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Stereocontrolled glycoside synthesis by activation of glycosyl sulfone donors with scandium(III) triflate†

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The activation of aryl glycosyl sulfone donors has been achieved using scandium(III) triflate and has led to the selective preparation of α-mannosides resulting from a post-glycosylation anomerization.

Introduction

Because of the implication of carbohydrates in many crucial biological events (*e.g.*, immune response, bacterial and viral infections, animal and plant development, fertilization), the formation of the glycosidic bond is one of the most important aspects of carbohydrate chemistry.[1–4] The synthesis of a glycoconjugate often involves a glycosyl donor that, upon activation with a suitable reagent, generates an intermediate oxacarbenium ion. The nucleophilic attack of an acceptor (ROH) to this flattened cation usually results in a mixture of the α- and β-anomers. The stereocontrolled synthesis of only one anomer is a difficult task and the stereoselectivity of the glycosylation can be tuned by many factors such as the leaving group, the protecting groups, the promoter, as well as the solvent without or with additives.[5,6] One of the most reliable methods to control the approach of the acceptor is to install on the donor a neighboring participating 2-*O*-carboxylate ester group, which shields one face through the formation of a stable acyloxonium cation and provides a 1,2-*trans*-glycoside.[5–7] However, this kind of protecting group deactivates the donor leading sometimes to a decreased reaction yield. In contrast, use of an ether-type protecting group that activates the donor often leads to a mixture of both anomers that results from the approach of the alcohol from both sites of the oxacarbonium ion. In this paper, we describe the selective synthesis of α-D-mannosides, which are ubiquitous in nature, *via* the activation of mannosyl sulfone donors and without the assistance of a neighboring-group effect.[8,9–19] Anomeric phenyl sulfones were prepared a long time ago.[20,21] They were mainly used as the starting glycosyl donors for the direct preparation of *C*-glycosides[22,23] by lithiation–desulfonylation,[24] reductive metallation with lithium,[25] samarium(II)[26] reagents and by using the Ramberg–Bäcklund rearrangement.[27] In contrast to the thioaryl(heteroaryl) and arylsulfoxide anomeric substituents, widely used in chemical *O*-glycosylation reactions,[5,6] the sulfone group has, however, rarely been used as an anomeric leaving group in *O*-glycosylations, mostly because of the inefficient activation of the glycosyl–sulfur bond cleavage.[28,29] Groundwork of Ferrier *et al.* first showed that the phenylsulfonyl group was not displaced from the 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside phenyl sulfone in the presence of mercury(II) acetate.[28] However, starting with more reactive deoxyglycoside substrates, the activation of anomeric phenylsulfones was successfully described using 2 equiv. of $MgBr_2 \cdot Et_2O$ in THF.[30,31] These conditions were inefficient for the activation of the more stable perbenzoylated glucosyl sulfone.[32] Also, activation of glycosyl 2-pyridyl sulfones by 1 equiv. of $Sm(OTf)_3$ at 70 °C in toluene with alcohols is possible, providing the corresponding α/β mixture of glycosides in good yields, presumably as a result of a complexation of the samarium salt with the 2-pyridyl sulfone group.[33]

We now report that scandium(III) triflate can effectively activate armed aryl glycosyl sulfone donors and we have established reaction conditions that can provide an α-selective synthesis of D-mannopyranosyl glycosides, through a post-glycosylation anomerization.

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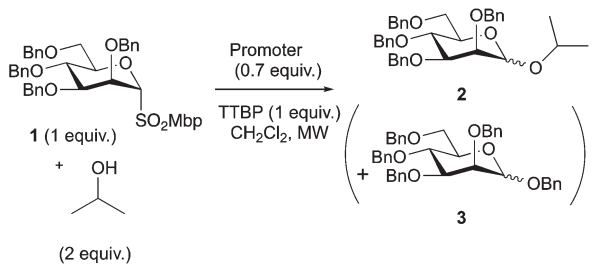
†Electronic supplementary information (ESI) available: NMR spectra of all new compounds and preparation of intermediate compounds. See DOI: 10.1039/c7ob02792c



Scheme 1 Glycosylation of i-PrOH with the sulfone **1**. Mbp = 2-methyl-5-*tert*-butylphenyl.

Results and discussion

Initial experiments to examine the possibility of activating anomeric sulfones were conducted with sulfone **1** (Scheme 1, Table 1). This latter was prepared by a one-step oxidation of the corresponding thioarylether, obtained from the nonmalodorous 2-methyl-5-*tert*-butylphenylthiol (HSMbp).[34,35] The reaction conditions (solvent, temperature, concentration, catalytic charge ...) were first optimized with $Fe(OTf)_3$ as a promoter (results not shown) that was previously used in our studies on the glycosylation with *N*-acetyl glycosamine donors.[36–38] With this Lewis acid, the best results for the glycosylation of iso-propanol (2 equiv./donor) were obtained using 0.7 equiv. of $Fe(OTf)_3$ and 1 equiv. of 2,4,6-tri-*tert*-butylpyrimidine (TTBP) as an acid scavenger in dry CH_2Cl_2 (0.5 M) (Table 1, entry 1). When the reaction was carried out at 100 °C under microwave irradiation (MW) for 90 min, the glycosylation adducts **2** were obtained in 71% yield and in a good α/β ratio of 49/1. The compound was also accompanied by a small amount (5%) of the by-product **3**, arising from a debenzylation of the starting donor under these conditions.[28,39]

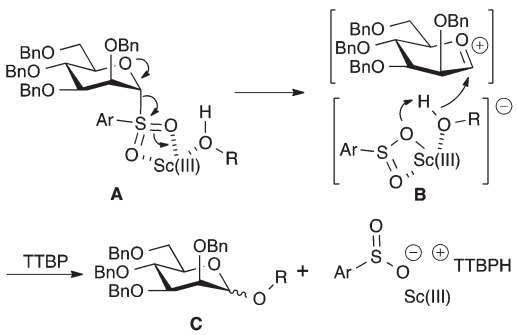
Table 1 Influence of the promoter for the glycosylation of i-PrOH with the sulfone **1**

Entry	Promoter[a]	**1**/**2** ratio[c]	α/β ratio[d]	**2**[e] (yield %)
1	$Fe(OTf)_3$	0/1	49/1	71
2	$Fe(OTf)_3$·6.2DMSO	1/0	—	—
3	$FeCl_3$	2.3/1	1.1/1	—
4	$Bi(OTf)_3$[b]	5.2/1	16/1	—
5	$Sm(OTf)_3$	0.9/1	2/1	—
6	$La(OTf)_3$	99/traces	1/1	—
7	$In(OTf)_3$	0.5/1	32/1	—
8	$Cu(OTf)_2$	0.8/1	8/1	—
9	$Yb(OTf)_3$	19/1	1.2/1	—
10	$Sc(OTf)_3$	0/1	32/1	85
11	TfOH[f]	Degradation	—	—

[a] Reaction conditions: Donor **1** (1 equiv.), i-PrOH (2 equiv.), TTBP (1 equiv.), activator (0.7 equiv.) in CH_2Cl_2 (*c* 0.5 M) under microwave irradiation (100 °C; 90 min) unless otherwise stated. [b] 90 °C for 90 min. At 100 °C, degradation of products in the reaction mixture were observed. [c] Determined by ^1H NMR analysis of the crude mixture. [d] Determined by UPLC-UV analysis of the crude mixture. [e] After chromatography on silica gel. [f] 2.1 equiv.

For this reason, we considered the use of other promoters for activating the arylsulfone. No glycosylation reaction occurred under these optimized conditions when using 70 mol% of $Fe(OTf)_3$·6.2DMSO (Table 1, entry 2). $FeCl_3$ (Table 1, entry 3) was also checked but led to a low conversion rate and a 1.1 : 1 mixture of the α/β anomers. We examined the glycosylation with other metallic triflates that were previously described as promotors in glycosylation reactions (70 mol% of $Yb(OTf)_3$,[33] $Bi(OTf)_3$, $Sm(OTf)_3$,[33] $La(OTf)_3$, $In(OTf)_3$, $Cu(OTf)_2$)[40–44] under the same set of reaction conditions (Table 1, entries 4–9) but we obtained lower conversion rates and stereoselectivites than with $Fe(OTf)_3$. Finally, $Sc(OTf)_3$, turned out to be an active promoter, providing the glycosylation adducts in 85% yield in an α/β ratio of 32/1 and no trace of the compound **3** (Table 1, entry 10). It is also worth to note that degradation was only observed when TfOH (2.1 equiv.) was used to promote the reaction (Table 1, entry 11).

$Sc(OTf)_3$ is known for its oxophilicity and a higher Lewis acidity, which is attributed to its small ionic radius compared to other rare-earth metal triflates.[45] A possible mechanism for the glycoside formation may be rationalized by the formation of complex **A** shown in Scheme 2. Both the donor and acceptor



Scheme 2 Proposed mechanism for the activation of glycosyl sulfones by scandium triflate in the presence of the alcohol nucleophile. TTBP = 2,4,6-tri-*tert*-butylpyrimidine.

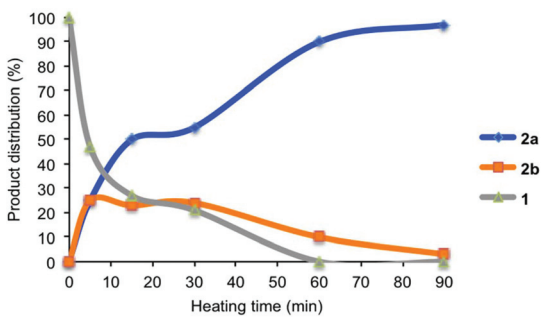
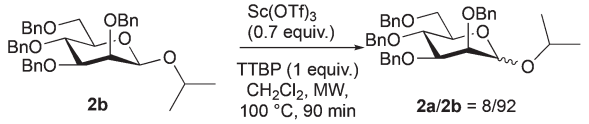


Fig. 1 Product distribution (**1**[a], **2a**[b], **2b**[b]) as a function of the operating time. Conditions: Donor **1** (1 equiv.), i-PrOH (2 equiv.), TTBP (1 equiv.), $Sc(OTf)_3$ (0.7 equiv.) in CH_2Cl_2 (*c* 0.5 M) under microwave irradiation (100 °C). [a] Determined by ^1H NMR analysis of the crude mixture. [b] Determined by UPLC-UV analysis of the crude mixture. **2a** = α-glycoside, **2b** = β-glycoside.

could be complexed to the Sc(III) atom *via* the oxygen atoms of the sulfone group of the donor as well as the oxygen of the alcohol acceptor as in **A**. Cleavage of the C–S bond[46] would lead to the oxacarbenium/scandium arenesulfinate ion pair **B**. The glycosylation reaction follows by a nucleophilic attack of the alcohol, producing an α/β mixture of glycosides **C** along with arylsulfinic acid neutralized by TTBP and the scandium promoter.

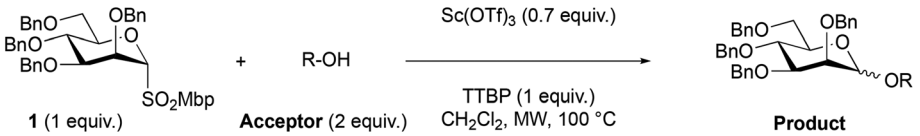
Under the optimized conditions with $Sc(OTf)_3$ at 100 °C (Scheme 1), Fig. 1 shows the product distribution as a function of the heating time (5, 10, 30, 60 and 90 min) and indicates an increase of the ratio of the α-glycoside **2a** in the reaction mixture. This is accompanied by the corresponding decrease of the ratio of the β-glycoside **2b**, which is probably the consequence of a post-glycosylation transformation of the β-anomer. This anomerization can occur through an oxocarbenium ion and involves an exocyclic bond cleavage and/or an endocyclic bond cleavage-recyclization process to the α-glycoside.[47]

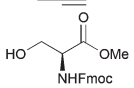
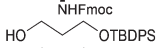
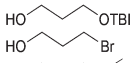
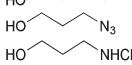
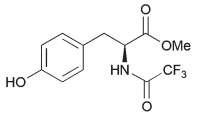
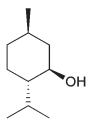
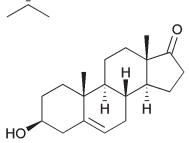
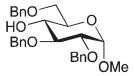
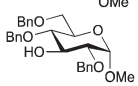


Scheme 3 Attempt of anomerization of **2b** using $Sc(OTf)_3$ (0.7 equiv.) under MW at 100 °C for 90 min. **2a** = α-glycoside, **2b** = β-glycoside.

The anomerization was further studied by treating the pure β-glycoside **2b** under the glycosylation conditions at 100 °C for 90 min (Scheme 3). However, $Sc(OTf)_3$ alone was not able to induced a complete anomerization and the reaction led to the α-glycoside **2a** in only 8%. This may indicate that a species including the anomeric leaving group and the scandium ion might be more efficient in promoting the anomerization than $Sc(OTf)_3$ alone. It is also worth to note that the presence of the base is essential otherwise only degradation is observed.

Table 2 Glycosylation of different acceptors with the sulfone **1**

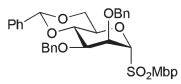
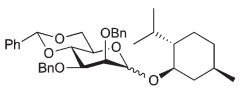
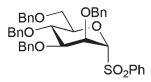
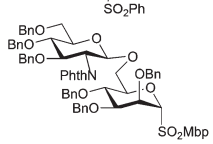
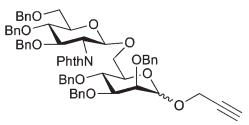
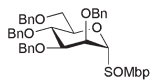
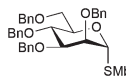
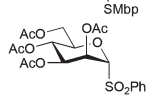
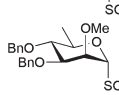
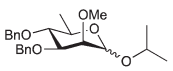
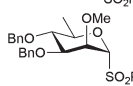
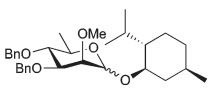
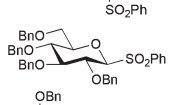
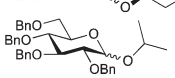
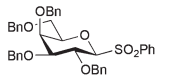
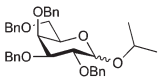
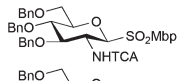
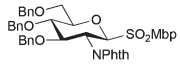
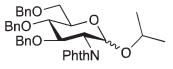


Entry	Acceptor		Reaction time[a] (min)	Ratio α/β [b,c]	Product[d] (yield %)
1		**4**	90	24/1	**5** (91)
2		**6**	90	9/1	**7** (70)
3		**8**	90	24/1	**9** (48)
4		**10**	120	16/1	**11** (82)
5		**12**	120	6/1	**13** (81)
6		**14**	180	13/1	**15** (60)
7		**16**	210	3/1	**17** (68)
8		**18**	90	8/1	**19** (65)
9		**20**	90	19/1	**21** (70)
10		**22**	150	10/1	**23** (84)
11		**24**	90	49/1	**25** (46)
12		**26**	90	6/1	**27** (43)

[a] Reaction conditions: Donor **1** (1 equiv.), acceptor (2 equiv.), TTBP (1 equiv.), activator (0.7 equiv.) in CH_2Cl_2 (*c* 0.5 M) under microwave irradiation at 100 °C. [b] Determined by UPLC-UV analysis. [c] The stereochemistry was determined by measurement of the $^1J_{C1,H1}$ coupling, which indicated an H-1 whether axial (≈160 Hz) or equatorial (≈170 Hz).[51] [d] After chromatography on silica gel.

With $Sc(OTf)_3$ as the standard activator, we further explored the scope of the reaction of sulfone **1** with a variety of functionalized acceptors (Table 2). The reaction proceeded smoothly with primary acceptors such as propargyl alcohol **4** (entry 1) or with L-serine derivative **6** (Table 2, entry 2) leading, under the optimized conditions (MW, 100 °C, 90 min), to the corresponding mannosides **5** [48] and **7** in 91 and 70% yields and in α/β ratios of 24/1 and 9/1 respectively. Glycosylation of the acceptor **8** containing OTBDPS group could also be achieved but in a moderate 48% yield (Table 2, entry 3), due to the possible cleavage of the silylether group by $Sc(OTf)_3$.[49] For the glycosylation of 3-bromopropan-1-ol (**10**) and 4-penten-1-ol (**12**) (Table 2, entries 4 and 5), we observed a difference in the anomerization rate of the β-glycosides compared to the preceding examples with the production of the desired glycosides in a lower α/β selectivity. The reaction was then carried out for 120 min instead of 90 min to obtain anomeric ratios of 16/1 and 6/1 respectively for the products **11** and **13**. The same trend was observed with acceptors **14** and **16** bearing N_3 (Table 2, entry 6) or NHCbz (Table 2, entry 7) functional groups. For these substrates, the reaction time was increased to 180 and 210 minutes to obtain the glycosylation adducts **15** and **17** in 60 and 68% yield and α/β ratios of 13/1 and 3/1. The reactivity of the phenol **18** derived from L-tyrosine was also checked and the glycosylation reaction gave after 90 min at 100 °C under microwave irradiation, the expected compound **19** in 65% yield and α/β ratio of 8/1 (Table 2, entry 8). An efficient reaction took also place with secondary alcohols such as L-menthol (**20**) (**21**, 70% yield, α/β ratio of 19/1 after 90 min, Table 2, entry 9) or with 3β-hydroxy-5-androsten-17-one **22** (**23**, 84% yield, α/β ratio of 10/1 after 150 min, Table 2, entry 10). Unfortunately, this procedure was not compatible with sugar alcohols acceptors unprotected at the 6-position for the synthesis of 1,6-disaccharides and the reaction led only to degradation adducts.[50] However, with acceptors **24** and **26**, the glycosylation could take place and led to the 1,4- and 1,3-disac-

Table 3 Glycosylation using various glycosyl sulfone donors with $Sc(OTf)_3$

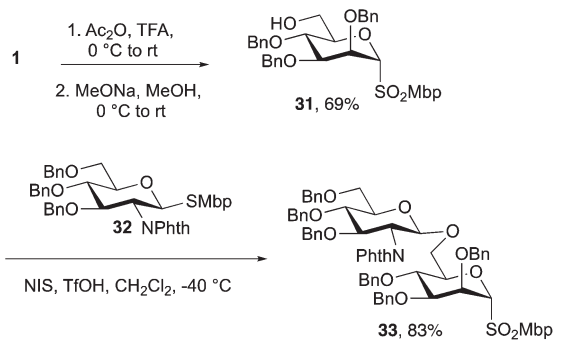
Entry	Donor		Acceptor	Reaction time[a] (min)	Ratio α/β[b,d]	Product[c] (yield %)
1		**28**	**20**	180	6.7/1	 **29** (52)
2		**30**	i-PrOH	40	32/1	**2** (70)
3		**33**	**4**	90	4.5/1	 **34** (78)
4		**35**	i-PrOH	90	2/1	**2** (57)
5		**36**	i-PrOH	90	—	—
6		**37**	i-PrOH	90	—	—
7		**38**	i-PrOH	90	13/1	 **39** (82)
8		**38**	**20**	90	99/1	 **40** (81)
9		**41**	i-PrOH	90	1.7/1	 **42** (95)
10		**43**	i-PrOH	90	1.6/1	 **44** (76)
11		**45**	i-PrOH	60	1/8.1	 **46** (71)
12		**47**	i-PrOH	240	1/11.5	 **48** (60)

[a] Reaction conditions: Donor **X** (1 equiv.), acceptor (2 equiv.), TTBP (1 equiv.), activator (0.7 equiv.) in CH_2Cl_2 (*c* 0.5 M) under microwaves irradiation at 100 °C. [b] Determined by UPLC-UV analysis. [c] After chromatography on silica gel. [d] For entries 1–8, the stereochemistry was determined by measurement of the $^1J_{C1,H1}$ coupling, which indicates whether H-1 is axial (≈160 Hz) or equatorial (≈170 Hz).[51]

charides **25** and **27** in 46 and 43% yields and α/β ratios of 49/1 and 6/1 respectively (Table 2, entries 11 and 12).

To further explore the synthetic utility of this method, the glycosylation with other donors was examined (Table 3). The reaction was carried out with the sulfone donor **28** containing a 4,6-*O*-benzylidene group (Table 3, entry 1). Using L-menthol (**20**) as an acceptor under microwave irradiation at 100 °C for 180 min, it led to the expected glycosides **29** in a 6.7/1 α/β ratio and a moderate 52% yield, which can be attributed to the instability of the *O*-benzylidene protecting group under these conditions. Compared to the corresponding SO_2Mbp donor **1**, phenyl sulfone **30** allowed a faster reaction (Table 3, entry 2). After only 40 min at 100 °C under microwave irradiation, glycosylation of iso-propanol was completed giving the desired compounds **2** in 70% yield and a α/β ratio of 32/1 along with some traces of the perbenzylated adduct **3** (3%).

The glycosylation of the propargylic alcohol **4** could also be carried out with the disaccharidic donor **33** giving the expected compound **34** in 78% yield and an unoptimized 4.5/1 α/β ratio (Table 3, entry 3). This donor **33** was obtained in 83% yield by coupling the sulfone acceptor **31** and the thioarylglycoside **32** with the standard NIS/TfOH promotor system (Scheme 4). This result showed that thioglycoside could be selectively activated in the presence of a sulfone group. We also checked the reactivity of 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl (2-methyl-5-*tert*-butylphenyl) sulfoxide **35** (Table 3, entry 4). The glycosylation was less efficient producing, after 90 min at 100 °C, the expected products **2** in 57% yield in a 2/1 mixture of anomers. It is also worth to note that no reaction occurred with the benzylated thioaryl mannoside **36** or with the disarmed acetylated mannosyl sulfone donor **37** (Table 3, entries 5 and 6). The activation of the D-rhamnoside sulfone **38** was also carried out with i-PrOH or L-menthol as acceptors and the reaction provided the glycosylated adducts **39** and **40** in good yields (82 and 81% respectively) and α/β ratio of 13/1 and 99/1 (Table 3, entries 7 and 8). Glucoside or galactoside sulfones **41** and **43** could also be efficiently activated but yielded a mixture of anomeric adducts with low selectivity that could not be improved with longer heating time (Table 3, entries 9 and 10). Finally, the glycosylation of i-PrOH using glucosamine derivatives **45** and **47** was carried out, providing selectively the β-glycosides **46** and **48**.



Scheme 4 Preparation of the donor **33**.

Conclusions

In summary, we have reported a novel glycosylation procedure starting from aryl glycosyl sulfone donors. Using scandium triflate as a promoter, the reaction is particularly efficient for the α-mannosylation without a neighboring participating group. Various acceptors have been used to give simple glycosides and disaccharides in excellent to moderate yields. The selectivity is partly due to a post anomerization process during the extending heating time, which needs, however, to be demonstrated by more experimental studies. This procedure is consistent with many functional groups (NHFmoc, NHCbz, NHTFA, NHTCA, NPhth, N_3, OTBDPS, Br, alkene, alkyne) and with gluco- and galactosyl sulfone donors but with much lower α/β selectivities. For the glucosamine derivatives **45** and **47**, the effect of the participating *N*-acyl groups dominates, providing selectively the β-glycosides. These new donors are very stable and can tolerate reaction conditions that are not compatible with thioglycosides such as palladium-catalyzed hydrogenolysis (results not shown). Moreover, we have demonstrated that the aryl glycosyl sulfones are not activated by the standard method that activates thioglycosides (*N*-iodosuccinimide/TfOH) and these latter are not activated using our procedure. We are currently investigating the application of this method for the synthesis of oligosaccharidic mimics.

Experimental section

General methods

Reactions were monitored with analytical thin-layer chromatography (TLC) on silica gel 60 F_{254} plates and visualized under UV (254 nm) and/or by staining with $KMnO_4$ or vanillin. Silica gel SDS 60 ACC 35–70 mm was used for column chromatography. Preparative TLC was done using Merck 60 F_{254} 0.5 mm. NMR spectra were recorded with AVANCE 300 and AVANCE 500 Bruker spectrometers. Chemical shifts are given in parts per million, referenced to the solvent peak of $CDCl_3$, defined at 77.23 ppm (^{13}C NMR) and 7.26 ppm (^{1}H NMR). Microwave reactions were carried out with an Anton Paar Monowave 300 instrument. Melting points (uncorrected) were determined with the aid of a Büchi B-540 apparatus. IR spectra were recorded on a PerkinElmer Spectrum BX instrument with an FT-IR system. Optical rotations were measured on an Anton Paar MCP300 polarimeter using a cell of 1 dm-length path. All the reagent grade chemicals obtained from commercial sources were used as received.

The ratio of α/β were determined by Reversed Phase (RP)-UPLC-MS analyses. The instrument used for all the analysis was an UPLC system equipped with a PDA and a triple quadrupole mass spectrometer detector (Acquity UPLC-TQD, Waters).

RP-UPLC (HSS T3 column, 1.8 μm, 2.1 mm × 100 mm) with 0.1% formic acid in CH_3CN and 0.1% formic acid in water as eluents at a flow rate of 0.6 mL min^{-1}. The detection was performed by PDA and using the TQD mass spectrometer operated in electrospray ionization positive mode at 3.2 kV capillary voltage.

The experimental procedures for the preparation of compounds **1**, **2b**, **28**, **30–33**, **35**, **38**, **45**, **47** are included within the ESI.†

General procedure for the glycosylation

To the donor (1 equiv.) in dry CH_2Cl_2 (0.5 M) was added successively the promoter (0.7 equiv.), TTBP (1 equiv.) and the acceptor (2 equiv.). The mixture was heated under microwave irradiation at 100 °C for the required time (see Table 1). After completion of the reaction, the solution was diluted in CH_2Cl_2 and a saturated solution of $NaHCO_3$ was added. After the separation of the organic layer, the aqueous layer was extracted with CH_2Cl_2 (3×). The combined organic layer were washed with a saturated aqueous solution of NaCl and dried with Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the product was purified by flash chromatography on silica gel.

Iso-propyl 2,3,4,6-tetra-*O*-benzyl-D-mannopyranoside 2

The general procedure was followed using donor **1** (92 mg, 0.125 mmol), TTBP (31 mg, 0.125 mmol), $Sc(OTf)_3$ (43 mg, 0.087 mmol) and i-PrOH (20 μL, 0.25 mmol) in CH_2Cl_2 (0.25 mL) for 90 min. After purification (toluene/acetone 90 : 10), **2** [52] (62 mg, 0.106 mmol, 85%, α/β: 32/1) was obtained as a colorless oil.

Gram-scale preparation of propargyl 2,3,4,6-tetra-*O*-benzyl-D-mannopyranoside 5

The general procedure was followed using donor **1** (0.85 g, 1.15 mmol), TTBP (0.286 g, 1.15 mmol), $Sc(OTf)_3$ (0.4 g, 0.86 mmol) and acceptor **4** (0.13 mL, 2.3 mmol) in CH_2Cl_2 (2.3 mL) for 90 min. After purification (EtOAc/heptane 30 : 70), **5** [53] (0.60 g, 1.05 mmol, 91%, α/β: 24/1) was obtained as a colorless oil.

N-(9-Fluorenylmethoxycarbonyl) 2,3,4,6-tetra-*O*-benzyl-D-mannopyranosyl-L-serine methyl ester 7

The general procedure was followed using donor **1** (92 mg, 0.125 mmol), TTBP (31 mg, 0.125 mmol), $Sc(OTf)_3$ (43 mg, 0.087 mmol) and acceptor **6** (85 mg, 0.25 mmol) in CH_2Cl_2 (0.25 mL) for 90 min. After purification (EtOAc/heptane 30 : 70), **7** (76 mg, 0.087 mmol, 70%, α/β: 9/1) was obtained as a colorless oil. **7α**: $[\alpha]_D^{22}$ = +31.5 (c = 1.2, $CHCl_3$). IR: ν = 3337 (N–H), 3063 and 3030 (=C–H), 2955 (C–H), 1732 (C=O) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, α-anomer): δ 7.73 (d, 2H, J = 7.5 Hz, H_{aro}), 7.57 (d, 2H, J = 7.5 Hz, H_{aro}), 7.36–7.21 (m, 22H, H_{aro}), 7.15–7.12 (m, 2H, H_{aro}), 5.80 (d, 1H, J = 8.5 Hz, N*H*), 4.83 (d, 1H, J = 10.5 Hz, OCH_2Ph), 4.80–4.79 (brs, 1H, *H*1), 4.74–4.45 (m, 8H, OCH_2Ph + C*H* (Fmoc)), 4.35–4.30 (m, 2H, OCH_2CHN), 4.18 (brt, 1H, J = 7.0 Hz, C*H*N), 3.99–3.69 (m, 8H, *H*2, *H*3, *H*4, *H*5, *H*6, *H*6′, OCH_2Ph), 3.67 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, α-anomer): δ 170.7 (*C*O), 156.2 (*C*O, Fmoc), 144.0 (2 × Cq_{aro}), 141.4 (2 × Cq_{aro}), 138.55 (Cq_{aro}), 138.46 (Cq_{aro}), 138.40 (Cq_{aro}), 138.38 (Cq_{aro}), 128.60, 128.57, 128.54, 128.5, 128.1, 128.00, 127.97, 127.95, 127.9, 127.7, 127.3 (26 × CH_{aro}), 120.1 (2 × CH_{aro}), 99.5 (*C*1), 79.9 (*C*3), 75.2 (O*C*H_2Ph), 74.93, 74.90 (2 × CH, *C*4 and *C*2 or *C*5), 73.5 (O*C*H_2Ph), 72.9 (O*C*H_2Ph), 72.6 (*C*2 or *C*5), 72.5 (O*C*H_2Ph), 69.3, 69.2 (2 × CH_2, *C*6 and *C*H_2 (Fmoc)), 67.4 (O*C*H_2CHN), 54.5 (*C*H (Fmoc)), 52.8 (O*C*H_3), 47.3 (*C*HN); gated decoupled ^{13}C NMR spectroscopy indicated a J_{C1-H1} value of 167.0 Hz. HRMS (ESI): calcd for $C_{53}H_{53}NO_{10}Na$ $[M + Na]^+$ 886.3567; found 886.3585.

(3′-((*tert*-Butyldiphenylsilyl)oxy)propyl) 2,3,4,6-tetra-*O*-benzyl-D-mannopyranoside 9

The general procedure was followed using donor **1** (92 mg, 0.125 mmol), TTBP (31 mg, 0.125 mmol), $Sc(OTf)_3$ (43 mg, 0.087 mmol) and acceptor **8** (79 mg, 0.25 mmol) in CH_2Cl_2 (0.25 mL) for 90 min. After purification (heptane/EtOAc 100 : 0 to 85 : 15), **9** (50 mg, 0.06 mmol, 48%, α/β: 24/1) was obtained as a colorless oil. **9α**: $[\alpha]_D^{22}$ = +19.6 (c = 0.9, $CHCl_3$). IR: ν = 3067 and 3031 (=C–H), 2929 and 2858 (C–H) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz, α-anomer): δ 7.59–7.53 (m, 4H, H_{aro}), 7.30–7.15 (m, 24H, H_{aro}), 7.10–7.05 (m, 2H, H_{aro}), 4.80 (d, 1H, J = 10.5 Hz, OCH_2Ph), 4.79 (d, 1H, J = 2.0 Hz, *H*1), 4.64 (brs, 2H, OCH_2Ph), 4.59 (d, J = 12.0 Hz, 1H, OCH_2Ph), 4.51 (brs, 2H, OCH_2Ph), 4.44 (d, J = 12.0 Hz, 1H, OCH_2Ph), 4.43 (d, J = 10.5 Hz, 1H, OCH_2Ph), 3.93 (t, 1H, J = 9.0 Hz, *H*4), 3.80–3.59 (m, 8H, *H*2, *H*3, *H*5, *H*6, *H*6′, OCH_2CH_2CH_2OTBDPS), 3.48–3.41 (m, 1H, OCH_2CH_2CH_2OTBDPS), 1.74–1.65 (m, 2H, OCH_2CH_2CH_2OTBDPS), 0.95 (s, 9H, SiC(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 75 MHz, α-anomer): δ 138.80 (Cq_{aro}), 138.78 (Cq_{aro}), 138.67 (Cq_{aro}), 138.64 (Cq_{aro}), 134.05 (Cq_{aro}), 135.03 (Cq_{aro}), 135.7, 128.50, 128.47, 128.2, 128.0, 127.9, 127.84, 127.81, 127.7, 127.6 (30 × CH_{aro}), 98.1 (*C*1), 80.5 (*C*3), 75.3 (O*C*H_2Ph), 75.13 (*C*4), 75.07 (*C*2 or *C*5), 73.6 (O*C*H_2Ph), 72.7 (O*C*H_2Ph), 72.4 (O*C*H_2Ph), 72.0 (*C*2 or *C*5), 69.4 (*C*6), 64.4 (O*C*H_2CH_2CH_2OTBDPS), 60.8 (OCH_2CH_2*C*H_2OTBDPS), 32.6 (OCH_2*C*H_2CH_2OTBDPS), 27.1 (SiC(*C*H_3)$_3$), 19.4 ((Si*C*CH_3)$_3$); gated decoupled ^{13}C NMR spectroscopy indicated a J_{C1-H1} value of 167.0 Hz. HRMS (ESI): calcd for $C_{53}H_{60}O_7NaSi$ $[M + Na]^+$ 859.4006; found 859.4024.

(3′-Bromopropyl) 2,3,4,6-tetra-*O*-benzyl-D-mannopyranoside 11

The general procedure was followed using donor **1** (92 mg, 0.125 mmol), TTBP (31 mg, 0.125 mmol), $Sc(OTf)_3$ (43 mg, 0.087 mmol) and acceptor 10 (23 μL, 0.25 mmol) in CH_2Cl_2 (0.25 mL) for 120 min. After purification (toluene/acetone 90 : 10), **11** (68 mg, 0.102 mmol, 82%, α/β: 16/1) was obtained as a colorless oil. **11α**: $[\alpha]_D^{20}$ = +26.5 (c = 0.8, $CHCl_3$). IR: ν = 3063 and 3030 (=C–H), 2918 and 2861 (C–H) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.40–7.25 (m, 18H, Ph), 7.18–7.15 (m, 2H, Ph), 4.88 (d, J = 10.5 Hz, 1H, CH_2Ph), 4.87 (s, 1H, H1), 4.77 (d, J = 12.5 Hz, 1H, CH_2Ph), 4.71 (d, J = 12.5 Hz, 1H, CH_2Ph), 4.67 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.63 (s, 2H, CH_2Ph), 4.55 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.51 (d, J = 10.5 Hz, 1H, CH_2Ph), 3.99 (t, $J_{4,3}$ = $J_{4,5}$ = 9.0 Hz, 1H, H4), 3.86 (dd, J = 9.0 Hz and J = 3.0 Hz,

1H, H3), 3.82–3.71 (m, 5H, H2, H6, H6′, H7 and H5), 3.49 (dt, $J_{7',7}$ = 10.0 Hz and $J_{7',8}$ = 6.0 Hz, 1H, H7′), 3.41 (t, $J_{8,9}$ = 6.5 Hz, 2H, H9), 2.05 (m, 2H, H8). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 138.8 (C, Ph), 138.8 (C, Ph), 138.7 (C, Ph), 138.7 (C, Ph), 128.7 (6 × CH, Ph), 128.7 (2 × CH, Ph), 128.4 (2 × CH, Ph), 128.2 (2 × CH, Ph), 128.1 (2 × CH, Ph), 128.0 (2 × CH, Ph), 128.0 (2 × CH, Ph), 128.0 (CH, Ph), 127.8 (CH, Ph), 98.5 (CH, C1), 80.4 (CH, C3), 75.5 (CH_2, CH_2Ph), 75.3 (CH, C4), 75.1 (CH, C2), 73.7 (CH_2, CH_2Ph), 73.0 (CH_2, CH_2Ph), 72.6 (CH_2, CH_2Ph), 72.4 (CH, C5), 69.6 (CH_2, C6), 65.4 (CH_2, C7), 32.8 (CH_2, C8), 30.6 (CH_2, C9); gated decoupled ^{13}C NMR spectroscopy indicated a J_{C1-H1} value of 169.5 Hz. HRMS (ESI): calcd for $C_{37}H_{41}BrNaO_6$ $[M + Na]^+$: 683.1984. Found: 683.1968.

(Pent-4′-enyl) 2,3,4,6-tetra-*O*-benzyl-D-mannopyranoside 13

The general procedure was followed using donor **1** (92 mg, 0.125 mmol), TTBP (31 mg, 0.125 mmol), $Sc(OTf)_3$ (43 mg, 0.087 mmol) and acceptor **12** (26 μL, 0.25 mmol) in CH_2Cl_2 (0.25 mL) for 120 min. After purification (toluene/acetone 90 : 10), **13** [54] (61 mg, 0.101 mmol, 81%, α/β: 6/1) was obtained as a colorless oil.

(3′-Azidopropyl) 2,3,4,6-tetra-*O*-benzyl-D-mannopyranoside 15

The general procedure was followed using donor **1** (92 mg, 0.125 mmol), TTBP (31 mg, 0.125 mmol), $Sc(OTf)_3$ (43 mg, 0.087 mmol) and acceptor **14** (31.6 mg, 0.31 mmol) in CH_2Cl_2 (0.25 mL) for 180 min. After purification (EtOAc/heptane 0 : 100 to EtOAc/heptane 20 : 80), **15** (57 mg, 0.089 mmol, 60%, α/β: 13/1) was obtained as a colorless oil. **15α**: $[\alpha]_D^{22}$ = +34.8 (c = 0.6, $CHCl_3$). IR: ν = 3088, 3059 and 3031 (=C–H), 2924 and 2870 (C–H), 2095 (N=N=N) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, α-anomer): δ 7.37–7.12 (m, 20H, H_{aro}), 4.87–4.82 (m, 2H, OCH_2Ph + H1), 4.76–4.46 (m, 7H, OCH_2Ph), 3.95 (t, 1H, J = 9.0 Hz, H4), 3.87–3.82 (dd, 1H, J = 9.0, 3.0 Hz, H3), 3.80–3.66 (m, 5H, H2, H5, H6, H6′, OCH_2CH_2CH_2N$_3$), 3.46–3.37 (m, 1H, OCH_2CH_2CH_2N$_3$), 3.34–3.22 (m, 2H, OCH_2CH_2CH_2N$_3$), 1.81–1.73 (m, 2H, OCH_2CH_2CH_2N$_3$). ^{13}C NMR ($CDCl_3$, 75 MHz, α-anomer): δ 138.7 (1 × Cq_{aro}), 138.6 (2 × Cq_{aro}), 138.5 (Cq_{aro}), 128.54, 128.50, 128.2, 128.0, 127.94, 127.90, 127.8, 127.7 (20 × CH_{aro}), 98.2 (C1), 80.3 (C3), 75.4 (OCH_2Ph), 75.1 (C4), 75.0 (C2 or C5), 73.6 (OCH_2Ph), 72.9 (OCH_2Ph), 72.4 (OCH_2Ph), 72.2 (C2 or C5), 69.5 (C6), 64.4 (OCH_2CH_CH$_2$N$_3$), 48.6 (O-CH$_2$CH$_2$$CH_2N_3$), 29.0 (OCH$_2$$CH_2CH_2N_3$); gated decoupled ^{13}C NMR spectroscopy indicated a J_{C1-H1} value of 170.0 Hz. HRMS (ESI): calcd for $C_{37}H_{41}N_3O_6Na$ $[M + Na]^+$ 646.2893; found 646.2885.

(3′-(*N*-Carbobenzyloxy)propyl) 2,3,4,6-tetra-*O*-benzyl-D-mannopyranoside 17

The general procedure was followed using donor **1** (92 mg, 0.125 mmol), TTBP (31 mg, 0.125 mmol), $Sc(OTf)_3$ (43 mg, 0.087 mmol) and acceptor **16** (52 mg, 0.25 mmol) in CH_2Cl_2 (0.25 mL) for 90 min. After purification (toluene/acetone 95 : 5), **17** (62 mg, 0.085 mmol, 68%, α/β: 3/1) was obtained as a colorless oil. **17α**: $[\alpha]_D^{22}$ = +36.6 (c = 0.5, $CHCl_3$). IR: ν = 3340 (NH), 3063 and 3030 (=C–H), 2913 (C–H), 1716 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, α-anomer): δ 7.38–6.97 (m, 25H, H_{aro}), 5.24–5.12 (m, 1H, NHCbz), 5.07–4.89 (m, 2H, OCH_2Ph), 5.80–4.71 (m, 2H, OCH_2Ph and H1), 4.66 (d, J = 12.5 Hz, 1H, OCH_2Ph), 4.60 (d, J = 12.5 Hz, 1H, OCH_2Ph), 4.55–4.47 (m, 4H, OCH_2Ph), 4.39 (d, J = 11.0 Hz, 1H, OCH_2Ph), 3.85–3.52 (m, 7H, H2, H3, H4, H5, H6 and OCH_2CH_2), 3.41–3.30 (m, 1H, OCH_2CH_2), 3.30–3.17 (m, 1H, CH_2NHCBz), 3.16–3.01 (m, 1H, CH_2NHCBz), 1.75–1.59 (m, 2H, CH_2CH_2NHCBz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 156.4 (CO), 138.5 (Cq_{aro}), 138.3 (Cq_{aro}), 138.2 (Cq_{aro}), 136.6 (Cq_{aro}), 128.4 (CH_{aro}), 128.3 (CH_{aro}), 128.1 (CH_{aro}), 128.0 (CH_{aro}), 127.8 (CH_{aro}), 127.7 (CH_{aro}), 127.6 (CH_{aro}), 127.5 (CH_{aro}), 127.4 (CH_{aro}), 98.2 (C1), 80.3 (C3), 75.1, 75.0 (C5, C2 and OCH_2Ph), 73.3 (OCH_2Ph), 72.8 (OCH_2Ph), 72.3 and 72.2 (OCH_2Ph and C4), 69.3 (C6), 66.6 (OCH_2Ph), 65.2 (OCH_2CH_2), 38.3 (CH_2NHCBz), 29.4 (CH_2CH_2NHCBz); gated decoupled ^{13}C NMR spectroscopy indicated a J_{C1-H1} value of 170.0 Hz. HRMS (ESI): calcd for $C_{45}H_{49}NO_8Na$ $[M + Na]^+$ 754.3356; found 754.3361.

Trifluoroacetamido 2,3,4,6-tetra-*O*-benzyl-D-mannopyranosyl-L-tyrosine methyl ester 19

The general procedure was followed using donor **1** (92 mg, 0.125 mmol), TTBP (31 mg, 0.125 mmol), $Sc(OTf)_3$ (43 mg, 0.087 mmol) and acceptor **18** (73 mg, 0.25 mmol) in CH_2Cl_2 (0.25 mL) for 90 min. After purification (heptane/EtOAc 8 : 2), **19** [55] (66 mg, 0.081 mmol, 65%, α/β: 8/1) was obtained as a colorless oil.

(+)-Menthyl 2,3,4,6-tetra-*O*-benzyl-D-mannopyranoside 21

The general procedure was followed using donor **1** (92 mg, 0.125 mmol), TTBP (31 mg, 0.125 mmol), $Sc(OTf)_3$ (43 mg, 0.087 mmol) and acceptor **20** (39 mg, 0.25 mmol) in CH_2Cl_2 (0.25 mL) for 90 min. After purification (toluene/acetone 90 : 10), **21** [56] (59 mg, 0.087 mmol, 70%, α/β: 19/1) was obtained as a colorless oil.

3β-(2′,3′,4′,6′-Tetra-*O*-benzyl-D-mannopyranosyl) 5-androsten-17-one 23

The general procedure was followed using donor **1** (92 mg, 0.125 mmol), TTBP (31 mg, 0.125 mmol), $Sc(OTf)_3$ (43 mg, 0.087 mmol) and acceptor dehydroepiandrosterone (ster) **22** (72 mg, 0.25 mmol) in CH_2Cl_2 (0.25 mL) for 150 min. After purification (heptane/EtOAc 80 : 20) then preparative HPLC, **23** (85 mg, 0.105 mmol, 84%, α/β: 10/1) was obtained as a colorless oil. **23α**: $[\alpha]_D^{22}$ = +39.7 (c = 0.8, $CHCl_3$). IR: ν = 3063 and 3031 (=C–H), 2927 and 2855 (C–H), 1734 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, α-anomer): δ 7.32–7.07 (m, 20H, H_{aro}), 5.21 (brd, 1H, J = 5.0 Hz, CHO, ster), 4.96–4.93 (brs, 1H, H1), 4.80 (d, J = 11.0 Hz, 1H, OCH_2Ph), 4.70–4.55 (m, 5H, OCH_2Ph), 4.44 (d, J = 12.0 Hz, 1H, OCH_2Ph), 4.43 (d, J = 11.0 Hz, 1H, OCH_2Ph), 3.91 (dd, 1H, J_{43} = 9.0 Hz, J_{45} = 3.0 Hz, H4), 3.85 (dd, 1H, J_{32} = 9.0 Hz, J_{34} = 3.0 Hz, H3), 3.82–3.63 (m, 4H, H2, H5, H6, H6′), 3.45–3.34 (m, 1H, CHO, ster), 2.37 (dd, J = 19.0, 9.0 Hz, 1H, =CH–CH_2 (ster)), 2.30–1.09 (m, 18H, ster), 0.92 (s, 3H, CH_3 (ster)), 0.79 (s, 3H, CH_3 (ster)). ^{13}C NMR ($CDCl_3$, 75 MHz, α-anomer): δ 221.6 (C=O), 141.0 (C=CH,

ster), 138.8 (*Cq*$_{aro}$), 138.6 (3 × *Cq*$_{aro}$), 128.5, 128.4, 128.2, 128.0, 127.9, 127.7, 127.6, 127.5 (20 × *C*H$_{aro}$), 121.2 (*C*=*C*H, ster), 96.1 (*C*1), 80.5 (*C*3), 76.6 (*C*HO, ster), 75.4 (*C*5), 75.3 (*C*4, OCH$_2$Ph), 73.4 (OCH$_2$Ph), 72.7 (OCH$_2$Ph), 72.3 (OCH$_2$Ph), 72.0 (*C*2), 69.6 (*C*6), 51.9 (*C*H, ster), 50.3 (*C*H, ster), 47.7 (*Cq*, ster), 40.0 (*C*H$_2$, ster), 37.1 (*C*H$_2$, ster), 36.9 (*Cq*, ster), 36.0 (*C*H$_2$, ster), 31.64 (*C*H$_2$, ster), 30.9 (*C*H, ster), 29.8 (*C*H$_2$, ster), 27.8 (*C*H$_2$, ster), 22.0 (*C*H$_2$, ster), 20.5 (*C*H$_2$, ster), 19.5 (*C*H$_3$, ster), 13.7 (*C*H$_3$, ster); gated decoupled ^{13}C NMR spectroscopy indicated a J_{C1-H1} value of 169.0 Hz. HRMS (ESI): calcd for $C_{53}H_{62}O_7Na$ $[M + Na]^+$ 833.4393; found 833.4412.

Methyl (2,3,4,6-tetra-*O*-benzyl-D-mannopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside 25

The general procedure was followed using donor **1** (92 mg, 0.125 mmol), TTBP (31 mg, 0.125 mmol), Sc(OTf)$_3$ (43 mg, 0.087 mmol) and acceptor **24** (116 mg, 0.25 mmol) in CH_2Cl_2 (0.25 mL) for 90 min. After purification (toluene/acetone 95 : 5), **25** [19] (58 mg, 0.058 mmol, 46%, α/β: 49/1) was obtained as a colorless oil.

Methyl (2,3,4,6-tetra-*O*-benzyl-D-mannopyranosyl)-(1 → 3)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside 27

The general procedure was followed using donor **1** (92 mg, 0.125 mmol), TTBP (31 mg, 0.125 mmol), Sc(OTf)$_3$ (43 mg, 0.087 mmol) and acceptor **26** (116 mg, 0.25 mmol) in CH_2Cl_2 (0.25 mL) for 90 min. After purification (toluene/acetone 95 : 5), **27** [19] (54 mg, 0.054 mmol, 43%, α/β: 6/1) was obtained as a colorless oil.

(+)-Menthyl 2,3,di-*O*-benzyl-4,6-*O*-benzylidene-D-mannopyranoside 29

The general procedure was followed using donor **28** (81 mg, 0.125 mmol), TTBP (31 mg, 0.125 mmol), Sc(OTf)$_3$ (43 mg, 0.087 mmol) and acceptor **20** (39 mg, 0.25 mmol) in CH_2Cl_2 (0.25 mL) for 180 min. After purification (heptane/EtOAc 9 : 1 to 7 : 3), **29** (38 mg, 0.065 mmol, 52%, α/β: 6.7/1) was obtained as a colorless oil. **29α**: $[\alpha]_D^{22}$ = +43.6 (*c* = 0.6, $CHCl_3$). IR: ν = 3063 and 3032 (=C–H), 2953, 2924, and 2868 (C–H) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, α-anomer): δ 7.62–7.19 (m, 15H, *H*$_{aro}$), 5.68 (s, 1H, C*H*Ph), 4.89 (d, *J* = 12.5 Hz, 1H, OC*H*$_2$Ph), 4.84 (d, *J* = 12.5 Hz, 1H, OC*H*$_2$Ph), 4.78 (d, *J* = 1.5 Hz, 1H, *H*1), 4.74 (d, *J* = 12.5 Hz, 1H, OC*H*$_2$Ph), 4.69 (d, *J* = 12.5 Hz, 1H, OC*H*$_2$Ph), 4.31–4.21 (m, 2H, *H*6 and *H*5), 3.97 (dd, *J* = 3.0 and 10 Hz, 1H, *H*3), 3.94–3.84 (m, 2H, *H*6 and *H*4), 3.78 (dd, *J* = 3.0 and 1.5 Hz, 1H, *H*2), 3.23 (td, *J* = 11.0 and 5.0 Hz, 1H, OC*H*$_{ment}$), 2.05–1.93 (m, 1H, C*H*$_{2ment}$), 1.79–1.67 (m, 1H, C*H*$_{ment}$), 1.66–1.58 (m, 2H, 2 × C*H*$_{2ment}$), 1.44–1.32 (m, 1H, C*H*$_{ment}$), 1.20–0.98 (m, 3H, 2 × C*H*$_{2ment}$ and C*H*$_{ment}$), 0.89 (d, *J* = 6.5 Hz, 3H, CH(C*H*$_3$)), 0.86–0.72 (m, 4H, CH(C*H*$_3$)$_2$ and C*H*$_{2ment}$), 0.63 (d, *J* = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$, 75 MHz, α-anomer): δ 138.0 (*Cq*$_{aro}$), 137.8 (*Cq*$_{aro}$), 128.8, 128.4, 128.3, 128.2, 128.1, 127.8, 127.4, 126.0 (*C*H$_{aro}$), 101.4, 101.3 (PhCHO$_2$ and *C*1), 81.1 (OCH$_{ment}$), 79.4 (*C*5), 76.5 (*C*3), 76.0 (*C*2), 73.4, 73.3 (2 × OCH$_2$Ph), 68.8 (*C*6), 64.2 (*C*4), 48.6 (*C*H$_{ment}$), 43.0 (*C*H$_{2ment}$), 34.2 (*C*H$_{2ment}$), 31.6 (*C*H$_{ment}$), 25.7 (*C*H$_{ment}$), 23.2 (*C*H$_{2ment}$), 22.2 (CH*C*H$_3$), 21.0 (CH(*C*H$_3$)$_2$), 16.2 (CH(*C*H$_3$)$_2$); gated decoupled ^{13}C NMR spectroscopy indicated a J_{C1-H1} value of 164.0 Hz. HRMS (ESI): calcd for $C_{37}H_{46}O_6Na$ $[M + Na]^+$ 609.3192; found 609.3190.

Propargyl (3,4,6-tri-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1 → 4)-2,3,4,6-tetra-*O*-benzyl-D-mannopyranoside 34

The general procedure was followed using donor **33** (75 mg, 0.062 mmol), TTBP (15 mg, 0.062 mmol), Sc(OTf)$_3$ (21 mg, 0.043 mmol) and acceptor **10** (7 μL, 0.124 mmol) in CH_2Cl_2 (0.12 mL) for 90 min. After purification (heptane/EtOAc 1 : 0 to 7 : 3), **34** (51 mg, 0.048 mmol, 78%, α/β: 4.5/1) was obtained as a colorless oil. **34α**: $[\alpha]_D^{22}$ = +44.4 (*c* = 0.3, $CHCl_3$). IR: ν = 3082, 3061 and 3027 (=C–H), 2939 and 2867 (C–H), 1776 and 1714 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, α-anomer): δ 7.60–7.41 (brm, 4H, *H*$_{aro}$), 7.30–7.15 (m, 25H, *H*$_{aro}$), 6.94–6.89 (m, 2H, *H*$_{aro}$), 6.84–6.75 (m, 3H, *H*$_{aro}$), 5.10 (d, 1H, *J* = 8.5 Hz, *H*1*B*), 4.75 (d, 1H, *J* = 11.0 Hz, OC*H*$_2$Ph), 4.71 (d, *J* = 12.0 Hz, 1H, OC*H*$_2$Ph), 4.61–4.54 (m, 4H, OC*H*$_2$Ph + *H*1*A*), 4.49 (s, 2H, OC*H*$_2$Ph), 4.48 (d, *J* = 12.0 Hz, 1H, OC*H*$_2$Ph), 4.39–4.24 (m, 5H), 4.16 (dd, 1H, J_{2B3B} = 10.5 Hz, J_{2B1B} = 8.5 Hz, *H*2*B*), 4.09–4.01 (m, 2H), 3.85 (dd, 1H, *J* = 16.0, 2.5 Hz, *H*6*A or H*6*B*), 3.75–3.43 (m, 10H), 2.19 (t, *J* = 2.5 Hz, 1H, CC*H*). ^{13}C NMR (CD_3CN, 75 MHz, α-anomer): δ 169.1 (*C*=O), 169.0 (*C*=O), 139.7, 139.6, 139.4, 139.2 (6 × *Cq*$_{aro}$), 135.2 (2 × *C*H$_{aro}$), 132.3 (2 × *Cq*$_{aro}$), 129.4, 129.3, 129.2, 129.1, 128.8, 128.63, 128.58, 128.5, 128.4, (25 × *C*H$_{aro}$), 124.2 (2 × *C*H$_{aro}$), 99.3 (*C*1*B*), 97.5 (*C*1*A*), 80.8, 80.6, 80.2 (*C*3*A*, *C*3*B*, *C*5*B*), 80.0 (*C*CH), 76.2 (C*C*H), 75.9, 75.8 (2 × *C*H), 75.6 (2 × OCH$_2$Ph), 75.3 (OCH$_2$Ph and *C*H), 73.9, 73.6, 72.3 (3 × OCH$_2$Ph), 72.1 (*C*H), 69.9, 69.3 (*C*6*A* and *C*6*B*), 56.9 (*C*2*B*), 54.9 (OCH$_2$CCH); gated decoupled ^{13}C NMR spectroscopy indicated a $J_{C1A-H1A}$ value of 172.0 Hz. HRMS (ESI): calcd for $C_{65}H_{63}NO_{12}Na$ $[M + Na]^+$ 1072.4248; found 1072.4249.

Iso-propyl 3,4-di-*O*-benzyl-2-*O*-methyl-D-rhamnopyranoside 39

The general procedure was followed using donor **38** (60 mg, 0.125 mmol), TTBP (31 mg, 0.125 mmol), Sc(OTf)$_3$ (43 mg, 0.087 mmol) and i-PrOH (19 μL, 0.25 mmol) in CH_2Cl_2 (0.25 mL) for 90 min. The crude product was purified by preparative TLC (heptane/EtOAc 8 : 2) to afford the desired product **39** (43 mg, 0.102 mmol, 82%, α/β: 13/1) as a colorless oil. **39α**: $[\alpha]_D^{22}$ = +43.7 (*c* = 1.05, $CHCl_3$). IR: ν = 3062 and 3030 (=C–H), 2973 and 2920 (C–H) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, α-anomer): δ 7.42–7.38 (m, 2H, *H*$_{aro}$), 7.37–7.28 (m, 8H, *H*$_{aro}$), 4.94 (d, *J* = 10.5 Hz, 1H, OC*H*$_2$Ph), 4.92 (s, 1H, *H*1), 4.73 (s, 2H, OC*H*$_2$Ph), 4.62 (d, *J* = 10.5 Hz, 1H, OC*H*$_2$Ph), 3.94–3.85 (m, 2H, *H*3 and C*H*(CH$_3$)$_2$), 3.74 (dq, *J* = 9.5, 6.0 Hz, 1H, *H*5), 3.55–3.49 (5H OC*H*$_3$, *H*4 and *H*2), 1.31 (d, *J* = 6.0 Hz, 3H, CH(C*H*$_3$)), 1.18 (d, *J* = 6.0 Hz, 3H, CH(C*H*$_3$)$_2$), 1.14 (d, *J* = 6.0 Hz, 3H, CH(C*H*$_3$)$_2$). ^{13}C NMR ($CDCl_3$, 75 MHz, α-anomer): δ 138.6 (2 × *Cq*$_{aro}$), 128.3 (4 × *C*H$_{aro}$), 128.1 (2 × *C*H$_{aro}$), 127.7 (2 × *C*H$_{aro}$), 127.6 (*C*H$_{aro}$), 127.5 (*C*H$_{aro}$), 95.2 (*C*1), 80.7 (*C*4), 80.2 (*C*3), 78.7 (*C*2), 75.5 (OCH$_2$Ph), 72.2 (OCH$_2$Ph), 68.8 (*C*H(CH$_3$)$_2$), 67.8 (*C*5), 59.4 (OCH$_3$), 23.2 (CH(*C*H$_3$)$_2$), 21.3 (CH

(CH_3)$_2$), 17.9 (CH(CH_3)); gated decoupled ^{13}C NMR spectroscopy indicated a J_{C1-H1} value of 168.5 Hz. HRMS (ESI): calcd for $C_{24}H_{32}O_5Na$ $[M + Na]^+$ 423.2147; found 423.2112.

(+)-Menthyl 3,4-di-*O*-benzyl-2-*O*-methyl-D-rhamnopyranoside 40

The general procedure was followed using donor **38** (60 mg, 0.125 mmol), TTBP (31 mg, 0.125 mmol), Sc(OTf)$_3$ (43 mg, 0.087 mmol) and acceptor **20** (39 mg, 0.25 mmol) in CH_2Cl_2 (0.25 mL) for 90 min. The crude product was purified (heptane/EtOAc 95 : 5 to 9 : 1) to afford the desired product **40** (50 mg, 0.101 mmol, 81%, α/β: 99/1) as a colorless oil. **40α**: $[\alpha]_D^{22}$ = +21.0 (c = 1.1, $CHCl_3$). IR: ν = 3063 and 3028 (=C–H), 2955 and 2919 (C–H) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, α-anomer): δ 7.42–7.38 (m, 2H, H_{aro}), 7.36–7.28 (m, 8H, H_{aro}), 4.95 (d, J = 11.0 Hz, 1H, OCH_2Ph), 4.83 (d, J = 1.5 Hz, 1H, $H1$), 4.75 (d, J = 12.0 Hz, 1H, OCH_2Ph), 4.70 (d, J = 12.0 Hz, 1H, OCH_2Ph), 4.63 (d, J = 11.0 Hz, 1H, OCH_2Ph), 3.88–3.77 (m, 2H, $H3$ and $H5$), 3.51 (ap. t, J = 9.5 Hz, 1H, $H4$), 3.49 (s, 3H, OCH_3), 3.42 (dd, J = 3.0, 2.0 Hz, 1H, $H2$), 3.28 (td, J = 10.5, 4.3 Hz, 1H, OCH_{ment}), 2.07–1.96 (m, 1H, CH_{2ment}), 1.94–1.81 (m, 1H, CH_{ment}), 1.67–1.58 (m, 2H, 2 × CH_{2ment}), 1.37–1.28 (m, 1H, CH_{ment}), 1.30 (d, J = 6.5 Hz, 3H, CH(CH_3)), 1.17–1.03 (m, 1H, CH_{ment}), 1.04–0.94 (m, 2H, 2 × CH_{2ment}), 0.91 (d, J = 7.5 Hz, 3H, CH(CH_3)$_2$), 0.88 (d, J = 7.0 Hz, 3H, CH(CH_3)$_2$), 0.82–0.72 (m, 1H, CH_{2ment}), 0.75 (d, J = 7.0 Hz, 3H, CH(CH_3)). ^{13}C NMR ($CDCl_3$, 75 MHz, α-anomer): δ 138.7 (Cq_{aro}), 138.6 (Cq_{aro}), 128.3 (4 × CH_{aro}), 128.0 (2 × CH_{aro}), 127.9 (2 × CH_{aro}), 127.6 (2 × CH_{aro}), 98.9 ($C1$), 81.2 (OCH_{ment}), 80.7 ($C4$), 79.8 ($C3$), 78.7 ($C2$), 75.5 (OCH_2Ph), 72.4 (OCH_2Ph), 68.0 ($C5$), 59.0 (OCH_3), 48.6 (CH_{ment}), 42.9 (CH_{2ment}), 34.3 (CH_{2ment}), 31.6 (CH_{ment}), 25.9 (CH_{ment}), 23.3 (CH_{2ment}), 22.2 (CH(CH_3)$_2$), 21.0 (CH(CH_3)$_2$), 17.8 (CH(CH_3)), 16.3 (CH(CH_3)); gated decoupled ^{13}C NMR spectroscopy indicated a J_{C1-H1} value of 168.0 Hz. HRMS (ESI): calcd for $C_{31}H_{44}O_5Na$ $[M + Na]^+$ 519.3086; found 519.3081.

Iso-propyl 2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside 42

The general procedure was followed using donor **41** (83 mg, 0.125 mmol), TTBP (31 mg, 0.125 mmol), Sc(OTf)$_3$ (43 mg, 0.087 mmol) and i-PrOH (19 μL, 0.25 mmol) in CH_2Cl_2 (0.25 mL) for 90 min. After purification (heptane/EtOAc 8 : 2), **42** [57] (69 mg, 0.119 mmol, 95%, α/β: 1.7/1) was obtained as a colorless oil.

Iso-propyl 2,3,4,6-tetra-*O*-benzyl-D-galactopyranoside 44

The general procedure was followed using donor **43** (83 mg, 0.125 mmol), TTBP (31 mg, 0.125 mmol), Sc(OTf)$_3$ (43 mg, 0.087 mmol) and i-PrOH (19 μL, 0.25 mmol) in CH_2Cl_2 (0.25 mL) for 90 min. After purification (heptane/EtOAc 8 : 2), **44** [18] (55 mg, 0.095 mmol, 76%, α/β: 1.6/1) was obtained as a colorless oil.

Iso-propyl 3,4,6-tri-*O*-benzyl-2-trichloroacetamido-2-deoxy-D-glucopyranoside 46

The general procedure was followed using donor **45** (53 mg, 0.067 mmol), TTBP (16 mg, 0.067 mmol), Sc(OTf)$_3$ (23 mg, 0.047 mmol) and i-PrOH (10 μL, 0.13 mmol) in CH_2Cl_2 (0.13 mL) for 180 min. After purification (heptane/EtOAc 1 : 0 to 8 : 2), **46** (30 mg, 0.045 mmol, 71%, α/β: 1/8.1) was obtained as a colorless oil. **46β**: $[\alpha]_D^{22}$ = +3.7 (c = 0.7, $CHCl_3$). IR: ν = 3305 (N–H), 3096, 3065 and 3032 (=C–H), 2870 (C–H), 1692 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27–7.10 (m, 15H, H_{aro}), 6.94 (d, J = 8.0 Hz, 1H, NH), 4.91 (d, $J_{1,2}$ = 8.0 Hz, 1H, $H1$), 4.72 (d, J = 11.0 Hz, 1H, CH_2Ph), 4.71 (d, J = 11.0 Hz, 1H, CH_2Ph), 4.69 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.66 (d, J = 11.0 Hz, 1H, CH_2Ph), 4.61 (d, J = 11.0 Hz, 1H, CH_2Ph), 4.54 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.51 (d, J = 11.0 Hz, 1H, CH_2Ph), 4.47 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.17 (dd, $J_{3,2}$ = 10.0 Hz, $J_{3,4}$ = 8.0 Hz, 1H, $H3$), 3.88 (tt, J = 6.0 Hz, 1H, CH$_3$CHOCH$_3$), 3.71–3.60 (m, 2H, $H6$, $H6'$), 3.56 (dd, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1H, $H4$), 3.51 (dd, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 4.0 Hz, $J_{5,6'}$ = 2.5 Hz, 1H, $H5$), 3.17 (dd, $J_{2,3}$ = 10.0 Hz, $J_{2,1}$ = 8.0 Hz, $J_{2,NH}$ = 8.0 Hz, 1H, $H2$), 1.16 (d, J = 6.0 Hz, 3H, CH_3CHOCH$_3$), 1.06 (d, J = 6.0 Hz, 3H, CH$_3$CHOCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.9 (brs, C=O), 138.4 (Cq_{aro}), 138.1 (2 × Cq_{aro}), 128.7, 128.6, 128.5, 128.16, 128.1, 128.04, 127.98, 127.9, 127.8 (15 × CH_{aro}), 97.8 ($C1$), 92.7 (CCl_3), 79.8 ($C3$), 78.9 ($C5$), 75.2 (CH_2Ph), 75.0 ($C4$), 74.8 (CH_2Ph), 73.6 (CH_2Ph), 72.5 (CH$_3$CHOCH$_3$), 69.1 ($C6$), 59.3 ($C2$), 23.6 (CH_3CHOCH$_3$), 22.2 (CH$_3$CHOCH_3). HRMS (ESI): calcd for $C_{32}H_{36}NO_6Cl_3Na$ $[M + Na]^+$ 658.1506; found 658.1509.

Iso-propyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-phthalimido-D-glucopyranoside 48

The general procedure was followed using donor **47** (76 mg, 0.098 mmol), TTBP (24 mg, 0.098 mmol), Sc(OTf)$_3$ (34 mg, 0.069 mmol) and i-PrOH (15 μL, 0.20 mmol) in CH_2Cl_2 (0.25 mL) for 240 min. After purification (heptane/EtOAc 1 : 0 to 8 : 2), **48** (36 mg, 0.056 mmol, 60%, α/β: 1/11.5) was obtained as a colorless oil. **48β**: $[\alpha]_D^{22}$ = +34.3 (c = 0.4, $CHCl_3$). IR: ν = 3089, 3058 and 3020 (=C–H), 2976, 2932 and 2871 (C–H), 1776 and 1714 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85–7.74 (brs, 1H, H_{aro}), 7.73–7.62 (brs, 1H, H_{aro}), 7.38–7.25 (m, 12H, H_{aro}), 7.08–6.99 (m, 2H, H_{aro}), 6.95–6.86 (m, 3H, H_{aro}), 5.22 (d, $J_{1,2}$ = 8.5 Hz, 1H, $H1$), 4.86 (d, J = 11.0 Hz, 1H, CH_2Ph), 4.81 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.69 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.66 (d, J = 11.0 Hz, 1H, CH_2Ph), 4.62 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.46 (d, J = 12.0 Hz, 1H, CH_2Ph), 4.37 (dd, $J_{3,2}$ = 11.0 Hz, $J_{3,4}$ = 8.5 Hz, 1H, $H3$), 4.18 (dd, $J_{2,3}$ = 11.0 Hz, $J_{2,1}$ = 8.5 Hz, 1H, $H2$), 3.88 (tt, J = 6.0 Hz, 1H, CH$_3$CHOCH$_3$), 3.83–3.72 (m, 3H, $H6$, $H6'$, $H4$), 3.67 (ddd, $J_{4,5}$ = 10.0 Hz, $J_{5,6}$ = 4.0 Hz, $J_{5,6'}$ = 2.5 Hz, 1H, $H5$), 1.15 (d, J = 6.0 Hz, 3H, CH_3CHOCH$_3$), 0.88 (d, J = 6.0 Hz, 3H, CH$_3$CHOCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.4 (brs, C=O), 167.9 (brs, C=O), 138.5 (Cq_{aro}), 138.2 (2 × Cq_{aro}), 133.8 (brs, 2 × CH_{aro}), 131.9 (Cq_{aro}), 131.8 (Cq_{aro}), 128.6, 128.5, 128.21, 128.16, 128.11, 128.0, 128.0, 127.9, 127.7, 127.5, 123.4 (brs) (17 × CH_{aro}), 97.2 ($C1$), 80.1 ($C5$), 79.6 ($C3$), 75.2 ($C4$), 75.1 (CH_2Ph), 74.9 (CH_2Ph), 73.7

(CH_2Ph), 72.0 (CH_3CHOCH_3), 69.1 (*C*6), 56.4 (*C*2), 23.5 (CH_3CHOCH_3), 22.0 (CH_3CHOCH_3). HRMS (ESI): calcd for $C_{38}H_{39}NO_7Na$ $[M + Na]^+$ 644.2624; found 644.2645.

Conflicts of interest

There are no conflicts of interest to declare.

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