.44–1.49 [2H, m, $CH_2$(CDA)], 1.66–1.70 [4H, m, 2 × $CH_2$(CDA)], 3.08 [3H, s, $OCH_3$(CDA)], 3.23 [3H, s, $OCH_3$-(CDA)], 3.32 (3H, s, 1-$OCH_3$), 3.75 (1H, d, $J_{6a',6b'}$ 10.8, 6′-$H_b$), 3.83 (1H, dd, $J_{5',6a'}$ 4.3, $J_{6a',6b'}$ 10.8, 6′-$H_a$), 3.86 (1H, m, 5-H), 3.89–3.96 (2H, m, 6-$H_2$), 4.01 (1H, dd, $J_{4',5'}$ 9.6, $J_{5',6a'}$ 4.3, 5′-H), 4.06 (1H, s, 2-H), 4.16 (1H, t, *J* 9.1, 4′-H), 4.17 (1H, s, 2′-H), 4.21 (2H, m, 3- and 4-H), 4.51 (1H, d, *J* 10.8, $OCH_aH_bPh_A$), 4.52 (1H, d, *J* 12.6, $OCH_aH_bPh_B$), 4.54 (1H, d, *J* 12.1, $OCH_aH_b$-$Ph_C$), 4.70 (1H, d, *J* 10.8, $OCH_aH_bPh_A$), 4.71 (1H, d, *J* 12.1, $OCH_aH_bPh_C$), 4.75 (1H, s, 1-H), 4.77 (1H, d, *J* 12.6, $OCH_aH_b$-$Ph_B$), 5.53 (1H, s, 1′-H), 5.56 (1H, dd, $J_{2',3'}$ 2.8, $J_{3',4'}$ 8.8, 3′-H) and 7.07–8.03 (30H, m, 6 × Ph); $\delta_C$(100 MHz; $CDCl_3$) 19.3 [$C(CH_3)_3$], 21.3 [$CH_2$(CDA)], 21.4 [$CH_2$(CDA)], 26.7 [$C(CH_3)_3$], 26.9 [$CH_2$(CDA)], 27.2 [$CH_2$(CDA)], 46.8 [$OCH_3$(CDA)], 46.9 [$OCH_3$(CDA)], 54.2 (1-$OCH_3$), 62.6 ($CH_2$), 64.4 (CH), 69.2 ($CH_2$), 69.9 (CH), 71.5 (CH), 72.3 ($CH_2$), 72.4 (CH), 73.5 ($CH_2$), 73.9 (2CH), 74.5 ($CH_2$), 74.6 (CH), 75.9 (CH), 98.3 [C(CDA)], 98.6 [C(CDA)], 98.7 (1′-C), 100.3 (1-C), 127.3–128.3 (24CH, Ph), 129.3 (2CH, Ph), 129.7 (CH, Ph), 130.4 [C, OC(O)*Ph*], 133.7 (C, SiPh), 132.8 (CH, Ph), 134.0 (C, SiPh), 135.6 (CH, Ph), 135.9 (CH, Ph), 137.9 (C, $OCH_2Ph$), 138.2 (C, $OCH_2Ph$), 138.3 (C, $OCH_2Ph$) and 165.2 [O*C*(O)Ph]; *m/z* (FAB) 1131 (42%, $MNa^+$), 1077 (75, $[M - OCH_3]^+$), 1045 (22, $[M - (2OCH_3)]^+$), 988 (6, $\{M - [2OCH_3 + C(CH_3)_3 + H]\}^+$), 911 (3, $\{M - [2OCH_3 + C(CH_3)_3 + Ph + H]\}^+$), 537 {89, $[C_6H_7O_5 + 3CH_2Ph + C(O)Ph]^+$}, 339 {86, $[(C_6H_7O_5 + 2CH_2$-$Ph) - 2H]^+$} and 241 (100) (Found: $MNa^+$, 1131.4834).

**Preparation of methyl 2-*O*-(4-*O*-benzoyl-2,3,6-di-*O*-benzyl-α-D-mannopyranosyl)-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 37.** Compound **27** (42 mg, 0.070 mmol) was used to prepare title compound **37** as a pale yellow oil (78 mg, 63%) *via* the general procedure described above. After 16 h, some of the mannopyranoside starting material remained and additional TfOH solution (10 μl) was added. Two further additions of TfOH solution (10 μl) were made after 24 and 48 h. After a total reaction time of 52 h the reaction was worked up to afford *compound* **37**, $[\alpha]_D^{26}$ +34.8 (*c* 1.0, $CHCl_3$) (Found: C, 70.21; H, 6.97%); $\nu_{max}$(film)/$cm^{-1}$ 3066 and 3010 (aromatic C–H), 2932 and 2858 (C–H), 1728 (C=O), 1602, 1589 and 1496 (aromatic C–C), 1453, 1428 and 1360 (C–H), 1267 (Si–C), 1173, 1112 and 1069 (ether C–O, cyclic C–C, Si–O), 883 (Si–O), 823 (Si–C) and 755 and 702 (aromatic C–H); $\delta_H$(500 MHz; $CDCl_3$) 1.06 [9H, s, $C(CH_3)_3$], 1.21–1.75 [8H, m, 4 × $CH_2$(CDA)], 3.11 (3H, s, $OCH_3$), 3.23 (3H, s, $OCH_3$), 3.28 (3H, s, $OCH_3$), 3.68 (1H, dd, $J_{5',6'b}$ 3.2, $J_{6'a,6'b}$ 10.9, 6′-$H_b$), 3.71 (1H, dd, $J_{5',6'a}$ 6.0, $J_{6'a,6'b}$ 10.9, 6′-$H_a$), 3.80 (1H, ddd, $J_{4,5}$ 7.8, $J_{5,6a}$ 4.2, $J_{5,6b}$ 2.0, 5-H), 3.91 (1H, dd, $J_{5,6b}$ 1.9, $J_{6a,6b}$ 11.2, 6-$H_b$), 3.95 (1H, dd, $J_{5,6a}$ 4.4, $J_{6a,6b}$ 11.3, 6-$H_a$), 4.03 (1H, dd, $J_{2',3'}$ 3.1, $J_{3',4'}$ 9.2, 3′-H), 4.05–4.07 (2H, m, 2- and 2′-H), 4.16 (1H, ddd, $J_{4',5'}$ 9.6, $J_{5',6'a}$ 6.0, $J_{5',6'b}$ 3.2, 5′-H), 4.23 (1H, dd, $J_{2,3}$ 2.6, $J_{3,4}$ 10.5, 3-H), 4.30 (1H, t, *J* 10.2, 4-H), 4.38 (1H, d, *J* 11.9, $OCH_aH_bPh_A$), 4.44 (1H, d, *J* 11.9, $OCH_a$-$H_bPh_A$), 4.53 (2H, d, *J* 12.2, $OCH_2Ph_B$), 4.65 (1H, d, *J* 12.4, $OCH_aH_bPh_C$), 4.78 (1H, d, *J* 12.4, $OCH_aH_bPh_C$), 5.48 (1H, d, $J_{1',2'}$ 1.0, 1′-H), 4.82 (1H, s, 1-H), 5.63 (1H, t, *J* 9.6, 4′-H) and 7.07–7.98 (30H, m, 6 × Ph); $\delta_C$(100 MHz; $CDCl_3$) 19.4

[$C(CH_3)_3$], 21.3 [$CH_2$(CDA)], 21.4 [$CH_2$(CDA)], 26.8 [$CH_2$-(CDA)], 27.0 [$C(CH_3)_3$], 27.2 [$CH_2$(CDA)], 46.9 [2 × $OCH_3$-(CDA)], 54.3 (1-$OCH_3$), 62.3 (6-C), 64.0 (4-C), 69.6 (3-C), 69.7 (4′-C), 70.3 (6′-C), 70.9 (5′-C), 71.6 ($OCH_2Ph_A$), 71.9 (5-C), 72.3 ($OCH_2Ph_C$), 73.5 ($OCH_2Ph_B$), 74.8 (2- or 2′-C), 75.3 (2′- or 2-C), 77.3 (3′-C), 98.5 [C(CDA)], 98.7 [C(CDA)], 99.2 (1′-C), 100.4 (1-C), 127.2–128.3 (24CH, Ph), 129.5 (CH, Ph), 129.6 (CH, Ph), 129.8 (CH, Ph), 130.0 [C, OC(O)*Ph*], 132.9 (CH, Ph), 133.3 (C, SiPh), 134.1 (C, SiPh), 135.5 (CH, Ph), 136.0 (CH, Ph), 138.1 (C, $OCH_2Ph$), 138.2 (C, $OCH_2Ph$), 138.5 (C, $OCH_2Ph$) and 165.6 [O*C*(O)Ph]; *m/z* (FAB) 1131 (67%, $MNa^+$), 1077 (69, $[M - OCH_3]^+$), 1045 {11, $[M - (2OCH_3 + H)]^+$}, 987 (6, $[M - (OCH_3 + CH_2Ph)]^+$ or $\{M - [2OCH_3 + C(CH_3)_3 + 2H]\}^+$), 893 {3, $[M - (OCH_3 + OCH_2Ph + Ph)]^+$}, 537 {74, $[C_6H_7O_5 + 3CH_2Ph + C(O)Ph]^+$}, 339 ($[C_6H_7O_5 + 2CH_2Ph - 2H]^+$) and 241 (100) (Found: $MNa^+$, 1131.4837).

**Preparation of methyl 2-*O*-(6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 38.** Compound **28** (85 mg, 0.142 mmol) was used to prepare title compound **38** (157 mg, 46%) *via* the general procedure as described above. After 16 h, some of the mannopyranoside starting material remained and extra TfOH solution (10 μl) was added. Two further additions of TfOH solution (10 μl) were made after 24 and 48 h. After a total reaction time of 52 h the reaction was worked up to give *compound* **38**, $[\alpha]_D^{26}$ +50.0 (*c* 2.0, $CHCl_3$) (Found: C, 69.39; H, 6.70. $C_{65}H_{76}O_{14}Si{\cdot}1H_2O$ requires C, 69.26; H, 6.97%); $\nu_{max}$(film)/$cm^{-1}$ 3066 and 3029 (aromatic C–H), 2933, 2859 and 2832 (C–H), 1722 (C=O), 1602, 1588 and 1496 (aromatic C–C), 1453, 1428 and 1360 (C–H), 1275 (Si–C), 1173, 1112 and 1069 (ether C–O, cyclic C–C, Si–O), 883 (Si–O), 823 (Si–C) and 754 and 701 (aromatic C–H); $\delta_H$(500 MHz; $CDCl_3$) 1.03 [9H, s, $C(CH_3)_3$], 1.32–1.36 [2H, m, $CH_2$(CDA)], 1.49–1.53 [2H, m, $CH_2$(CDA)], 1.64–1.72 [4H, m, 2 × $CH_2$(CDA)], 3.10 (3H, s, $OCH_3$), 3.20 (3H, s, $OCH_3$), 3.30 (3H, s, $OCH_3$), 3.78–3.81 (1H, m, 5-H), 3.88–3.93 (2H, m, 6-$H_2$), 4.04–4.11 (5H, m, 2-, 2′-, 3′-, 4′- and 5′-H), 4.20 (1H, dd, $J_{2,3}$ 2.5, $J_{3,4}$ 10.5, 3-H), 4.26 (1H, t, *J* 10.1, 4-H), 4.50 (1H, d, *J* 11.5, $OCH_aH_bPh_A$), 4.54 (1H, d, *J* 11.5, $OCH_aH_bPh_A$), 4.57–4.65 (2H, m, 6′-$H_2$), 4.61 (1H, d, *J* 10.8, $OCH_aH_bPh_B$), 4.64 (1H, d, *J* 12.4, $OCH_aH_bPh_C$), 4.71 (1H, s, 1-H), 4.75 (1H, d, *J* 12.4, $OCH_aH_bPh_C$), 4.95 (1H, d, *J* 10.8, $OCH_aH_bPh_B$), 5.54 (1H, s, 1′-H), 7.20–8.06 (30H, m, 6 × Ph); $\delta_C$(100 MHz; $CDCl_3$) 19.3 [$C(CH_3)_3$], 21.3 [$CH_2$(CDA)], 21.4 [$CH_2$(CDA)], 26.8 [$C(CH_3)_3$], 26.9 [$CH_2$(CDA)], 27.2 [$CH_2$-(CDA)], 46.9 [$OCH_3$(CDA)], 47.0 [$OCH_3$(CDA)], 54.3 (1-$OCH_3$), 62.3 (6-C), 64.0 (4′- and 6′-C), 69.9 (3-C), 70.4 (5′-C), 71.7 ($OCH_2Ph_A$), 71.9 ($OCH_2Ph_C$), 72.0 (5-C), 74.5, 74.4 and 74.1 (2-, 2′- and 4′-C), 75.3 ($OCH_2Ph_B$), 79.8 (3′-C), 98.0 (1′-C), 98.4 [C(CDA)], 98.6 [C(CDA)], 100.4 (1-C), 127.4–128.4 (24CH, Ph), 129.5 (2CH, Ph), 129.7 (CH, Ph), 130.1 [C, OC(O)*Ph*], 132.9 (CH, Ph), 133.3 (C, SiPh), 134.0 (C, SiPh), 135.5 (CH, Ph), 135.9 (CH, Ph), 138.2 (C, $OCH_2Ph$), 138.4 (C, $OCH_2Ph$) and 166.4 [O*C*(O)Ph]; *m/z* (FAB) 1131 (69%, $MNa^+$), 1077 (75, $[M - OCH_3]^+$), 1045 {15, $[M - (2OCH_3 + H)]^+$}, 987 (6, $\{M - [2OCH_3 + C(CH_3)_3 + 2H]\}^+$), 911 (4, $\{M - [2OCH_3 + C(CH_3)_3 + Ph + H]\}^+$), 537 {53, $[C_6H_7O_5 + 3CH_2Ph + C(O)Ph]^+$}, 339 (100, $[C_6H_7O_5 + 2CH_2Ph - 2H]^+$) and 241 (100) (Found: $MNa^+$, 1131.4886).

**Preparation of methyl 2-*O*-{2,6-di-*O*-benzyl-3,4-*O*-[(1‴*S*,2‴*S*)-1‴,2‴-dimethoxycyclohexane-1‴,2‴-diyl]-α-D-mannopyranosyl}-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 39.** Compound **29** (38 mg, 0.070 mmol) was used to prepare *title compound* **39** (58 mg, 78%) *via* the general procedure described above. The mannopyranoside starting material was consumed within 48 h (Found: C, 67.02; H, 7.52. $C_{59}H_{78}O_{15}Si$ requires C, 67.15; H, 7.45%); $\nu_{max}$(film)/$cm^{-1}$ 3008 (aromatic C–H), 2937, 2860 and 2831 (C–H), 1589 and 1496 (aromatic C–C), 1462, 1429, 1357 and 1342 (C–H), 1265 (Si–C), 1173, 1114, 1094 and 1070 (ether C–O, cyclic C–C, Si–O), 884 (Si–O), 822 (Si–C) and 755 and 701 (aromatic C–H); $\delta_H$(500 MHz; $CDCl_3$) 1.03 [9H, s, $C(CH_3)_3$], 1.33–1.52 [8H, m, 4 × $CH_2$(CDA)], 1.65–1.84 [8H, m, 4 × $CH_2$(CDA)], 2.98 [3H, s, $OCH_3$(CDA)], 3.07 [3H, s, $OCH_3$(CDA)], 3.16 [3H, s, $OCH_3$(CDA)], 3.20 [3H, s, $OCH_3$-(CDA)], 3.31 (3H, s, 1-$OCH_3$), 3.79–3.84 (4H, m, 5-H, 6-$H_b$ and 6′-$H_2$), 3.91 (1H, d, *J* 10.2, 6-$H_a$), 3.92 (1H, s, 2′-H), 4.03 (2H, br s, 2- and 5′-H), 4.10 (1H, t, *J* 10.0, 4-H), 4.16 (1H, d, $J_{3,4}$ 10.5, 3-H), 4.27 (1H, dd, $J_{2',3'}$ 2.0, $J_{3',4'}$ 10.6, 3′-H), 4.42 (1H, t, *J* 10.4, 4′-H), 4.57 (1H, d, *J* 11.9, $OCH_aH_bPh_A$), 4.65 (1H, d, *J* 11.9, $OCH_aH_bPh_A$), 4.72 (1H, s, 1-H), 4.73 (1H, d, *J* 12.4, $OCH_aH_bPh_B$), 4.87 (1H, d, *J* 12.4, $OCH_aH_bPh_B$), 5.42 (1H, s, 1′-H), 7.23–7.47 (16H, m, Ph) and 7.69–7.73 (4H, m, Ph); $\delta_C$(100 MHz; $CDCl_3$) 19.3 [$C(CH_3)_3$], 21.3 [$CH_2$(CDA)], 21.4 [2 × $CH_2$(CDA)], 21.5 [$CH_2$(CDA)], 26.8 [$C(CH_3)_3$], 27.0 [$CH_2$(CDA)], 27.1 [3 × $CH_2$(CDA)], 46.6 [$OCH_3$(CDA)], 46.7 [$OCH_3$(CDA)], 46.8 [$OCH_3$(CDA)], 47.0 [$OCH_3$(CDA)], 54.4 (1-$OCH_3$), 62.7 (6-C), 64.4 (4-C), 64.6 (4′-C), 68.8 (6-C), 69.2 (3′-C), 69.9 (3-C), 71.4 (5′-C), 72.2 (5-C), 72.3 ($OCH_2Ph_B$), 73.4 ($OCH_2Ph_A$), 74.1 (2-C), 76.6 (2′-C), 98.3 [C(CDA)], 98.5 [2C(CDA)], 98.7 [C(CDA)], 99.4 (1′-C), 100.5 (1-C), 128.2–127.0 (17CH, Ph), 129.5 (CH, Ph), 133.7 (C, SiPh), 133.9 (C, SiPh), 135.6 (CH, Ph), 135.7 (CH, Ph), 138.7 (C, $OCH_2Ph$) and 139.2 (C, $OCH_2Ph$); *m/z* (FAB) 1078.2 (50%, $MNa^+$), 1024 {18 $[M - (OCH_3 + H)]^+$}, 992 {7, $[M - (2OCH_3 + 4H)]^+$}, 569 {4, $[C_6H_7O_5 + OCH_3 + CDA + SiPh_2C(CH_3)_3]^+$}, 483 (11, $[C_6H_7O_5 + 2CH_2Ph + CDA]^+$), 307 (24, $\{M - [OSiPh_2C(CH_3)_3 + 2OCH_2Ph + 2CDA + 2H]\}^+$) and 135 (100) (Found: $MH^+ + Na$, 1078.5039. $C_{59}H_{78}NaO_{15}Si$ requires *M*H + Na, 1077.5007).

**Preparation of methyl 2-*O*-{2,6-di-*O*-benzyl-3,4-*O*-[(2‴*S*,2‴*S*)-octahydro-2‴,2‴-bi-2*H*-pyran-2‴,2‴-diyl]-α-D-mannopyranosyl}-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 40.** Compound **30** (10 mg, 0.0175 mmol) was used to prepare title compound **40** (6 mg, 32%) *via* the general procedure described above. After 4 h, some of the mannopyranoside starting material remained and extra TfOH solution (6 μl) was added. Two further additions of TfOH solutin (10 μl) were made after 24 and 36 h. After a total reaction time of 52 h the reaction was worked up and gave *compound* **40**; $\nu_{max}$(film)/$cm^{-1}$ 3010 (aromatic C–H), 2930 (C–H), 1589 and 1496 (aromatic C–C), 1453, 1428 and 1355 (C–H), 1215 (Si–C), 1154, 1113, 1071 and 1040 (ether C–O, cyclic C–C, Si–O), 882 (Si–O), 822 (Si–C) and 757 and 702 (aromatic C–H); $\delta_H$(600 MHz; $CDCl_3$) 1.00 [9H, s, $C(CH_3)_3$], 1.23–1.90 [20H, m, 10 × $CH_2$(dispoke/CDA)], 2.93 (3H, s, $OCH_3$), 3.21 (3H, s, $OCH_3$), 3.29 (3H, s, $OCH_3$), 3.45–3.64 [4H, m, 2 × $OCH_2$(dispoke)], 3.77–3.93 (6H, m, 5-H, 6-$H_2$, 2′-H, 6′-$H_2$), 3.96–4.00 (1H, m, 5′-H), 4.08 (1H, br s, 2′-H), 4.12–4.18 (3H, m, 3-, 4- and 3′-H), 4.24 (1H, t, *J* 10.2, 4′-H), 4.58 (1H, d, *J* 11.9, $CH_aH_bPh_A$), 4.66 (1H, d, *J* 11.9, $CH_aH_b$-$Ph_A$), 4.71 (1H, s, 1-H), 4.77 (1H, d, *J* 13.1, $CH_aH_bPh_B$), 4.82 (1H, d, *J* 13.1, $CH_aH_bPh_A$), 5.53 (1H, s, 1′-H), 7.22–7.50 (16H, m, Ph) and 7.68–7.72 (4H, m, Ph); $\delta_C$(150 MHz; $CDCl_3$) 18.1 [$CH_2$(dispoke)], 18.2 [$CH_2$(dispoke)], 19.3 [$C(CH_3)_3$], 21.3 [$CH_2$(CDA)], 21.4 [$CH_2$(CDA)], 24.9 [$CH_2$(dispoke)], 25.0 [$CH_2$(dispoke)], 26.8 [$C(CH_3)_3$], 26.9 [$CH_2$(CDA)], 27.2 [$CH_2$(CDA)], 28.7 [$CH_2$(dispoke)], 29.7 [$CH_2$(dispoke)], 46.7 [$OCH_3$(CDA)], 46.9 [$OCH_3$(CDA)], 54.3 (1-$OCH_3$), 60.5 [$OCH_2$-(dispoke)], 60.7 [$OCH_2$(dispoke)], 62.5 (6-C), 62.8 (CH), 64.2 (CH), 65.8 (CH), 67.6 (CH), 69.0 (6′-C), 70.0 (CH), 73.4 (CH), 73.5 (CH), 75.6 (CH), 69.9 (C, dispoke), 97.0 (C, dispoke), 98.2 (C, CDA), 98.5 (C, CDA), 99.1 (1′-C), 100.5 (1-C), 127.5–128.1 (24CH, Ph), 129.5 (CH, Ph), 129.7 (CH, Ph), 133.3 (C, SiPh), 134.0 (C, SiPh), 135.5 (2CH, Ph), 135.7 (2CH, Ph), 138.2 (C, $OCH_2Ph$) and 138.4 (C, $OCH_2Ph$); *m/z* (FAB) 1104 (26%, $MH^+ + Na$), 1050 (79, $[MH - OCH_3]^+$), 1018 {46, $[M - (2OCH_3)]^+$}, 992 (8, $\{M - [OCH_3 + C(CH_3)_3]\}^+$), 881 {3, $[M - (OCH_3 + CH_2Ph + Ph)]^+$}, 509 (30, $C_6H_7O_5 + 2CH_2$-Ph + dispoke), 241.0 {5, $[SiPh_2C(CH_3)_3 + 2H]$}, 197 (26) and

167 (100) (Found: $MH^+ + Na$, 1104.5362. $C_{61}H_{81}NaO_{15}Si$ requires *M*Na, 1104.5242).

**Preparation of methyl 2-*O*-{2,6-di-*O*-benzyl-3,4-*O*-[(2‴*S*,3‴*S*)-2‴,3‴-dimethoxybutan-2‴,3‴-diyl]-α-D-mannopyranosyl}-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 41.** Compound **31** (36 mg, 0.070 mmol) was used to prepare *title compound* **41** (30.4 mg, 42%) *via* the general procedure described above. The mannopyranoside starting material was consumed within 24 h (Found: C, 66.80; H, 7.53. $C_{57}H_{76}O_{15}Si$ requires C, 66.58; H, 7.35%); $\nu_{max}$(film)/cm$^{-1}$ 3008 (aromatic C–H), 2934, 2859 and 2832 (C–H), 1589 and 1496 (aromatic C–C), 1454, 1428, 1376 and 1342 (C–H), 1264 (Si–C), 1114, 1086, 1070 and 1038 (ether C–O, cyclic C–C, Si–O), 883 (Si–O), 822 (Si–C) and 755 and 701 (aromatic C–H); $\delta_H$(500 MHz; $CDCl_3$) 1.02 [9H, s, $C(CH_3)_3$], 1.29 [3H, s, $CH_3$(BDA)], 1.32 [3H, s, $CH_3$(BDA)], 1.27–1.32 [2H, m, $CH_2$(CDA)], 1.48–1.53 [2H, m, $CH_2$(CDA)], 1.67–1.69 [4H, m, 2 × $CH_2$(CDA)], 2.96 (3H, s, $OCH_3$), 3.12 (3H, s, $OCH_3$), 3.20 (6H, s, 2 × $OCH_3$), 3.31 (3H, s, 1-$OCH_3$), 3.78–3.83 (4H, m, 5-H, 6-$H_b$ and 6′-$H_2$), 3.88–3.91 (2H, m, 6-$H_a$ and 2′-H), 3.98–4.00 (1H, m, 5′-H), 4.04 (1H, s, 2-H), 4.09–4.12 (2H, m, 3′- and 4-H), 4.16 (1H, dd, $J_{2,3}$ 2.0, $J_{3,4}$ 10.4, 3-H), 4.23 (1H, t, *J* 10.2, 4′-H), 4.58 (1H, d, *J* 11.9, $OCH_aH_bPh_A$), 4.65 (1H, d, *J* 11.9, $OCH_aH_bPh_A$), 4.72 (1H, s, 1-H), 4.74 (1H, d, *J* 12.7, $OCH_aH_bPh_B$), 4.82 (1H, d, *J* 12.7, $OCH_aH_bPh_B$), 5.44 (1H, s, 1′-H), 7.23–7.47 (16H, m, Ph) and 7.70–7.72 (4H, m, Ph); $\delta_C$(100 MHz; $CDCl_3$) 17.9 ($2CH_3$, BDA), 19.4 [$C(CH_3)_3$], 21.4 [$2CH_2$(CDA)], 26.8 [$C(CH_3)_3$], 27.0 [$CH_2$(CDA)], 27.1 [$CH_2$(CDA)], 46.7 [$OCH_3$(CDA)], 47.0 [$OCH_3$(CDA)], 47.8 ($OCH_3$, BDA), 47.9 ($OCH_3$, BDA), 54.4 ($OCH_3$, 1-C), 62.7 (6-C), 63.8 (4′-C), 64.4 (4-C), 68.5 (3′-C), 68.9 (6-C), 69.9 (3-C), 71.1 (5′-C), 72.2 (5-C), 72.2 ($OCH_2Ph_B$), 73.4 ($OCH_2Ph_A$), 74.1 (2-C), 76.1 (2′-C), 98.3 [C(CDA)], 98.5 [C(CDA)], 99.3 (1′-C), 99.5 (C, BDA), 99.8 (C, BDA), 100.4 (1-C), 127.0–129.5 (18-CH, Ph), 133.6 (C, SiPh), 133.9 (C, SiPh), 135.6 (CH, Ph), 135.8 (CH, Ph), 138.6 (C, $OCH_2Ph$) and 139.2 (C, $OCH_2Ph$); *m*/*z* (FAB) 1027 (10%, $MH^+$), 997 (29, $[M - OCH_3]^+$), 965 {19, $[M - (2OCH_3 + H)]^+$}, 875 {3, $[M - (2OCH_3 + CH_2Ph)]^+$}, 817 (2, $\{M - [2OCH_3 + CH_2Ph + C(CH_3)_3 + H]\}^+$), 789 (2, $\{M - [SiPh_2C(CH_3)_3]\}^+$), 757 (2, $\{M - [SiPh_2C(CH_3)_3 + OCH_3 + H]\}^+$), 599 (2, $\{M - [SiPh_2C(CH_3)_3 + CDA]\}^+$), 569 (43), 553 (7), 523 (28), 457 (10), 365 (24), 241 (17), 181 (45), 135 (100) and 114 (69) (Found: $M^+ - OCH_3$, 997.4801. $C_{56}H_{73}O_{14}Si$ requires *m*/*z*, 997.4769).

### Preparation of disaccharides from selenomannoside donors

**Preparation of methyl 2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 42.** Compound **1** (100 mg, 0.147 mmol) was used to prepare *title compound* **42** (86 mg, 53%) *via* the general procedure described above. The mannopyranoside starting material was consumed within 5 min; $[\alpha]_D^{20}$ +40.2 (*c* 1.7, $CHCl_3$) (Found: $M^+$, 1094.5176; C, 71.6; H, 7.3. $C_{65}H_{78}O_{13}Si$ requires *M*, 1094.5211; C, 71.3; H, 7.2%); $\nu_{max}$(film)/cm$^{-1}$ 2932 and 2858 (C–H), 1605, 1588 and 1496 (aromatic C–C), 1389 (C–H), 1290 (Si–C) and 1111, 1070 and 1036 (ether C–O, cyclic C–C, Si–O); $\delta_H$(500 MHz; $CDCl_3$) 1.00 [9H, s, $C(CH_3)_3$], 1.20–1.53 [4H, m, 2 × $CH_2$(CDA)], 1.64–1.78 [4H, m, 2 × $CH_2$(CDA)], 3.07 (3H, s, $OCH_3$), 3.21 (3H, s, $OCH_3$), 3.28 (3H, s, $OCH_3$), 3.73–3.93 (6H, m, 5-, 5′-H and 6- and 6′-$H_2$), 3.94–4.07 (4H, m, 2-, 2′-, 3′- and 4′-H), 4.15–4.27 (2H, m, 3- and 4-H), 4.43–4.74 (6H, m, 6 × OC*H*HPh), 4.70 (1H, s, 1-H), 4.77 (1H, d, *J* 12.5, OC*H*HPh), 4.87 (1H, d, *J* 10.8, OC*H*HPh), 5.53 (1H, s, 1′-H), 7.12–7.47 (26H, m, Ph) and 7.66–7.77 (4H, m, Ph); $\delta_C$(100 MHz; $CDCl_3$) 19.3 [$C(CH_3)_3$], 21.3 ($CH_2$, CDA), 21.4 ($CH_2$, CDA), 26.8 [$C(CH_3)_3$], 27.0 ($CH_2$, CDA), 27.2 ($CH_2$, CDA), 46.9, 54.3 (3 × $OCH_3$), 62.3 (6-C), 64.1 (4-C), 69.4 (6′-C), 69.9 (3-C), 71.7 ($OCH_2Ph$), 71.8 ($OCH_2Ph$), 71.9 (5- and 5′-C), 73.4 ($OCH_2Ph$), 74.0, 74.4 and 74.9 (2′-, 2- and 4-C), 75.0 ($OCH_2Ph$), 79.8 (3′-C), 98.2 (1′-C), 98.4 (C, CDA), 98.6 (C, CDA), 100.5 (1-C), 127.3–129.6 (28CH), 133.3 (C), 134.0 (C), 135.6 (CH), 136.0 (CH), 138.4 (C), 138.5 (C), 138.6 (C) and 138.7 (C); *m*/*z* (FAB) 1095 (10%, $M^+$), 1065 (80, $[MH - OCH_3]^+$), 1033 (20, $[M - 2 \times OCH_3]^+$), 523 (70), 431 (95) and 181 (100).

**Preparation of methyl 2-*O*-[6-*O*-(4′-methoxybenzoyl)-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl]-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 43.** Compound **32** (50 mg, 0.069 mmol) was used to prepare *title compound* **43** (48 mg, 61%) *via* the general procedure described above. The mannopyranoside starting material was consumed within 5 min; $[\alpha]_D^{25}$ +44.6 (*c* 1.34, $CHCl_3$) (Found: C, 69.8; H, 7.0. $C_{66}H_{78}O_{15}Si$ requires C, 69.6; H, 6.9%); $\nu_{max}$(film)/cm$^{-1}$ 2932 (C–H), 1725 (C=O), 1605 and 1511 (aromatic C–H), 1428 (C–H), 1256 (Si–C) and 1112 and 1033 (ether C–O, cyclic C–C); $\delta_H$(500 MHz; $CDCl_3$) 1.02 [9H, s, $C(CH_3)_3$], 1.20–1.55 [4H, m, 4 × $CH_2$(CDA)], 1.65–1.78 [4H, m, 4 × $CH_2$(CDA)], 3.09 (3H, s, $OCH_3$), 3.20 (3H, s, $OCH_3$), 3.30 (3H, s, $OCH_3$), 3.77–3.82 (1H, m, 5-H), 3.84 (3H, s, $OCH_3$), 3.85–3.93 (2H, m, 6-$H_2$), 4.00–4.13 (5H, m, 2-, 2′-, 3-, 4′- and 5′-H), 4.20 (1H, dd, $J_{2,3}$ 2.4, $J_{3,4}$ 10.6, 3-H), 4.25 (1H, t, *J* 10.0, 4-H), 4.46–4.66 (6H, m, 6′-$H_2$ and 4 × OC*H*HPh), 4.70 (1H, s, 1-H), 4.75 (1H, d, *J* 12.2, OC*H*HPh), 4.94 (1H, d, *J* 10.7, OC*H*HPh), 5.55 (1H, s, 1′-H), 6.79–6.83 (2H, m, Ph) and 7.05–8.03 (27H, m, Ph); $\delta_C$(100 MHz; $CDCl_3$), 19.3 [$C(CH_3)_3$], 21.3, 21.4 [2 × $CH_2$(CDA)], 26.8 [$C(CH_3)_3$], 27.0 ($CH_2$, CDA), 27.2 ($CH_2$, CDA), 46.9, 47.0, 54.4 and 55.4 (4 × $OCH_3$), 62.3 (6-C), 63.7 (6′-C), 64.0 (4-C), 69.9 (3-C), 70.5 (5′-C), 71.7 ($OCH_2Ph$), 71.9 ($OCH_2Ph$), 72.0 (5-C), 74.1 (4′-C), 74.5 (2- and 2′-C), 75.3 ($OCH_2Ph$), 79.8 (3′-C), 98.0 (1′-C), 98.4 (C, CDA), 98.6 (C, CDA), 100.4 (1-C), 113.5 (2CH), 122.5 (C), 127.4–129.5 (24CH), 131.8 (CH), 133.3 (C), 134.0 (C), 135.5 (CH), 135.9 (CH), 138.2 (C), 138.5 (C), 163.3 (C) and 166.2 (C); *m*/*z* (FAB) 1138 (4%, $M^+$), 1108 (60, $[MH - OCH_3]^+$), 1076 {10, $[M - (2OCH_3)]^+$}, 1032 (10, $[MH - Ph]^+$), 567 [70, $C_6H_7O_5$ + $3CH_2Ph$ + C(O)Ar], 181 (45) and 135 (100, $[C(O)Ar]^+$) (Found: $[MH - OCH_3]^+$, 1108.5099. $C_{65}H_{76}O_{14}Si$ requires *m*/*z*, 1108.5004).

**Preparation of methyl 2-*O*-[6-*O*-(4′-methylbenzoyl)-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl]-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 44.** Compound **33** (50 mg, 0.070 mmol) was used to prepare *title compound* **44** (33 mg, 41%) *via* the general procedure described above. The mannopyranoside starting material was consumed within 5 min; $[\alpha]_D^{20}$ +38.7 (*c* 0.30, $CHCl_3$) (Found: $M^+$, 1122.5231; C, 70.4; H, 7.2. $C_{66}H_{78}O_{14}Si$ requires *M*, 1122.5161; C, 70.6; H, 7.0%); $\nu_{max}$(film)/cm$^{-1}$ 3018 (aromatic C–H), 2930 (C–H), 1455 and 1428 (C–H), 1277 (Si–C) and 1111 and 1034 (ether C–O, cyclic C–C); $\delta_H$(500 MHz; $CDCl_3$), 1.01 [9H, s, $C(CH_3)_3$], 1.24–1.56 [4H, m, 2 × $CH_2$(CDA)], 1.60–1.78 [4H, m, 2 × $CH_2$(CDA)], 2.39 (3H, s, $CH_3$), 3.09 (3H, s, $OCH_3$), 3.19 (3H, s, $OCH_3$), 3.30 (3H, s, $OCH_3$), 3.76–3.82 (1H, m, 5-H), 3.84–3.93 (2H, m, 6-$H_2$), 3.98–4.11 (5H, m, 2-, 2′-, 3′-, 4′- and 5′-H), 4.19 (1H, dd, $J_{2,3}$ 2.4, $J_{3,4}$ 10.5, 3-H), 4.24 (1H, t, *J* 10.1, 4-H), 4.46–4.65 (6H, m, 6′-$H_2$ and 4 × OC*H*HPh), 4.70 (1H, s, 1-H), 4.74 (1H, d, *J* 12.1, OC*H*HPh), 4.94 (1 H, d, *J* 10.6, OC*H*HPh), 5.53 (1H, s, 1′-H), 7.12–7.46 (23H, m, Ph), 7.68–7.77 (4H, m, Ph) and 7.90–7.97 (2H, m, Ph); $\delta_C$(100 MHz; $CDCl_3$) 19.3 [$C(CH_3)_3$], 21.3 ($CH_2$, CDA), 21.4 ($CH_2$, CDA), 21.7 ($CH_3$), 26.8 [$C(CH_3)_3$], 26.9 ($CH_2$, CDA), 27.2 ($CH_2$, CDA), 46.9 ($OCH_3$), 47.0 ($OCH_3$), 54.4 ($OCH_3$), 62.3 (6-C), 63.9 (6′-C), 64.0 (4-C), 69.9 (3-C), 70.5 (5′-C), 71.7 and 71.9 (2 × $OCH_2Ph$), 72.0 (5-C), 74.1, 74.4 and 74.6 (2-, 2′- and 4′-C), 75.3 ($OCH_2Ph$), 79.8 (3′-C), 97.9 (1′-C), 98.4 (C, CDA), 98.6 (C, CDA), 100.4 (1-C), 127.4–129.8 (27CH), 133.3 (C), 134.0 (C), 135.5 (CH), 135.9 (CH), 138.2 (C), 138.4 (C), 143.5 (C) and 166.5 [O*C*(O)Ar]; *m*/*z* (FAB) 1122 (15%, $M^+$), 1092 (45,

$[MH - OCH_3]^+$), 551 [45, $C_6H_7O_5$ + $3CH_2Ph$ + C(O)Ar] and 181 (100).

**Preparation of methyl 2-*O*-[6-*O*-(4′-nitrobenzoyl)-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl]-3,4-*O*-[(1″*S*,2″*S*)-1″,2″-dimethoxycyclohexane-1″,2″-diyl]-6-*O*-(*tert*-butyldiphenylsilyl)-α-D-mannopyranoside 45.** Compound **34** (80 mg, 0.108 mmol) was used to prepare title compound **45** (108 mg, 87%) *via* the general procedure described above. The mannopyranoside starting material was consumed within 5 min; $[\alpha]_D^{20}$ +50.3 (*c* 1.6, $CHCl_3$); $\nu_{max}$(film)/$cm^{-1}$ 2930 (C–H), 1728 (C=O), 1528 (aromatic C–C), 1277 (Si–C) and 1103, 1070 and 1036 (ether C–O, cyclic C–C, Si–O); $\delta_H$(500 MHz; $CDCl_3$), 1.04 [9H, s, $C(CH_3)_3$], 1.09–1.78 [8H, m, 4 × $CH_2$(CDA)], 3.11 (3H, s, $OCH_3$), 3.20 (3H, s, $OCH_3$), 3.32 (3H, s, $OCH_3$), 3.77–3.82 (1H, m, 5-H), 3.87–3.94 (2H, m, 6-$H_2$), 4.00–4.11 (5H, m, 2-, 2′-, 3′-, 4′- and 5′-H), 4.21 (1H, dd, $J_{2,3}$ 2.5, $J_{3,4}$ 10.5, 3-H), 4.26 (1H, t, *J* 9.9, 4-H), 4.52–4.74 (8H, m, 1-H, 6′-$H_2$ and 5 × OC*H*HPh), 4.95 (1H, d, *J* 11.0, OC*H*HPh), 5.54 (1H, s, 1′-H) and 7.10–8.10 (29H, m, Ph); $\delta_C$(100 MHz; $CDCl_3$), 19.3 [*C*$(CH_3)_3$], 21.3 ($CH_2$, CDA), 21.3 ($CH_2$, CDA), 26.8 [C(*C*$H_3)_3$], 26.9 ($CH_2$, CDA), 27.2 ($CH_2$, CDA), 46.9, 47.0 and 54.3 (3 × $OCH_3$), 62.3 (6-C), 64.0 (4-C), 64.6 (6′-C), 69.9 (3-C), 70.2 (5′-C), 71.6 (O*C*$H_2$Ph), 72.0 (5-C), 72.2 (O*C*$H_2$Ph), 73.7 (4′-C), 74.5 (2- and 2′-C), 75.0 (O*C*$H_2$Ph), 79.8 (3′-C), 98.1 (1′-C), 98.4 (C, CDA), 98.6 (C, CDA), 100.4 (1-C), 123.4 (CH), 127.5–129.5 (25CH), 130.7 (CH), 133.3 (C), 133.9 (C), 135.4 (C), 135.5 (CH), 135.9 (CH), 138.0 (C), 138.9 (C), 150.4 (C) and 164.4 (C); *m*/*z* (FAB) 1153 (5%, $M^+$), 1123 (40, $[MH - OCH_3]^+$), 271 (90) and 135 (100) (Found: $[MH - OCH_3]^+$, 1123.4645. $C_{64}H_{73}NO_{15}Si$ requires *m*/*z*, 1123.4749).

**General procedure for competition reactions**

A mixture of two glycoside donors (2.0 equiv. of each), acceptor **6** (1.0 equiv.) and powdered molecular sieves (4 Å) in DCE–diethyl ether (1 : 1; ~1 ml per 0.02 mmol of acceptor) was stirred for 2 h at room temp. NIS (2.0 equiv.) was dissolved in DCE–diethyl ether (3 : 2; 1 ml per 0.08 mmol of NIS) and a solution of TfOH in DCE (30 μl in 1 ml, 10 μl) was added. The freshly prepared NIS–TfOH solution was added to the reaction mixture. After consumption of the acceptor the reaction mixture was diluted with diethyl ether (10 ml), filtered, washed successively with saturated aq. sodium thiosulfate (10 ml) and saturated aq. sodium hydrogen carbonate (10 ml), dried ($MgSO_4$), and concentrated *in vacuo*.

**Thiorhamnoside competition reactions (Table 1).**

*Note:* The residues were chromatographed on silica gel (light petroleum–diethyl ether mixtures) to give the disaccharide products in one fraction from which the ratio was determined by $^1$H NMR spectrometry (500 MHz).

*Entry* 1. *Ethyl* 2,3,4-*tri*-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **7** vs. *ethyl* 3-O-*benzoyl*-2,4-*di*-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **9**.—Compounds **7** (70 mg, 0.146 mmol) and **9** (72 mg, 0.146 mmol) were treated *via* the general procedure described above. An extra portion of TfOH solution (10 μl) was added after 2 h, and after 3.5 h the reaction mixture was worked up. The integrals of the following $^1$H NMR signals revealed a ratio of 3.1 : 1.0 (**16** : **18**).

**16**: $\delta_H$(500 MHz; $CDCl_3$) 3.06 (s, $OCH_3$), 3.22 (s, $OCH_3$), 3.33 (s, $OCH_3$).

**18**: $\delta_H$(500 MHz; $CDCl_3$) 3.17 (s, $OCH_3$), 3.23 (s, $OCH_3$), 3.36 (s, $OCH_3$).

*Entry* 2. *Ethyl* 2,3,4-*tri*-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **7** vs. *ethyl* 4-O-*benzoyl*-2,3-*di*-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **10**.—Compounds **7** (70 mg, 0.146 mmol) and **10** (72 mg, 0.146 mmol) were treated *via* the general procedure described above. Three extra portions of TfOH solution (10 μl) were added over the reaction time and after 7 h the reaction mixture was worked up. The integrals of the following $^1$H NMR signals revealed a ratio of 8.9 : 1.0 (**16** : **19**).

**16**: $\delta_H$(500 MHz; $CDCl_3$) 3.06 (s, $OCH_3$) and 3.33 (s, $OCH_3$).

**19**: $\delta_H$(500 MHz; $CDCl_3$) 3.03 (s, $OCH_3$) and 3.35 (s, $OCH_3$).

*Entry* 3. *Ethyl* 2,3,4-*tri*-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **7** vs. *ethyl* 2-O-*benzoyl*-3,4-*di*-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **8**.—Compounds **7** (70 mg, 0.146 mmol) and **8** (72 mg, 0.146 mmol) were treated *via* the general procedure described above. An extra portion of TfOH solution (10 μl) was added after 1.5 h, and after 3 h the reaction mixture was worked up. The integrals of the following $^1$H NMR signals revealed a ratio of 26.6 : 1.0 (products **16** : **17**).

**16**: $\delta_H$(500 MHz; $CDCl_3$) 3.22 (s, $OCH_3$) and 3.33 (s, $OCH_3$).

**17**: $\delta_H$(500 MHz; $CDCl_3$) 3.24 (s, $OCH_3$) and 3.36 (s, $OCH_3$).

*Entry* 4. *Ethyl* 2,4-*di*-O-*benzoyl*-3-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **12** vs. *ethyl* 2,3,4-*tri*-O-*benzoyl*-1-*thio*-α-L-*rhamnopyranoside* **14**.—Compounds **12** (74 mg, 0.146 mmol) and **14** (76 mg, 0.146 mmol) were treated *via* the general procedure described above. Extra portions of TfOH solution (10 μl) were added hourly over a period of 8 h. After 4 days the reaction mixture was worked up. A small amount of the acceptor was still present. The integrals of the following $^1$H NMR signals revealed a ratio of 2.5 : 1.0 (**21** : **23**).

**21**: $\delta_H$(500 MHz; $CDCl_3$) 2.97 (s, $OCH_3$), 3.23 (s, $OCH_3$) and 3.39 (s, $OCH_3$).

**23**: $\delta_H$(500 MHz; $CDCl_3$) 3.26 (s, $OCH_3$), 3.34 (s, $OCH_3$) and 3.38 (s, $OCH_3$).

*Entry* 5. *Ethyl* 2,3-*di*-O-*benzoyl*-4-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **11** vs. *ethyl* 2,3,4-*tri*-O-*benzoyl*-1-*thio*-α-L-*rhamnopyranoside* **14**.—Compounds **11** (74 mg, 0.146 mmol) and **14** (76 mg, 0.146 mmol) were allowed to react *via* the general procedure described above. Extra portions of TfOH solution (10 μl) were added hourly over a period of 8 h. After 4 days the reaction mixture was worked up. A small amount of the acceptor was still present. The integrals of the following $^1$H NMR signals revealed a ratio of 13.0 : 1.0 (**20** : **23**).

**20**: $\delta_H$(500 MHz; $CDCl_3$) 3.20 (s, $OCH_3$).

**23**: $\delta_H$(500 MHz; $CDCl_3$) 3.34 (s, $OCH_3$).

*Entry* 6. *Ethyl* 3,4-*di*-O-*benzoyl*-2-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **13** vs. *ethyl* 2,3,4-*tri*-O-*benzoyl*-1-*thio*-α-L-*rhamnopyranoside* **14**.—Compounds **13** (74 mg, 0.146 mmol) and **14** (76 mg, 0.146 mmol) were allowed to react *via* the general procedure described above. Extra portions of TfOH solution (10 μl) were added over a period of 8 h. After 4 days the reaction mixture was worked up. A small amount of the acceptor was still present. The integrals of the following $^1$H NMR signals revealed a ratio of 24.2 : 1.0 (**22** : **23**).

**22**: $\delta_H$(500 MHz; $CDCl_3$) 3.28 (s, $OCH_3$).

**23**: $\delta_H$(500 MHz; $CDCl_3$) 3.26 (s, $OCH_3$).

*Entry* 7. *Ethyl* 3-O-*benzoyl*-2,4-*di*-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **9** vs. *ethyl* 4-O-*benzoyl*-2,3-*di*-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **10**.—Compounds **9** (72 mg, 0.146 mmol) and **10** (72 mg, 0.146 mmol) were treated *via* the general procedure described above. Extra portions of TfOH solution (10 μl) were added over a period of 8 h. After 3 days the reaction mixture was worked up. A small amount of the acceptor was still present. The integrals of the following $^1$H NMR signals revealed a ratio of 2.5 : 1.0 (**18** : **19**).

**18**: $\delta_H$(500 MHz; $CDCl_3$) 3.17 (s, $OCH_3$).

**19**: $\delta_H$(500 MHz; $CDCl_3$) 3.03 (s, $OCH_3$).

*Entry* 8. *Ethyl* 3-O-*benzoyl*-2,4-*di*-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **9** vs. *ethyl* 2-O-*benzyl*-3,4-*di*-O-*benzoyl*-1-*thio*-α-L-*rhamnopyranoside* **13**.—Compounds **9** (72 mg, 0.146 mmol) and **13** (74 mg, 0.146 mmol) were allowed to react *via* the general procedure described above. Extra portions of TfOH solution (10 μl) were added during 8 h. After 24 h the reaction mixture was worked up. The integrals of the following $^1$H NMR signals revealed a ratio of 5.1 : 1.0 (**18** : **22**).

**18**: $\delta_H$(500 MHz; $CDCl_3$) 3.17 (s, $OCH_3$), 3.23 (s, $OCH_3$) and 3.36 (s, $OCH_3$).

**22**: $\delta_H$(500 MHz; $CDCl_3$) 3.24 (s, $OCH_3$), 3.28 (s, $OCH_3$) and 3.37 (s, $OCH_3$).

*Entry* 9. *Ethyl* 4-O-*benzoyl*-2,3-*di*-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **10** vs. *ethyl* 3,4-*di*-O-*benzoyl*-2-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **13**.—Compounds **10** (72 mg, 0.146 mmol) and **13** (74 mg, 0.146 mmol) were treated *via* the general procedure described above. Extra portions of TfOH solution (10 μl) were added over a period of 8 h. After 24 h the reaction mixture was worked up. The integrals of the following $^1$H NMR signals revealed a ratio of 2.1 : 1.0 (**19** : **22**).

**19**: $\delta_H$(500 MHz; $CDCl_3$) 3.03 (s, $OCH_3$), 3.22 (s, $OCH_3$) and 3.35 (s, $OCH_3$).

**22**: $\delta_H$(500 MHz; $CDCl_3$) 3.24 (s, $OCH_3$), 3.28 (s, $OCH_3$) and 3.37 (s, $OCH_3$).

*Entry* 10. *Ethyl* 4-O-*benzoyl*-2,3-*di*-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **10** vs. *ethyl* 2-O-*benzyl*-3,4-O-(1′,2′-*dimethoxycyclohexane*-1′,2′-*diyl*)-1-*thio*-α-L-*rhamnopyranoside* **15**.—Compounds **10** (31 mg, 0.070 mmol) and **15** (35 mg, 0.070 mmol) were allowed to react *via* the general procedure described above. Extra portions of TfOH solution (10 μl) were added during 8 h. After 24 h the reaction mixture was worked up. The integrals of the following $^1$H NMR signals revealed a ratio of 2.6 : 1.0 (**19** : **24**).

**19**: $\delta_H$(500 MHz; $CDCl_3$) 3.03 (s, $OCH_3$), 3.22 (s, $OCH_3$) and 3.35 (s, $OCH_3$).

**24**: $\delta_H$(500 MHz; $CDCl_3$) 3.11 (s, $OCH_3$), 3.20 (s, $OCH_3$) and 3.31 (s, $OCH_3$).

*Entry* 11. *Ethyl* 4-O-*benzoyl*-2,3-*di*-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **10** vs. *ethyl* 2-O-*benzoyl*-3,4-*di*-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **8**.—Compounds **10** (72 mg, 0.146 mmol) and **8** (72 mg, 0.146 mmol) were treated *via* the general procedure described above. Extra portions of TfOH solution (10 μl) were added over 8 h. After 3 days the reaction mixture was worked up. The integrals of the following $^1$H NMR signals revealed a ratio of 3.9 : 1.0 (**19** : **17**).

**19**: $\delta_H$(500 MHz; $CDCl_3$) 3.03 (s, $OCH_3$).

**17**: $\delta_H$(500 MHz; $CDCl_3$) 3.06 (s, $OCH_3$).

*Entry* 12. *Ethyl* 3,4-*di*-O-*benzoyl*-2-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **13** vs. *ethyl* 2-O-*benzyl*-3,4-O-(1′,2′-*dimethoxycyclohexane*-1′,2′-*diyl*)-1-*thio*-α-L-*rhamnopyranoside* **15**.—Compounds **13** (41 mg, 0.081 mmol) and **15** (76 mg, 0.081 mmol) were treated *via* the general procedure described above. Extra portions of TfOH solution (10 μl) were added over a period of 8 h. After 30 h the reaction mixture was worked up. The integrals of the following $^1$H NMR signals revealed a ratio of 1.7 : 1.0 (**22** : **24**).

**22**: $\delta_H$(500 MHz; $CDCl_3$) 3.28 (s, $OCH_3$) and 3.37 (s, $OCH_3$).

**24**: $\delta_H$(500 MHz; $CDCl_3$) 3.20 (s, $OCH_3$) and 3.31 (s, $OCH_3$).

*Entry* 13. *Ethyl* 3,4-*di*-O-*benzoyl*-2-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **13** vs. *ethyl* 2-O-*benzoyl*-3,4-*di*-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **8**.—Compounds **13** (40 mg, 0.081 mmol) and **8** (41 mg, 0.081 mmol) were treated *via* the general procedure described above. Extra portions of TfOH solution (10 μl) were added during 8 h. After 2 days the reaction mixture was worked up. A small amount of the acceptor was still present. The integrals of the following $^1$H NMR signals revealed a ratio of 2.1 : 1.0 (**22** : **17**).

**22**: $\delta_H$(500 MHz; $CDCl_3$) 3.28 (s, $OCH_3$).

**17**: $\delta_H$(500 MHz; $CDCl_3$) 3.06 (s, $OCH_3$).

*Entry* 14. *Ethyl* 3,4-*di*-O-*benzoyl*-2-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **13** vs. *ethyl* 2,3-*di*-O-*benzoyl*-4-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **11**.—Compounds **13** (74 mg, 0.146 mmol) and **11** (74 mg, 0.146 mmol) were allowed to react *via* the general procedure described above. Extra portions of TfOH solution (10 μl) were added over a period of 8 h. After 4 days the reaction mixture was worked up. A small amount of the acceptor was still present. The integrals of the following $^1$H NMR signals revealed a ratio of 2.8 : 1.0 (**22** : **20**).

**22**: $\delta_H$(500 MHz; $CDCl_3$) 3.28 (s, $OCH_3$).

**20**: $\delta_H$(500 MHz; $CDCl_3$) 3.20 (s, $OCH_3$).

*Entry* 15. *Ethyl* 3,4-*di*-O-*benzoyl*-2-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **13** vs. *ethyl* 2,4-*di*-O-*benzoyl*-3-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **12**.—Compounds **13** (74 mg, 0.146 mmol) and **12** (74 mg, 0.146 mmol) were allowed to react *via* the general procedure described above. Extra portions of TfOH solution (10 μl) were added over a period of 8 h. After 2 days the reaction mixture was worked up. The integrals of the following $^1$H NMR signals revealed a ratio of 27.3 : 1.0 (**22** : **21**).

**22**: $\delta_H$(500 MHz; $CDCl_3$) 3.28 (s, $OCH_3$).

**21**: $\delta_H$(500 MHz; $CDCl_3$) 2.97 (s, $OCH_3$).

*Entry* 16. *Ethyl* 2-O-*benzyl*-3,4-O-(1′,2′-*dimethoxycyclohexane*-1′,2′-*diyl*)-1-*thio*-α-L-*rhamnopyranoside* **15** vs. *ethyl* 2-O-*benzoyl*-3,4-*di*-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **8**.—Compounds **15** (12 mg, 0.024 mmol) and **8** (11 mg, 0.024 mmol) were treated *via* the general procedure described above. Extra portions of TfOH solution (10 μl) were added over a period of 8 h. After 24 h the reaction mixture was worked up. The integrals of the following $^1$H NMR signals revealed a ratio of 1.7 : 1.0 (**24** : **17**).

**24**: $\delta_H$(600 MHz; $CDCl_3$) 3.11 (s, $OCH_3$) and 3.31 (s, $OCH_3$).

**17**: $\delta_H$(600 MHz; $CDCl_3$) 3.06 (s, $OCH_3$) and 3.36 (s, $OCH_3$).

*Entry* 17. *Ethyl* 2-O-*benzoyl*-3,4-*di*-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **8** vs. *ethyl* 2,3-*di*-O-*benzoyl*-4-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **11**.—Compounds **8** (47 mg, 0.095 mmol) and **11** (48 mg, 0.095 mmol) were treated *via* the general procedure described above. Extra portions of TfOH solution (10 μl) were added during 8 h. After 24 h the reaction mixture was worked up. The integrals of the following $^1$H NMR signals revealed a ratio of 1.6 : 1.0 (**17** : **20**).

**17**: $\delta_H$(500 MHz; $CDCl_3$) 3.06 (s, $OCH_3$), 3.24 (s, $OCH_3$) and 3.36 (s, $OCH_3$).

**20**: $\delta_H$(500 MHz; $CDCl_3$) 3.20 (s, $OCH_3$), 3.25 (s, $OCH_3$) and 3.37 (s, $OCH_3$).

*Entry* 18. *Ethyl* 2,3-*di*-O-*benzoyl*-4-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **11** vs. *ethyl* 2,4-*di*-O-*benzoyl*-3-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **12**.—Compounds **11** (74 mg, 0.146 mmol) and **12** (74 mg, 0.146 mmol) were treated *via* the general procedure described above. Extra portions of TfOH solution (10 μl) were added over a period of 8 h. After 4 days the reaction mixture was worked up. A small amount of the acceptor was still present. The integrals of the following $^1$H NMR signals revealed a ratio of 5.3 : 1.0 (**20** : **21**).

**20**: $\delta_H$(500 MHz; $CDCl_3$) 3.20 (s, $OCH_3$) and 3.37 (s, $OCH_3$).

**21**: $\delta_H$(500 MHz; $CDCl_3$) 2.97 (s, $OCH_3$) and 3.39 (s, $OCH_3$).

**Thiomannoside competition reactions.**

*Note* 1: Consumption of the acceptor was monitored by TLC and up to 4 extra portions of TfOH solution were added through the day and the reaction mixture was worked up after 24 h.

*Note* 2: The ratio of the dissaccharide products was determined by $^1$H NMR (500 MHz) spectroscopy of the crude residue.

**Table 3**

*Entry* 1. *Ethyl* 2,3,4,6-*tetra*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **46** vs. *ethyl* 3-O-*benzoyl*-2,4,6-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **26**.—Compounds **46** (41 mg, 0.070 mmol) and **26** (42 mg, 0.070 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 1.1 : 1.0 (**42** : **36**).

**42**: $\delta_H$(500 MHz; $CDCl_3$) 3.07 (s, $OCH_3$), 3.21 (s, $OCH_3$) and 3.28 (s, $OCH_3$).

**36**: $\delta_H$(500 MHz; $CDCl_3$) 3.08 (s, $OCH_3$), 3.23 (s, $OCH_3$) and 3.32 (s, $OCH_3$).

*Entry* 2. *Ethyl* 2,3,4,6-*tetra*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **46** vs. *ethyl* 4-O-*benzoyl*-2,3,6-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **27**.—Compounds **46** (41 mg, 0.070 mmol) and **27** (42 mg, 0.070 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 4.6 : 1.0 (**42** : **37**).

**42**: $\delta_H$(500 MHz; $CDCl_3$) 3.07 (s, $OCH_3$) and 3.21 (s, $OCH_3$).

**37**: $\delta_H$(500 MHz; $CDCl_3$) 3.11 (s, $OCH_3$) and 3.28 (s, $OCH_3$).

*Entry* 3. *Ethyl* 2,3,4,6-*tetra*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **46** vs. *ethyl* 6-O-*benzoyl*-2,3,4-*tri*-O-*benzyl*-1-*thio*-α-

D-*mannopyranoside* **28**.—Compounds **46** (41 mg, 0.070 mmol) and **28** (42 mg, 0.070 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 10.2 : 1.0 (**42** : **38**).

**42**: $\delta_H$(500 MHz; $CDCl_3$) 3.07 (s, $OCH_3$), 3.21 (s, $OCH_3$) and 3.28 (s, $OCH_3$).

**38**: $\delta_H$(500 MHz; $CDCl_3$) 3.10 (s, $OCH_3$), 3.20 (s, $OCH_3$) and 3.30 (s, $OCH_3$).

*Entry* 4. *Ethyl* 2,3,4,6-*tetra*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **46** vs. *ethyl* 2-O-*benzoyl*-3,4,6-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **25**.—Compounds **46** (41 mg, 0.070 mmol) and **25** (42 mg, 0.070 mmol) were treated *via* the general procedure described above. The $^1$H NMR signals for the 2-benzoylated compound could not be distinguished so the ratio of products must be greater than 30.0 : 1.0 (**42** : **35**).

*Entry* 5. *Ethyl* 3-O-*benzoyl*-2,4,6-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **26** vs. *ethyl* 4-O-*benzoyl*-2,3,6-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **27**.—Compounds **26** (42 mg, 0.070 mmol) and **27** (42 mg, 0.070 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 4.5 : 1.0 (**36** : **37**).

**36**: $\delta_H$(500 MHz; $CDCl_3$) 3.08 (s, $OCH_3$), 3.23 (s, $OCH_3$) and 3.32 (s, $OCH_3$).

**37**: $\delta_H$(500 MHz; $CDCl_3$) 3.11 (s, $OCH_3$), 3.23 (s, $OCH_3$) and 3.28 (s, $OCH_3$).

*Entry* 6. *Ethyl* 3-O-*benzoyl*-2,4,6-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **26** vs. *ethyl* 6-O-*benzoyl*-2,3,4-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **28**.—Compounds **26** (42 mg, 0.070 mmol) and **28** (42 mg, 0.070 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 7.2 : 1.0 (**36** : **38**).

**36**: $\delta_H$(500 MHz; $CDCl_3$) 3.08 (s, $OCH_3$), 3.23 (s, $OCH_3$) and 3.32 (s, $OCH_3$).

**38**: $\delta_H$(500 MHz; $CDCl_3$) 3.10 (s, $OCH_3$), 3.20 (s, $OCH_3$) and 3.30 (s, $OCH_3$).

*Entry* 7. *Ethyl* 3-O-*benzoyl*-2,4,6-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **26** vs. *ethyl* 2-O-*benzoyl*-3,4,6-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **25**.—Compounds **26** (42 mg, 0.070 mmol) and **25** (42 mg, 0.070 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 32.6 : 1.0 (**36** : **35**).

**36**: $\delta_H$(500 MHz; $CDCl_3$) 3.08 (s, $OCH_3$) and 3.23 (s, $OCH_3$).

**35**: $\delta_H$(500 MHz; $CDCl_3$) 3.16 (s, $OCH_3$) and 3.20 (s, $OCH_3$).

*Entry* 8. *Ethyl* 4-O-*benzoyl*-2,3,6-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **27** vs. *ethyl* 6-O-*benzoyl*-2,3,4-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **28**.—Compounds **27** (42 mg, 0.070 mmol) and **28** (42 mg, 0.070 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 1.7 : 1.0 (**37** : **38**).

**37**: $\delta_H$(500 MHz; $CDCl_3$) 3.11 (s, $OCH_3$), 3.23 (s, $OCH_3$) and 3.28 (s, $OCH_3$).

**38**: $\delta_H$(500 MHz; $CDCl_3$) 3.10 (s, $OCH_3$), 3.20 (s, $OCH_3$) and 3.30 (s, $OCH_3$).

*Entry* 9. *Ethyl* 4-O-*benzoyl*-2,3,6-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **27** vs. *ethyl* 2-O-*benzoyl*-3,4,6-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **25**.—Compounds **27** (42 mg, 0.070 mmol) and **25** (42 mg, 0.070 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 5.4 : 1.0 (**37** : **35**).

**37**: $\delta_H$(500 MHz; $CDCl_3$) 3.11 (s, $OCH_3$), 3.23 (s, $OCH_3$) and 3.28 (s, $OCH_3$).

**35**: $\delta_H$(500 MHz; $CDCl_3$) 3.16 (s, $OCH_3$), 3.20 (s, $OCH_3$) and 3.32 (s, $OCH_3$).

*Entry* 10. *Ethyl* 6-O-*benzoyl*-2,3,4-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **28** vs. *ethyl* 2,6-*di*-O-*benzyl*-3,4-O-(1′,2′-*dimethoxycyclohexane*-1′,2′-*diyl*)-1-*thio*-α-D-*mannopyranoside* **29**.—Compounds **28** (42 mg, 0.070 mmol) and **29** (38 mg, 0.070 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 1.7 : 1.0 (**38** : **39**).

**38**: $\delta_H$(500 MHz; $CDCl_3$) 3.10 (s, $OCH_3$) and 3.30 (s, $OCH_3$).

**39**: $\delta_H$(500 MHz; $CDCl_3$) 3.07 (s, $OCH_3$) and 3.31 (s, $OCH_3$).

*Entry* 11. *Ethyl* 6-O-*benzoyl*-2,3,4-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **28** vs. *ethyl* 2-O-*benzoyl*-3,4,6-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **25**.—Compounds **28** (42 mg, 0.070 mmol) and **25** (42 mg, 0.070 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 3.2 : 1.0 (**38** : **35**).

**38**: $\delta_H$(500 MHz; $CDCl_3$) 3.10 (s, $OCH_3$), 3.20 (s, $OCH_3$) and 3.30 (s, $OCH_3$).

**35**: $\delta_H$(500 MHz; $CDCl_3$) 3.16 (s, $OCH_3$), 3.20 (s, $OCH_3$) and 3.32 (s, $OCH_3$).

*Entry* 12. *Ethyl* 2,6-*di*-O-*benzyl*-3,4-O-(1′,2′-*dimethoxycyclohexane*-1′,2′-*diyl*)-1-*thio*-α-D-*mannopyranoside* **29** vs. *ethyl* 2,6-*di*-O-*benzyl*-3,4-O-(*octahydro*-2′,2″-*bi*-2H-*pyran*-2′,2″-*diyl*)-1-*thio*-α-D-*mannopyranoside* **30**.—Compounds **29** (41 mg, 0.076 mmol) and **30** (43 mg, 0.076 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 1.1 : 1.0 (**39** : **40**).

**39**: $\delta_H$(500 MHz; $CDCl_3$) 2.98 (s, $OCH_3$) and 3.20 (s, $OCH_3$).

**40**: $\delta_H$(500 MHz; $CDCl_3$) 2.93 (s, $OCH_3$) and 3.21 (s, $OCH_3$).

*Entry* 13. *Ethyl* 2,6-*di*-O-*benzyl*-3,4-O-(1′,2′-*dimethoxycyclohexane*-1′,2′-*diyl*)-1-*thio*-α-D-*mannopyranoside* **29** vs. *ethyl* 2,6-*di*-O-*benzyl*-3,4-O-(2′,3′-*dimethoxybutane*-2′,3′-*diyl*)-1-*thio*-α-D-*mannopyranoside* **31**.—Compounds **29** (38 mg, 0.070 mmol) and **31** (36 mg, 0.070 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 1.2 : 1.0 (**39** : **41**).

**39**: $\delta_H$(500 MHz; $CDCl_3$) 2.98 (s, $OCH_3$), 3.07 (s, $OCH_3$) and 3.31 (s, $OCH_3$).

**41**: $\delta_H$(500 MHz; $CDCl_3$) 2.96 (s, $OCH_3$), 3.12 (s, $OCH_3$) and 3.31 (s, $OCH_3$).

*Entry* 14. *Ethyl* 2,6-*di*-O-*benzyl*-3,4-O-(1′,2′-*dimethoxycyclohexane*-1′,2′-*diyl*)-1-*thio*-α-D-*mannopyranoside* **29** vs. *ethyl* 2-O-*benzoyl*-3,4,6-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **25**.—Compounds **29** (38 mg, 0.070 mmol) and **25** (42 mg, 0.070 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 2.4 : 1.0 (**39** : **35**).

**39**: $\delta_H$(500 MHz; $CDCl_3$) 2.98 (s, $OCH_3$), 3.07 (s, $OCH_3$), 3.20 (s, $OCH_3$) and 3.31 (s, $OCH_3$).

**35**: $\delta_H$(500 MHz; $CDCl_3$) 3.20 (s, $OCH_3$) and 3.32 (s, $OCH_3$).

**Table 5**

*Entry* 1. *Ethyl* 6-O-*benzoyl*-2,3,4-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **28** vs. *ethyl* 6-O-(4′-*methoxybenzoyl*)-2,3,4-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **47**.—Compounds **28** (42 mg, 0.070 mmol) and **47** (44 mg, 0.070 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 0.8 : 1.0 (**38** : **43**).

**38**: $\delta_H$(500 MHz; $CDCl_3$) 3.30 (s, $OCH_3$).

**43**: $\delta_H$(500 MHz; $CDCl_3$) 3.30 (s, $OCH_3$).

*Entry* 2. *Ethyl* 6-O-*benzoyl*-2,3,4-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **28** vs. *ethyl* 6-O-(4′-*methylbenzoyl*)-2,3,4-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **48**.—Compounds **28** (42 mg, 0.070 mmol) and **48** (44 mg, 0.070 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 0.8 : 1.0 (**38** : **44**).

**38**: $\delta_H$(500 MHz; $CDCl_3$) 3.30 (s, $OCH_3$).

**44**: $\delta_H$(500 MHz; $CDCl_3$) 3.30 (s, $OCH_3$).

*Entry* 4. *Ethyl* 6-O-*benzoyl*-2,3,4-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **28** vs. *ethyl* 6-O-(4′-*nitrobenzoyl*)-2,3,4-*tri*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **49**.—Compounds **28** (42 mg, 0.070 mmol) and **49** (45 mg, 0.070 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 2.3 : 1.0 (**38** : **45**).

**38**: $\delta_H$(500 MHz; $CDCl_3$) 3.20 (s, $OCH_3$) and 3.30 (s, $OCH_3$).

**45**: $\delta_H$(500 MHz; $CDCl_3$) 3.20 (s, $OCH_3$) and 3.32 (s, $OCH_3$).

**Rhamnose *vs.* mannose reaction.**

*Ethyl* 2,3,4-*tri*-O-*benzyl*-1-*thio*-α-L-*rhamnopyranoside* **7** vs. *ethyl* 2,3,4,6-*tetra*-O-*benzyl*-1-*thio*-α-D-*mannopyranoside* **46**.—

Compounds **7** (34 mg, 0.070 mmol) and **46** (41 mg, 0.070 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 2.6 : 1.0 (**16** : **42**).

**16**: $\delta_H$(500 MHz; $CDCl_3$) 3.06 (s, $OCH_3$).

**42**: $\delta_H$(500 MHz; $CDCl_3$) 3.07 (s, $OCH_3$).

**Selenomannoside competition reactions (Table 6).**

*Note* 1: The acceptor was consumed within 5 min in all reactions.

*Note* 2: The residue was chromatographed on silica gel (light petroleum–diethyl ether mixtures) to give the disaccharide products in one fraction from which the ratio was determined by $^1$H NMR (500 MHz) spectroscopy.

*Entry* 1. *Phenyl* 2,3,4,6-*tetra*-O-*benzyl*-1-*seleno*-α-D-*manno*-*pyranoside* **1** vs. *phenyl* 2,3,4-*tri*-O-*benzyl*-6-O-(4′-*methoxy*-*benzoyl*)-1-*seleno*-α-D-*mannopyranoside* **32**.—Compounds **1** (100 mg, 0.147 mmol) and **32** (106 mg, 0.147 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 1.5 : 1.0 (**42** : **43**).

**42**: $\delta_H$(500 MHz; $CDCl_3$) 3.07 (s, $OCH_3$), 3.21 (s, $OCH_3$) and 3.28 (s, $OCH_3$).

**43**: $\delta_H$(500 MHz; $CDCl_3$) 3.09 (s, $OCH_3$), 3.20 (s, $OCH_3$) and 3.30 (s, $OCH_3$).

*Entry* 2. *Phenyl* 2,3,4,6-*tetra*-O-*benzyl*-1-*seleno*-α-D-*manno*-*pyranoside* **1** vs. *phenyl* 2,3,4-*tri*-O-*benzyl*-6-O-(4′-*methyl*-*benzoyl*)-1-*seleno*-α-D-*mannopyranoside* **33**.—Compounds **1** (100 mg, 0.147 mmol) and **33** (104 mg, 0.147 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 2.0 : 1.0 (**42** : **44**).

**42**: $\delta_H$(500 MHz; $CDCl_3$) 3.07 (s, $OCH_3$), 3.21 (s, $OCH_3$) and 3.28 (s, $OCH_3$).

**44**: $\delta_H$(500 MHz; $CDCl_3$) 3.09 (s, $OCH_3$), 3.19 (s, $OCH_3$) and 3.30 (s, $OCH_3$).

*Entry* 3. *Phenyl* 2,3,4,6-*tetra*-O-*benzyl*-1-*seleno*-α-D-*manno*-*pyranoside* **1** vs. *phenyl* 6-O-*benzoyl*-2,3,4-*tri*-O-*benzyl*-1-*seleno*-α-D-*mannopyranoside* **50**.—Compounds **1** (41 mg, 0.060 mmol) and **50** (42 mg, 0.060 mmol) were treated *via* the general procedure described above. The residue was chromatographed and the integrals of the following $^1$H NMR signals revealed a ratio of 2.4 : 1.0 (**42** : **38**).

**42**: $\delta_H$(500 MHz; $CDCl_3$) 3.07 (s, $OCH_3$), 3.21 (s, $OCH_3$) and 3.28 (s, $OCH_3$).

**38**: $\delta_H$(500 MHz; $CDCl_3$) 3.10 (s, $OCH_3$), 3.20 (s, $OCH_3$) and 3.30 (s, $OCH_3$).

*Entry* 4. *Phenyl* 2,3,4,6-*tetra*-O-*benzyl*-1-*seleno*-α-D-*manno*-*pyranoside* **1** vs. *phenyl* 2,3,4-*tri*-O-*benzyl*-6-O-(4′-*nitrobenzoyl*)-1-*seleno*-α-D-*mannopyranoside* **34**.—Compounds **1** (100 mg, 0.147 mmol) and **34** (108 mg, 0.147 mmol) were treated *via* the general procedure described above. The integrals of the following $^1$H NMR signals revealed a ratio of 3.8 : 1.0 (**42** : **45**).

**42**: $\delta_H$(500 MHz; $CDCl_3$) 3.07 (s, $OCH_3$), 3.21 (s, $OCH_3$) and 3.28 (s, $OCH_3$).

**45**: $\delta_H$(500 MHz; $CDCl_3$) 3.11 (s, $OCH_3$), 3.20 (s, $OCH_3$) and 3.32 (s, $OCH_3$).

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