CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200800365

Endohexosaminidase-Catalysed Glycosylation with Oxazoline Donors: Fine Tuning of Catalytic Efficiency and Reversibility

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Abstract: A complete series of oxazoline di-, tri-, tetra-, and hexasaccharides, corresponding to the core sections of *N*-linked glycoprotein high mannose glycans, together with the corresponding oligosaccharides containing a central glucose unit, were synthesised and tested as glycosyl donors for glycosylation of a GlcNAcAsn glycosyl amino acid catalysed by the endohexosaminidases M (Endo M), A (Endo A) and H (Endo H). Whilst Endo H did not catalyse any glycosylation reactions, both Endo M and Endo A efficiently catalysed glycosylations that were not limited to donors containing the Manβ(1→4)GlcNAc linkage. Precise structure activity relationships and time course studies have revealed fine-tuning of the efficiency of the synthetic processes which correlated both with the enzyme used and the precise oxazoline structure. Efficient irreversible glycosylation was achievable with both Endo M and Endo A, further demonstrating the use of structurally modified oxazoline donors as transition state mimics in order to promote enzyme-catalysed synthesis, whilst precluding product hydrolysis; enzymes in these cases display "glycoligase" activity.

Keywords: carbohydrates · enzyme catalysis · glycopeptides · glycoproteins · glycosylation

Introduction

Glycosylation of proteins, the most diverse form of post-translational modification, can play a key role in protein folding,[1] and can crucially affect important protein properties such as conformation and stability,[2] their susceptibility to proteases[3] and their circulatory lifetimes.[4,5] Moreover glycosylation is also fundamental to many other key biological processes such as cell–cell signalling,[6] and development and immune response.[7] However since the biosynthesis of glycans is not under direct genetic control, glycoproteins are produced intracellularly as heterogeneous mixtures of glycoforms, in which different oligosaccharide structures are linked to the same peptide chain. Access to pure single glycoforms of glycoproteins has now become a major scientific objective.[8] Not only is it a prerequisite for more precise biological investigations into the different effects glycans have on protein properties, but it is also becoming an increasingly important commercial goal in the field of glycoprotein therapeutics. These are currently marketed as heterogeneous mixtures of glycoforms, some of which may not produce the desired biological effects.[9]

Access to single glycoforms of glycoproteins can be achieved by total synthesis of both glycan and polypeptide components, and outstanding achievements in this area have recently been published.[10,11] However, such synthetic approaches are particularly arduous, and do not realistically represent a practical approach that could be applied to widespread and large-scale glycoprotein production. Approaches based on bioengineering of cell lines in order to optimise production of glycoproteins bearing particular oligosaccharide structures have also been reported,[12,13] and been exploited commercially, though such approaches have no guarantee of complete glycan homogeneity.

An alternative approach is one in which a defined synthetic oligosaccharide is attached to an expressed protein. To this end several chemoselective methods have been developed in order to synthetically access proteins glycosylated with defined oligosaccharides,[14,15] though these methods suffer from the disadvantage that the carbohydrates are connected to the peptide backbone by non-native linkages. An alternative method for achieving homogenous protein glycosylation in which glycans are attached via native linkages in-

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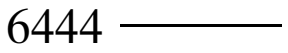

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volves the use of enzymatic catalysis,[16] and one particular class of enzymes which display considerable synthetic potential in this respect are the endohexosaminidases.[17] Endohexosaminidases are a class of enzyme which specifically cleave the chitobiose core [GlcNAcβ(1→4)GlcNAc] of *N*-linked glycans between the two *N*-acetyl glucosamine residues, and since they cleave this linkage they can also be used to selectively synthesise it. Two members of this class which have been demonstrated to display useful *synthetic* glycosylation activity are Endo M from *Mucor hiemalis*[18–21] and Endo A from *Arthrobacter protophormiae*.[22,23] The strategy involves the trimming of heterogeneous mixtures of *N*-glycans back to a single GlcNAc residue at asparagine *N*-glycosylation sites. Glycosylation of these GlcNAcAsn residues with a synthetic oligosaccharide donor bearing a single GlcNAc at the reducing terminus, can be catalysed by an endohexosaminidase, which then produces a protein bearing a defined natural *N*-glycan containing the GlcNAcβ(1→4)GlcNAcAsn linkage. Synthetic peptides which contain an asparagine residue bearing a GlcNAc unit can be similarly glycosylated enzymatically, allowing access to homogenous glycopeptides via a similar strategy.[24]

Seminal work in the field by Shoda and co-workers demonstrated that carbohydrate oxazolines are useful activated glycosyl donors for these enzymes, presumably since they mimic the putative oxazolinium ions which are intermediates in the enzymatic catalysed hydrolysis reaction.[25] Indeed the efficient synthesis of a series of glycopeptides has been achieved by transglycosylation with Endo A,[26,27] and investigations of a correlation of the efficiency of glycosylation with substrate structure have also been reported.[28] More recent work has also reported the application of the glycoprotein remodelling strategy using Endo A to access single glycoforms of ribonuclease B.[29]

However, as with many enzyme-catalysed transglycosylations one particular problem that can greatly reduce synthetic efficiency and utility is product hydrolysis, since in general the product is itself an enzyme substrate. One particularly elegant way of circumventing this problem is the use of specifically mutated enzymes called glycosynthases, as developed by Withers[30] and Planas,[31] which are not capable of product hydrolysis. However another potential solution to this problem is the use of highly activated donors that incorporate a slight structural modification as compared to the native glycan. In these cases an activated donor which is a transition state mimic may be processed by the enzyme at a reasonably efficient rate to effect synthesis, and yet the product may not be hydrolysed due to the minor structural modification.

As part of a long-term program aimed at developing synthetic routes to pure single glycoforms of glycopeptides and glycoproteins, interest recently focussed on the use of Endo M as a catalyst for the conjugation of synthetic oligosaccharides to glycopeptides and proteins bearing single GlcNAc residues. These studies first revealed the potential for the use of *gluco*-containing oxazolines as activated donors for irreversible glycosylation mediated by Endo M.[32] Herein are reported complete and comprehensive investigations into structure activity relationships for glycosylations catalysed by both Endo M and Endo A, using both natural and structurally modified oxazoline donors with a model glycosyl amino acid as acceptor.

Synthesis of Oxazolines

Enzymatic glycosylation was envisaged with the two complete series of oxazolines: natural *N*-glycans **1**–**4**, and **9** and those containing a "central" *gluco* unit **5**–**8**, and **10** (Figure 1) in which the "central" mannose residue, that is, the mannose residue directly β(1→4) linked to the *N*-acetyl glucosamine which itself is normally a 3,6-branch point to further mannoses, has been replaced by glucose.

In the natural series of oxazoline donors, containing a "central" mannose unit corresponding to fragments of natural high mannose *N*-glycans, the disaccharide **1**, (1→3)-linked trisaccharide **2** and hexasaccharide **5**, were synthetically accessed as previously described.[33] The (1→6)-linked trisaccharide **3** and tetrasaccharide **4** were synthesised as shown in Schemes 1 and 2, respectively. The previously described disaccharide **12**[33] underwent regioselective reductive ring opening after treatment with Et_3SiH and $PhBCl_2$ to yield the alcohol **13**, which was then glycosylated with the trichloroacetimidate donor **14** to give (1→6)-linked trisaccharide **15**. A series of protecting group manipulations that was common to most reaction sequences then followed. Removal of the phthalimide protection and complete acetylation produced acetamide **16**. Catalytic hydrogenation and subsequent acetylation then yielded acetate **17**, before removal of the anomeric *para*-methoxyphenyl (PMP) protection with ceric ammonium nitrate(CAN) and subsequent acetylation then yielded peracetate **18**. Conversion to the oxazoline **19** was achieved by treatment with TMSBr and boron trifluoride etherate in dichloroethane at 40°C, to yield oxazoline **19** which finally underwent global deacetylation by treatment with sodium methoxide in methanol to yield the *manno* (1→6)-linked trisaccharide oxazoline **3** (Scheme 1).

A similar series of reactions produced the *manno* tetrasaccharide oxazoline **4**[34] from the previously described trisaccharide diol **20**[33] which underwent regioselective glycosylation at the primary hydroxyl with donor **14**. An identical sequence of protecting group manipulations and oxazoline formation furnished *manno* tetrasaccharide oxazoline **4** (Scheme 2).

In the non-natural series containing a "central" glucose unit, the disaccharide **6**, and the (1→3) linked trisaccharide **7** were synthetically accessed as previously described.[32] The *gluco* (1→6) linked trisaccharide oxazoline **8** and the *gluco* tetrasaccharide oxazoline **9** were synthesised as shown in Schemes 3 and 4, respectively. Disaccharide **26**[32] was acetylated to give acetate **27** which underwent a sequence of regioselective reductive ring opening to yield alcohol **28**, and glycosylation with donor **14**, to give the *gluco* (1→6) linked

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Figure 1. Oxazoline donors **1**–**10** used for endohexosaminidase-catalysed glycosylation of GlcNAcAsn amino acid **11**.

Scheme 1. a) Et_3SiH, $PhBCl_2$, CH_2Cl_2, 4 Å MS, −78 °C, 30 min, 99 %; b) **14**, TMSOTf, 4 Å MS, CH_2Cl_2, −60 °C to RT, 2 h, quant.; c) i) $NH_2CH_2CH_2NH_2$, MeOH, reflux, 22 h; ii) Ac_2O, py, 21 h, 92 % (over two steps); d) i) H_2, Pd (10 % on C), MeOH, 20 h; ii) Ac_2O, py, 11 h, 85 % (over two steps); e) i) CAN, H_2O, MeCN, 3 d; ii) Ac_2O, py, CH_2Cl_2, 16 h, 75 % (over two steps); f) TMSBr, $BF_3{\cdot}OEt_2$, 2,4,6-collidine, DCE, 40 °C, 1 d, 81 %; g) Na, MeOH, 21 h, quant.

trisaccharide **29**. Protecting group manipulations identical to those previously described gave peracetate **32**, and subsequent oxazoline formation and finally deacetylation yielded the *gluco* (1→6) linked trisaccharide oxazoline **8** (Scheme 3).

The *gluco* tetrasaccharide oxazoline **9** was synthesised using an analogous reaction sequence to that used for the corresponding *manno* tetrasaccharide; the 4,6-benzylidene acetal was removed from *gluco* trisaccharide **34**[32] by treatment with aqueous acetic acid, to yield the diol **35** which underwent regioselective glycosylation[35] of the primary hydroxyl with donor **14**, to yield tetrasaccharide **36**. Standard protecting group manipulations and oxazoline formation furnished *gluco* tetrasaccharide oxazoline **9** (Scheme 4).

Finally the *gluco* hexasaccharide oxazoline **10** was synthesised as shown in Scheme 5. Regioselective glycosylation of diol **35** with the trisaccharide donor **41**[32] efficiently produced the *gluco* hexasaccharide **42**. A sequence of protecting group manipulations and oxazoline formation/deprotection similar to those employed previously then furnished the *gluco* hexasaccharide oxazoline donor **10**.

Enzyme catalysed glycosylation reactions: Endohexosaminidase-catalysed glycosylations were carried out using model glycosyl amino acid **11**[33] as the acceptor, which possessed Cbz protection to facilitate time course studies of the extent of reaction by UV/HPLC analysis.

Reactions catalysed by Endo M: Studies initially focussed on reactions catalysed by Endo M (Table 1). Previously[32] it had been demonstrated that Endo M catalysed glycosylation of **11** occurred in a high yielding irreversible[25,36] fashion with *manno* disaccharide donor **1** (95 %, Table 1, entry 1), less efficiently and reversibly[36] with *manno* (1→3) trisaccharide donor **2** (65 %, Table 1, entry 2), and considerably less efficiently and again reversibly with *manno* hexasaccharide donor **5** (24 %, Table 1, entry 5). Gly-

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Scheme 2. a) **14**, TMSOTf, 4 Å MS, CH_2Cl_2, −60°C to RT, 20 h, 76%; b) i) $NH_2CH_2CH_2NH_2$, MeOH, reflux, 25 h; ii) Ac_2O, py, 72 h, 90% (over two steps); c) i) H_2, Pd (10% on C), MeOH, 18 h; ii) Ac_2O, py, 1 d, 81% (over two steps); d) i) CAN, H_2O, MeCN, 21 h; ii) Ac_2O, py, CH_2Cl_2, 14 h, 67% (over two steps); e) TMSBr, $BF_3{\cdot}OEt_2$, 2,4,6-collidine, DCE, 40°C, 1 d, 73%; f) Na, MeOH, 21 h, quant.

Scheme 3. a) Ac_2O, py, 0°C to RT, 15 h, 87%; b) Et_3SiH, $PhBCl_2$, CH_2Cl_2, 4 Å MS, −78°C, 1 h, quant.; c) **14**, TMSOTf, 4 Å MS, CH_2Cl_2, −60°C to RT, 14 h, 99%; d) i) $NH_2CH_2CH_2NH_2$, MeOH, reflux, 19 h; ii) Ac_2O, py, 18 h, 84% (over two steps); e) i) H_2, Pd (10% on C), EtOAc, EtOH, 16 h; ii) Ac_2O, py, 4.5 h, 89% (over two steps); f) i) CAN, H_2O, MeCN, 3 d; ii) Ac_2O, py, 0°C to RT, 19 h, 88% (over two steps); g) TMSBr, $BF_3{\cdot}OEt_2$, 2,4,6-collidine, DCE, 40°C, 21 h, 75%; h) Na, MeOH, 13 h, quant.

cosylation with the *manno* (1→6) trisaccharide donor **3** proceeded more efficiently than with the corresponding (1→3)-linked trisaccharide, and produced tetrasaccharide **49** with a maximum yield of 89%, though again this reaction was reversible. However, glycosylation with the *manno* tetrasaccharide **4** only produced pentasaccharide **50** in a maximum yield of 36%. The conclusion reached in this study was that rapid competing hydrolysis of the product **50** by Endo M was responsible for the substantially lower yield obtained in this case, highlighting the underlying importance of irreversibility of glycosylation. However irreversibility was not the only prerequisite for an efficient synthetic process. Glycosylation catalysed by Endo M using both *gluco* donors **6** and **7** was irreversible, but glycosylation with the *gluco* disaccharide **6** only gave **52** in a very low 4% yield. Increasing the size of the oligosaccharide donor increased the efficiency of the process significantly; use of the *gluco* (1→3) linked trisaccharide donor **7** allowed formation of **53** in an excellent 88% yield (Table 1, entry 7) in an irreversible process and the irreversibility of this reaction contrasted with the result obtained for the corresponding *manno* donor **2** (Table 1, entry 2). In contrast use of the *gluco* (1→6) linked trisaccharide donor **8** only produced **54** in a very low 4% yield, albeit in an irreversible process (Table 1, entry 8). These three results indicate that it is the (1→3) mannose linkage that is largely responsible for enhanced synthetic efficiency by binding to the Endo M active site. Use of the *gluco* tetrasaccharide **9** as a donor produced pentasaccharide product **55** in 70% yield in an irreversible fashion, a considerable improvement on the efficiency of the reversible process using corresponding *manno* donor **4**. Finally use of the *gluco* hexasaccharide donor **10** produced heptasaccharide **56** in 60% yield in an irreversible fashion (Table 1, entry 10); again a considerable improvement on the use of the natural *manno* hexasaccharide oxazoline **5**. It can be concluded that the use of *gluco* containing oxazoline donors with Endo M in all cases results in irreversible glycosylation of **11**, and that the efficiency of the reaction is crucially dependent on the oxazoline structure, which must contain the Man(1→3)Glc linkage in order for the donor to be processed by Endo M at a useful rate.

Reactions catalysed by Endo A: Wang and co-workers[28] have previously published studies on the effect of donor structure on the efficiency of Endo A catalysed glycosylations for a selection of oxazolines. In the present study, glycosylation of glycosyl amino acid **11** was undertaken with the structural set of donors **1**–**4** and **6**–**9** in order to further delineate the effects of the natural N-glycan derived oxazoline structure on the efficiency and reversibility of reaction, and moreover to investigate the possibility of the use of *gluco* containing donors with Endo A (Table 2).

manno-Disaccharide donor **1** (Table 2, entry 1)[25] produced trisaccharide **47** in quantitative yield, but the product **47** was observed to be slowly hydrolysed by Endo A. This result contrasted somewhat with the original findings of Shoda and co-workers,[25] who found that using the same donor **1** a product was formed in 44% yield, which did not then undergo hydrolysis. However, in this case reported here hydrolysis of the product **47** did take place, but hydrolysis was slow; so slow that only after reaction times of greater than 3 h did the yield of **47** decrease below essentially quantitative. A time course plot of product yield for the formation of **47** is shown in Figure 2A. The use of the *manno*

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40: R=Ac
9: R=H

36: R=R^1=Phth, R^2=H, R^3=Lev, R^4=Bn, R^5=PMP
37: R=H, R^1=R^2=R^3=Ac, R^4=Bn, R^5=PMP
38: R=H, R^1=R^2=R^3=R^4=Ac, R^5=PMP
39: R=H, R^1=R^2=R^3=R^4=R^5=Ac

Scheme 4. a) 80% aqueous AcOH, 50°C, 16 h, 86%; b) **14**, TMSOTf, 4 Å MS, CH_2Cl_2, −60°C to RT, 16 h, 84%; c) i) $NH_2CH_2CH_2NH_2$, MeOH, reflux, 21 h; ii) Ac_2O, py, 0°C to RT, 1 d, 95% (over two steps); d) i) H_2, Pd (10% on C), EtOAc, EtOH, 19 h; ii) Ac_2O, py, 0°C to RT, 20 h, 91% (over two steps); e) i) CAN, H_2O, MeCN, 4 d; ii) Ac_2O, py, 0°C to RT, 18 h, 84% (over two steps); f) TMSBr, BF_3·OEt_2, 2,4,6-collidine, DCE, 40°C, 14 h, 74%; g) Na, MeOH, 17 h, quant.

(1→3) trisaccharide donor **2** (Table 2, entry 2) also proceeded in excellent yield (96%), and again was reversible; product **48** was a substrate for Endo A catalysed hydrolysis, and the yield of product decreased after reaching a maximum after 30 minutes as shown in Figure 2B. Glycosylation with the *manno* (1→6) trisaccharide donor **3** proceeded in a similar reversible fashion, with a maximum yield of 76% after 20 minutes, and, as shown in Figure 2C the rate of product hydrolysis was notably higher than in the case of the (1→3) linked donor **2**. Glycosylation with the *manno* tetrasaccharide **4**, as reported by Wang[34] was also efficient, but in fact was reversible and produced **50** with a maximum yield of 88%. Again an extended time course study revealed that the yield of product decreased markedly after rapidly initially reaching a maximum (Figure 2D). However, the high yield obtainable together with the time course study confirmed that the *manno* oxazoline **4** is a much better donor substrate for Endo A than it is for Endo M (see above), and in addition that product **50** is hydrolysed more rapidly by Endo M than it is by Endo A.

Turning to the non-natural donors, use of the *gluco* disaccharide **6** with Endo A gave product **52** in 48% yield in an irreversible process (Table 2, entry 5, Figure 2E). This result contradicted an earlier report from Wang and co-workers[28] who had previously indicated that **6** was not a substrate for Endo A catalysed glycosylation. In fact these findings indicate that Endo A is more tolerant of a *gluco* unit in a disaccharide donor than is Endo M, since Endo M was only capable of producing disaccharide **52** in 4% yield. Further investigations revealed that Endo A was indeed capable of processing all modified donors in which the *gluco* for *manno* substitution proximal to the *N*-acetyl glucosamine had been made. Endo A catalysed glycosylation of **11** with *gluco* (1→3) linked trisaccharide **7** produced **53** in 57% yield (Table 2, entry 6), again in an irreversible process (Figure 2F). Again the irreversibility of this reaction contrasted with the result obtained for the corresponding *manno* donor **2** (Table 2, entry 2), though the process was less efficient than the corresponding reaction catalysed by Endo M. The use of *gluco* (1→6) linked trisaccharide **8** with Endo A produced **54** in a moderate 38% yield (Table 2, entry 7), again in an irreversible process (Figure 2G), which was more efficient than the corresponding Endo M catalysed reaction. Finally use of the *gluco* tetrasaccharide **9** as

42: R=R^1=Phth, R^2 = Bn, R^3=H, R^4=Bz, R^5=Lev, R^6=PMP
43: R=H, R^1=Ac, R^2 = Bn, R^3=R^4=R^5=Ac, R^6=PMP
44: R=H, R^1=R^2=R^3=R^4=R^5=Ac, R^6=PMP
45: R=H, R^1=R^2=R^3=R^4=R^5=R^6=Ac

46: R = Ac
10: R = H

Scheme 5. a) TMSOTf, 4 Å MS, CH_2Cl_2, −60°C to RT, 15 h, 88%; b) i) $NH_2CH_2CH_2NH_2$, MeOH, reflux, 3 d; ii) Ac_2O, py, 0°C to RT, 1 d, 82% (over two steps); c) i) H_2, Pd (10% on C), MeOH, 21 h; ii) Ac_2O, py, 0°C to RT, 25 h, 92% (over two steps); d) i) CAN, H_2O, MeCN, 3 d; ii) Ac_2O, py, 0°C to RT, 20 h, 82% (over two steps); e) TMSBr, BF_3·OEt_2, 2,4,6-collidine, DCE, 40°C, 1 d, 81%; f) Na, MeOH, 18 h, quant.

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Table 1. Glycosylation of **11** with donors **1**–**10** catalysed by Endo M.

Entry	Oxazoline donor	Product	Max. yield [%][a]
1	**1**	**47**	95 →
2	**2**	**48**	65 ↘
3	**3**	**49**	89 ↘
4	**4**	**50**	36 ↘
5	**5**	**51**	24 ↘
6	**6**	**52**	4 →
7	**7**	**53**	88 →
8	**8**	**54**	4 →
9	**9**	**55**	70 →
10	**10**	**56**	60 →

[a] Yields determined by integration of acceptor and product peaks. → Yield stays constant, ↘ yield decreases after reaching the maximum stated by product hydrolysis.

donor with Endo A produced pentasaccharide product **55** in 67% yield, but time course studies revealed that glycosylation was reversible (Figure 2H), that is, that Endo A was capable of hydrolysing the *gluco* product **55** (albeit very slowly); again a result which contrasted with the corresponding Endo M catalysed process.

Endo H catalysed reactions: A variety of representative donors were investigated, but Endo H was not found to be capable of catalysing glycosylation of acceptor **11** in appreciable yield with any of the oxazoline donors investigated.

Conclusion

Endo M and Endo A, members of the family 85 of the glycohydrolases, are both able to effect glycosylation with a wide range of different oxazoline donors. Precise structure activity relationships and time course studies revealed fine-tuning of the efficiency of the synthetic processes which correlated both with the enzyme used and the precise structure of the oxazoline donor. With the natural series of donors containing a "central" mannose unit, Endo M catalysed irreversible glycosylation with a disaccharide donor. The use of Endo A gave in this case gave a reversible reaction, but the rate of hydrolysis was slow enough to enable an essentially quantitative yield of product to be obtained. Both enzymes catalysed glycosylation with larger natural oligosaccharide oxazolines, but in all cases in a reversible fashion. Glycosylations were generally more efficient with Endo A than with Endo M, particularly for pentasaccharide synthesis.

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Table 2. Glycosylation of **11** with *manno* donors **1–4** and *gluco* donors **6–9** catalysed by Endo A.

Entry	Oxazoline donor	Product	Max. yield[a]
1	**1**	**47**	100 ↘
2	**2**	**48**	96 ↘
3	**3**	**49**	76 ↘
4	**4**	**50**	88 ↘
5	**6**	**52**	48 →
6	**7**	**53**	57 →
7	**8**	**54**	38 →
8	**9**	**55**	67 ↘

[a] Yields determined by integration of acceptor and product peaks. → Yield stays constant, ↘ yield decreases after reaching the maximum stated by product hydrolysis.

In the unnatural series of oxazoline donors which contained a key glucose for mannose substitution, Endo M was capable of catalysing irreversible glycosyation (glycoligation) with all oxazoline donors which contained a Manα(1→3)Glc unit proximal to the GlcNAc derived oxazoline, indicating importance of the Man(1→3) residue for binding to the Endo M active site. Endo A was also capable of catalysing glycosylation of **11** with all *gluco* oxazoline donors, though once a pentasaccharide level was reached glycosylation was found to be reversible. In general Endo M catalysed reactions were more efficient than the corresponding processes catalysed by Endo A, but Endo A was capable of glycosylation with donors that did not possess the mannose unit at the 3-position of the "central" glucose residue. Endo H was found to be incapable of catalysing glycosylation with any of the oxazoline donors investigated. It is notable that Endo H is a member of a different family of glycohydrolases (family 18), the hydrolytic mechanism of which may not proceed via an oxazolinium type intermediate. Applications of both Endo M and Endo A catalysed glycoligation for the synthesis of a variety of neoglycoconjugates and homogenous neoglycoproteins are currently in progress, and the results will be reported in due course.

Figure 2. Time correlations of product yield for Endo A catalysed reactions of acceptor **11** with donors **1–4** (A–D) and **6–9** (E–H).

Experimental Section

General chemical procedures: Melting points were recorded on a Kofler hot block. Proton and carbon nuclear magnetic resonance (δ_H, δ_C) spectra were recorded on Bruker DPX250 (250 MHz), Bruker DPX400 (400 MHz), Bruker AV400 (400 MHz), Bruker AV500 (500 MHz) or Bruker DRX500 (500 MHz) spectrometers. All chemical shifts are quoted on the δ-scale in ppm using residual solvent as an internal standard. ^{1}H and ^{13}C spectra were assigned using 2D NMR experiments including COSY, NOESY, ROESY, HSQC, HSQC "non-decoupled", HSQC-TOCSY, TOCSY, HMBC, DEPT and APT. Identical proton coupling constants are averaged in each spectra and reported to the nearest 0.1 Hz. It should be noted that measured J values are limited by the digital resolution of 0.3 Hz per point. Carbohydrates and derivatives have been named in accordance with IUPAC recommendations and numbered according to the carbohydrate convention. The two protons on C-6 are labelled H-6 and H-6′. The individual components of oligosaccharides are distinguished by the assignment of a lowercase letter, given alphabetically starting from the

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reducing terminus. Low resolution mass spectra were recorded on a Micromass Platform 1 spectrometer using electrospray ionisation in either positive or negative polarity (ES^+ or ES^-), or by Dr Neil Oldham or Dr Jo Kirkpatrick using a VG Micromass spectrometer. High resolution mass spectra were recorded by Dr Neil Oldham on a Walters 2790-Micromass LCT electrospray ionisation mass spectrometer using either electrospray ionisation techniques as stated. *m*/*z* values are reported in Daltons and are followed by their percentage abundance in parentheses. Optical rotations were measured on a Perkin-Elmer 241 polarimeter with a path length of 1 dm. Concentrations are given in g per 100 mL. Microanalyses were performed by the Inorganic Chemistry Laboratory Elemental Analysis service. Thin Layer Chromatography (TLC) was carried out on Merck Kieselgel $60F_{254}$ pre-coated glass-backed plates. Visualisation of the plates was achieved using a UV lamp ($\lambda_{max}=254$ or 365 nm), and/or ammonium molybdate (5% in 2M sulfuric acid), or sulfuric acid (5% in ethanol). Flash column chromatography was carried out using Sorbsil C60 40/60 silica. CH_2Cl_2 was distilled from calcium hydride or dried via an alumina column. Anhydrous THF, DMF, pyridine, methanol and toluene were purchased from Fluka over molecular sieves. "Petrol" refers to the fraction of light petroleum ether boiling in the range of 40–60 °C.

General enzymatic procedures: Endohexosaminidase-catalysed glycosylations were monitored by HPLC using a Waters 2795 Alliance HT HPLC instrument using Empower software (version 5.0) connected to a Waters 2996 Photodiode Array Detector and a Waters 2420 ELS Detector. Analytical HPLC (Phenomenex Gemini 5 µ C-18 column, 250×4.6 mm) was used to monitor reactions performed at 23 °C, with aliquots taken every 30 min for a minimum of 3 h. The column was eluted with a linear gradient of 0–90% MeCN/H_2O at a flow rate of 1 mL/min over 20 min, which was then increased to 100% MeCN for a further 5 min followed by a re-equilibration with 95% H_2O for a further 5 min.

***p*-Methoxyphenyl 2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (13)**: Disaccharide **12** (448 mg, 458 µmol) was added to a flask containing activated 4 Å molecular sieves and anhydrous CH_2Cl_2 (15 mL). The solution was stirred for 30 min at room temperature and then cooled to −78 °C. Et_3SiH (219 µL, 1.37 mmol) and $PhBCl_2$ (202 µL, 1.56 mmol) were added successively. After 30 m, TLC (ethyl acetate/petrol 1:1) indicated formation of a major product ($R_f=0.35$) and full consumption of starting material ($R_f=0.45$). Triethylamine (500 µL) and methanol (500 µL) were added successively and the reaction mixture diluted with CH_2Cl_2 (50 mL) and washed with $NaHCO_3$ (2×50 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate/petrol 1:1) to yield alcohol **13** (445 mg, 99%) as a white amorphous solid. $[\alpha]_D^{22} = +24$ ($c=1.0$ in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): $\delta=2.16$ (s, 3H; $OC(O)CH_3$), 3.22 (ddd, $^3J_{4b,5b}=9.4$, $^3J_{5b,6b}=5.1$, $^3J_{5b,6'b}=2.6$ Hz, 1H; H-5b), 3.46 (dd, $^3J_{2b,3b}=3.1$, ^3J 9.3 Hz, 1H; H-3b), 3.51 (dd, $^2J_{6b,6'b}=12.0$ Hz, 1H; H-6b), 3.62 (at, $^3J=9.4$ Hz, 1H; H-4b), 3.68–3.71 (m, 1H; H-5a), 3.72 (s, 3H; OCH_3), 3.76–3.78 (m, 2H; H-6a, H-6'b), 3.81 (dd, $^3J_{5a,6'a}=2.9$, $^2J_{6a,6'a}=11.3$ Hz, 1H; H-6'a), 4.18 (at, $^3J=9.2$ Hz, 1H; H-4a), 4.33 (dd, $^3J_{2a,3a}=10.8$, $^3J_{3a,4a}=8.6$ Hz, 1H; H-3a), 4.40, 4.65 (ABq, $^2J=11.1$ Hz, 2H; $PhCH_2$), 4.41 (dd, $^3J_{1a,2a}=8.3$ Hz, 1H; H-2a), 4.48, 4.92 (ABq, $^2J=12.2$ Hz, 2H; $PhCH_2$), 4.50, 4.74 (ABq, $^2J=12.1$ Hz, 2H; $PhCH_2$), 4.56, 4.86 (ABq, $^2J=11.1$ Hz, 2H; $PhCH_2$), 4.68 (s, 1H; H-1b), 5.46–5.47 (m, 1H; H-2b), 5.63 (d, 1H; H-1a), 6.70–6.72 (m, 2H; 2×Ar-H), 6.81–6.82 (m, 2H; 2×Ar-H), 6.94–6.95 (m, 3H; 3×Ar-H), 7.03–7.04 (m, 2H; 2×Ar-H), 7.27–7.34 (m, 15H; 15×Ar-H), 7.57–7.87 ppm (m, 4H; 4×Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta=20.9$ (q, $OC(O)CH_3$), 55.6 (q, OCH_3), 55.6 (d, C-2a), 62.1 (t, C-6b), 68.2 (d, C-2b), 68.2 (t, C-6a), 71.5, 73.6 (2×t, 2×$PhCH_2$), 74.2 (d, C-4b), 74.6 (d, C-5a), 74.6, 75.1 (2×t, 2×$PhCH_2$), 75.5 (d, C-5b), 76.8 (d, C-3a), 78.1 (d, C-4a), 80.3 (d, C-3b), 97.6 (d, ^1J(C,H)=165 Hz; C-1a), 98.3 (d, ^1J(C,H)=160 Hz; C-1b), 114.3, 118.7, 123.4, 127.4, 127.5, 127.8, 127.8, 127.9, 127.9, 128.0, 128.0, 128.0, 128.2, 128.4, 128.4, 128.6 (16×d, 26×Ar-C), 131.5 (s, 2×Ar-C), 133.9 (d, 2×Ar-C), 137.6, 137.7, 138.2, 138.2, 150.8, 155.4 (6×s, 6×Ar-C), 170.3 ppm (s, 3×C=O); IR (KBr): $\tilde{\nu}=3459$ (br, OH), 1776, 1744, 1714 (s, C=O) (s, C=O); HRMS (ESI): *m*/*z*: calcd for $C_{57}H_{61}N_2O_{14}$: 997.4117; found 997.4123 $[M+NH_4]^+$.

***p*-Methoxyphenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)-2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (15)**: Alcohol **13** (226 mg, 231 µmol) and 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl trichloroacetimidate (**14**; 162 mg, 254 µmol) were dissolved in dry CH_2Cl_2 (10 mL) and transferred via cannula to a flame-dried round-bottomed flask containing activated 4 Å molecular sieves (50 mg). The solution was cooled to −60 °C and stirred under an atmosphere of argon. TMSOTf (4.18 µL, 23.1 µmol) was added and the temperature allowed to rise to 0 °C after 3 h. After 2 h, TLC (petrol/ethyl acetate 1:1) indicated formation of a major product ($R_f=0.45$) and complete consumption of **13** ($R_f=0.3$). Triethylamine (50 µL) was added and the solution stirred for a further 10 min. The reaction mixture was then filtered through Celite and the filtrate concentrated in vacuo. The residue was purified by flash column chromatography (petrol/ethyl acetate 1:1) to give trisaccharide **15** (335 mg, quant.) as a white foam. $[\alpha]_D^{22}=+38$ ($c=0.25$ in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): $\delta=1.84$, 2.20 (2×s, 6H; 2×$OC(O)CH_3$), 3.30 (ddd, $^3J_{4b,5b}=9.6$, $^3J=1.4$, $^3J=2.9$ Hz, 1H; H-5b), 3.44 (dd, $^3J_{2b,3b}=3.2$, $^3J_{3b,4b}=9.3$ Hz, 1H; H-3b), 3.55 (brd, $^2J_{6c,6'c}=9.7$ Hz, 1H; H-6c), 3.65–3.72 (m, 6H; H-5a, H-5c, H-6'c, OCH_3), 3.73 (at, $^3J=9.4$ Hz, 1H; H-4b), 3.76–3.84 (m, 5H; H-4c, H-6a, H-6b, H-6'a, H-6'b), 3.86 (dd, $^3J_{2c,3c}=2.9$, $^3J_{3c,4c}=9.4$ Hz, 1H; H-3c), 4.18 (at, $^3J=9.1$ Hz, 1H; H-4a), 4.28 (at, ^3J 9.6 Hz, 1H; H-3a), 4.32, 4.49 (ABq, $^2J=11.0$ Hz, 2H; $PhCH_2$), 4.33–4.35 (m, 1H; H-2a), 4.34, 4.63 (ABq, $^2J=10.8$ Hz, 2H; $PhCH_2$), 4.43, 4.54 (ABq, $^2J=12.1$ Hz, 2H; $PhCH_2$), 4.45, 4.63 (ABq, $^2J=11.0$ Hz, 2H; $PhCH_2$), 4.45, 4.84 (ABq, $^2J=11.0$ Hz, 2H; $PhCH_2$), 4.55, 4.82 (ABq, $^2J=12.6$ Hz, 2H; $PhCH_2$), 4.58, 4.73 (ABq, $^2J=11.6$ Hz, 2H; $PhCH_2$), 4.72 (s, 1H; H-1b), 4.99 (d, $^3J_{1c,2c}=1.8$ Hz, 1H; H-1c), 5.35 (dd, 1H; H-2c), 5.50 (brd, 1H; H-2b), 5.58 (d, $^3J_{1a,2a}=8.4$ Hz, 1H; H-1a), 6.67–6.70 (m, 2H; 2×Ar-H), 6.72–6.74 (m, 3H; 3×Ar-H), 6.76–6.78 (m, 2H; 2×Ar-H), 6.95–6.97 (m, 2H; 2×Ar-H), 7.12–7.14 (m, 2H; 2×Ar-H), 7.17–7.36 (m, 28H; 28×Ar-H), 7.46–7.77 ppm (m, 4H; 4×Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta=20.7$, 21.1 (2×q, 2×$OC(O)CH_3$), 55.5 (q, OCH_3), 55.6 (d, C-2a), 66.0 (t, C-6b), 68.2 (d, C-2c), 68.2 (d, C-2b), 68.5 (t, C-6a), 68.8 (t, C-6c), 71.3, 71.4 (2×t, 2×$PhCH_2$), 71.7 (d, C-5c), 73.3, 73.4 (2×t, 2×$PhCH_2$), 73.7 (d, C-4b), 74.1 (d, C-4c), 74.4 (t, $PhCH_2$), 74.5 (d, C-5a), 74.9, 75.0 (2×t, 2×$PhCH_2$), 75.1 (d, C-5b), 76.4 (d, C-3a), 77.7 (d, C-3c), 79.3 (d, C-4a), 80.5 (d, C-3b), 97.5 (d, ^1J(C,H)=166 Hz; C-1a), 98.0 (d, ^1J(C,H)=174 Hz; C-1c), 99.5 (d, ^1J(C,H)=159 Hz; C-1b), 114.3, 118.6, 123.2, 127.2, 127.4, 127.4, 127.5, 127.5, 127.6, 127.7, 127.7, 127.8, 127.8, 127.9, 128.2, 128.2, 128.2, 128.2, 128.3, 128.3, 128.4, 128.5 (22×d, 41×Ar-C), 131.6 (s, 2×Ar-C), 133.5 (d, 2×Ar-C), 137.6, 137.8, 138.0, 138.3, 138.3, 138.4, 138.6, 150.8, 155.3 (9×s, 9×Ar-C), 170.0, 170.6 ppm (2×s, 4×C=O); IR (KBr): $\tilde{\nu}=1742$, 1716 cm^{-1} (s, C=O); MS (ESI): *m*/*z*: species observed: $[M+MeCN/NH_4]^+$ (major), $[M+Na]^+$; peaks observed: *m*/*z* (%): 1476.6 (100), 1477.6 (91), 1478.6 (39), 1479.6 (10), 1480.6 (3); calcd for: 1476.6 (100), 1477.6 (95), 1478.6 (49), 1479.6 (18), 1480.6 (5).

***p*-Methoxyphenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)-2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (16)**: Phthalimide-protected trisaccharide **15** (226 mg, 224 µmol) was dissolved in methanol (7 mL), ethylene diamine (6.00 mL, 89.6 mmol) added and the solution refluxed at 65 °C. After 22 h, TLC (petrol/ethyl acetate 1:1) indicated formation of a major product ($R_f=0$) and complete consumption of starting material ($R_f=0.45$). The reaction mixture was concentrated in vacuo, and the residue dissolved in pyridine (8 mL). The solution was cooled to 0 °C, acetic anhydride (7 mL) added and the reaction mixture stirred and allowed to warm to room temperature. After 21 h, TLC (petrol/ethyl acetate 1:1) indicated formation of a major product ($R_f=0.2$) and complete consumption of starting material ($R_f=0.45$). The reaction mixture was poured onto ice/water (20 mL) and extracted with CH_2Cl_2 (2×10 mL). The organic layers were washed with hydrochloric acid (3×50 mL of a 1M solution), $NaHCO_3$ (3×50 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (petrol/ethyl acetate 1:1) to afford acetamide **16** (195 mg, 92%) as a white foam. $[\alpha]_D^{22}=+4$ ($c=0.25$ in $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): $\delta=1.61$, 2.05, 2.06 (3×s, 9H; 3×$C(O)CH_3$), 3.08 (dd, $^3J_{5c,6c}=1.0$, $^2J_{6c,6'c}=11.0$ Hz, 1H; H-6c), 3.40–3.43 (m, 2H; H-2a, H-5b), 3.50 (dd, $^3J_{5c,6'c}=3.2$ Hz, 1H; H-6'c), 3.54 (dd, $^3J_{2b,3b}=3.1$, $^3J_{3b,4b}=$

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9.1 Hz, 1H; H-3b), 3.63 (at, ^{3}J=9.3 Hz, 1H; H-4b), 3.65–3.69 (m, 2H; H-5a, H-6b), 3.75–3.80 (m, 7H; H-5c, H-6a, H-6′a, H-6′b, OCH_3), 3.92–3.93 (m, 2H; H-3c, H-4c), 4.14 (at, ^{3}J=7.5 Hz, 1H; H-4a), 4.17 (at, ^{3}J=7.8 Hz, 1H; H-3a), 4.29, 4.56 (ABq, ^{2}J=12.1 Hz, 2H; $PhCH_2$), 4.37, 4.48 (ABq, ^{2}J=11.4 Hz, 2H; $PhCH_2$), 4.39, 4.82 (ABq, ^{2}J=10.2 Hz, 2H; $PhCH_2$), 4.40, 4.67 (ABq, ^{2}J=10.8 Hz, 2H; $PhCH_2$), 4.45, 4.64 (ABq, ^{2}J=11.9 Hz, 2H; $PhCH_2$), 4.51, 4.90 (ABq, ^{2}J=12.2 Hz, 2H; $PhCH_2$), 4.52, 4.89 (ABq, ^{2}J=11.1 Hz, 2H; $PhCH_2$), 4.71 (s, 1H; H-1b), 4.91 (brs, 1H; H-1c), 5.12 (d, $^{3}J_{2a,NH}$=7.4 Hz, 1H; NH), 5.37 (d, $^{3}J_{1a,2a}$=7.5 Hz, 1H; H-1a), 5.37–5.39 (m, 1H; H-2c), 5.52 (brd, 1H; H-2b), 6.78–6.80 (m, 2H; 2×Ar-H), 6.90–6.93 (m, 2H; 2×Ar-H), 7.14–7.35 ppm (m, 35H; 35×Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ?=21.0, 21.0 (2×q, 2×OC(O)CH_3), 23.3 (q, NC(O)CH_3), 55.6 (q, OCH_3), 56.4 (d, C-2a), 66.3 (t, C-6b), 68.0 (d, C-2b), 68.4 (t, C-6c), 68.9 (d, C-2c), 68.9 (t, C-6a), 71.3 (d, C-5c), 71.6, 71.8, 73.3, 73.5 (4×t, 4×$PhCH_2$), 74.1 (d, C-5a), 74.2 (t, $PhCH_2$), 74.3 (d, C-4b), 74.6 (d, C-5b), 74.7 (d, C-4c), 74.9, 75.4 (2×t, 2×$PhCH_2$), 75.8 (d, C-4a), 77.2 (d, C-3a), 78.5 (d, C-3c), 80.7 (d, C-3b), 97.4 (d, ^{1}J(C,H)=160 Hz; C-1b), 97.6 (d, ^{1}J(C,H)=172 Hz; C-1c), 98.8 (d, ^{1}J(C,H)=167 Hz; C-1a), 114.4, 118.5, 127.4, 127.6, 127.7, 127.7, 127.9, 128.2, 128.2, 128.2, 128.2, 128.3, 128.3, 128.4, 128.5, 128.5 (16×d, 39×Ar-C), 137.4, 137.9, 138.0, 138.1, 138.4, 138.8, 139.0, 151.5, 155.1 (9×s, 9×Ar-C), 170.3, 170.4, 170.5 ppm (3×s, 3×C=O); IR (KBr): $\tilde{\nu}$=3420 (br, NH), 1743 cm^{-1} (s, C=O); MS (ESI): *m/z*: species observed: $[M+MeCN/NH_4]^+$ (major), $[M+Na]^+$; peaks observed: *m/z* (%): 1388.6 (100), 1389.6 (85), 1390.6 (36), 1391.6 (9), 1392.6 (2); calcd for: 1388.6 (100), 1389.6 (89), 1390.6 (43), 1391.6 (15), 1392.6 (4).

***p*-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-acetyl-β-D-mannopyranosyl-(1→4)-2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranoside (17)**: Benzyl ether **16** (180 mg, 132 μmol) was dissolved in ethyl acetate (7 mL) and ethanol (7 mL). Palladium (10% on carbon, 65 mg) was added and the reaction mixture stirred at room temperature under an atmosphere of hydrogen. After 20 h, TLC (petrol/ethyl acetate 1:1) indicated formation of a major product (R_f=0) and complete consumption of starting material (R_f=0.2). The reaction mixture was poured onto Celite, washed with ethyl acetate (2×20 mL) and ethanol (5×20 mL), filtered and concentrated in vacuo. The residue was dissolved in pyridine (7 mL), the solution cooled to 0°C and acetic anhydride (6 mL) added. The reaction mixture was stirred and allowed to warm to room temperature. After 21 h, TLC (ethyl acetate) indicated formation of a major product (R_f=0.5) and complete consumption of intermediate material (R_f=0). The reaction mixture was poured onto ice/water (10 mL) and extracted with CH_2Cl_2 (2×10 mL). The organic layers were washed with hydrochloric acid (2×20 mL of a 1 M solution), $NaHCO_3$ (2×20 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate) to give acetate **17** (115 mg, 85%) as a white amorphous foam. $[\alpha]_D^{24}$ = +11 (c=0.2 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.88, 1.94, 2.03, 2.06, 2.09, 2.10, 2.10, 2.11, 2.13, 2.17 (10×s, 30H; 10×C(O)CH_3), 3.48 (dd, $^{3}J_{5b,6b}$=1.9, $^{2}J_{6b,6'b}$=10.9 Hz, 1H; H-6b), 3.73 (ddd, $^{3}J_{4b,5b}$=10.2, $^{3}J_{5b,6'b}$=4.6 Hz, 1H; H-5b), 3.76 (s, 3H; OCH_3), 3.79 (dd, 1H; H-6′b), 3.88–3.93 (m, 1H; H-5c), 3.90 (at, ^{3}J=9.1 Hz, 1H; H-4a), 3.98 (ddd, $^{3}J_{4a,5a}$=9.2, $^{3}J_{5a,6a}$=4.9, $^{3}J_{5a,6'a}$=2.3 Hz, 1H; H-5a), 4.12 (dd, $^{3}J_{5c,6c}$=2.4, $^{2}J_{6c,6'c}$=12.2 Hz, 1H; H-6c), 4.23–4.28 (m, 1H; H-2a), 4.30 (dd, $^{3}J_{5c,6'c}$=5.2 Hz, 1H; H-6′c), 4.32 (d, $^{2}J_{6a,6'a}$=11.7 Hz, 1H; H-6a), 4.46 (dd, 1H; H-6′a), 4.86 (s, 1H; H-1b), 4.86 (s, 1H; H-1c), 5.12 (d, $^{3}J_{1a,2a}$=8.2 Hz, 1H; H-1a), 5.19 (at, ^{3}J=9.5 Hz, 1H; H-3a), 5.19 (dd, $^{3}J_{2b,3b}$=4.6, $^{3}J_{3b,4b}$=8.6 Hz, 1H; H-3b), 5.25 (dd, $^{3}J_{2c,3c}$=3.3, $^{3}J_{3c,4c}$=10.2 Hz, 1H; H-3c), 5.28 (brd, 1H; H-2b), 5.33 (at, ^{3}J=10.1 Hz, 1H; H-4c), 5.40 (at, ^{3}J=9.4 Hz, 1H; H-4b), 5.52 (brs, 1H; H-2c), 6.11 (d, $^{3}J_{2a,NH}$=9.6 Hz, 1H; NH), 6.78–6.81 (m, 2H; 2×Ar-H), 6.94–6.97 ppm (m, 2H; 2×Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ=20.4, 20.5, 20.7, 20.7, 20.8, 20.9, 21.0 (7×q, 9×OC(O)CH_3), 23.1 (q, NC(O)CH_3), 53.7 (d, C-2a), 55.6 (q, OCH_3), 62.4 (t, C-6c), 62.9 (t, C-6a), 65.5 (d, C-4c), 66.7 (t, C-6b), 66.9 (d, C-4b), 67.6 (d, C-2b), 68.8 (d, C-5c), 69.1 (d, C-2c), 69.6 (d, C-3c), 70.0 (d, C-3b), 71.9 (d, C-5b), 72.1 (d, C-5a), 73.4 (d, C-3a), 75.0 (d, C-4a), 96.9 (d, ^{1}J=165 Hz; C-1b), 97.9 (d, ^{1}J=175 Hz; C-1c), 99.8 (d, ^{1}J=163 Hz; C-1a), 114.4, 118.1 (2×d, 4×Ar-C), 151.3, 155.3 (2×s, 2×Ar-C), 169.5, 169.9, 170.0, 170.2, 170.2, 170.4, 170.6, 170.7, 170.7 ppm (9×s, 10×C=O); IR (KBr): $\tilde{\nu}$=3448 (br, NH), 1747 cm^{-1} (s, C=O); MS (ESI): species observed: $[M+MeCN/NH_4]^+$ (major), $[M+Na]^+$; peaks observed: *m/z* (%): 1052.3 (100), 1053.3 (50), 1054.3 (16), 1055.3 (3); calcd for: 1052.3 (100), 1053.3 (51), 1054.3 (18), 1055.3 (5).

2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-acetyl-β-D-mannopyranosyl-(1→4)-2-acetamido-1,3,6-tri-*O*-acetyl-2-deoxy-D-glucopyranose (18): PMP glycoside **17** (100 mg, 97.1 μmol) was dissolved in water (5 mL) and acetonitrile (10 mL). Ceric ammonium nitrate (160 mg, 291 μmol) was added and the solution stirred at room temperature. After 3 d, the reaction mixture was extracted with CH_2Cl_2 (2×20 mL). The organic portions were combined and washed with $NaHCO_3$ (2×20 mL of a saturated solution), sodium thiosulfate (2×10 mL of a 10% w/v solution), EDTA (2×30 mL of a 0.05 M solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate to ethyl acetate/methanol 9:1) and the product dissolved in pyridine (7 mL), the solution cooled to 0°C and acetic anhydride (5 mL) added. The reaction mixture was stirred and allowed to warm to room temperature. After 16 h, TLC (ethyl acetate) indicated formation of a major product (R_f=0.25) and complete consumption of starting material (R_f=0.5). The reaction mixture was poured onto ice/water (10 mL) and extracted with CH_2Cl_2 (2×10 mL). The organic layers were washed with hydrochloric acid (3×10 mL of a 1 M solution), $NaHCO_3$ (3×10 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate) to give peracetate **18** (70 mg, 75%) as a white foam and only the α anomer detected. ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.92, 1.99, 1.99, 2.07, 2.07, 2.11, 2.12, 2.14, 2.16, 2.16, 2.18 (11×s, 33H; 11×C(O)CH_3), 3.59–3.64 (m, 2H; H-5b, H-6b), 3.83 (dd, $^{3}J_{5b,6'b}$=5.6, $^{2}J_{6b,6'b}$=10.9 Hz, 1H; H-6′b), 3.92 (dat, $^{3}J_{4a,5a}$=10.1, ^{3}J=2.7 Hz, 1H; H-5a), 3.96–4.00 (m, 2H; H-4a, H-5c), 4.14 (dd, $^{3}J_{5c,6c}$=2.3, $^{2}J_{6c,6'c}$=12.4 Hz, 1H; H-6c), 4.23 (dd, $^{3}J_{5a,6a}$=3.4, $^{2}J_{6a,6'a}$=12.3 Hz, 1H; H-6a), 4.27 (dd, $^{3}J_{5c,6'c}$=4.7 Hz, 1H; H-6′c), 4.31 (dd, $^{3}J_{5a,6'a}$=2.3 Hz, 1H; H-6′a), 4.36 (ddd, $^{3}J_{1a,2a}$=3.6, $^{3}J_{2a,3a}$=11.1, $^{3}J_{2a,NH}$=9.2 Hz, 1H; H-2a), 4.75 (s, 1H; H-1b), 4.85 (d, $^{3}J_{1c,2c}$=1.6 Hz, 1H; H-1c), 5.04 (dd, $^{3}J_{2b,3b}$=3.2, $^{3}J_{3b,4b}$=9.8 Hz, 1H; H-3b), 5.19 (at, ^{3}J=9.8 Hz, 1H; H-4b), 5.24 (dd, $^{3}J_{3a,4a}$=9.0 Hz, 1H; H-3a), 5.27 (dd, $^{3}J_{2c,3c}$=2.8 Hz, 1H; H-2c), 5.30–5.33 (m, 1H; H-3c), 5.35 (at, ^{3}J=9.6 Hz, 1H; H-4c), 5.41 (brd, 1H; H-2b), 5.64 (d, 1H; NH), 6.09 ppm (d, 1H; H-1a); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ=20.5, 20.6, 20.7, 20.7, 20.7, 20.7, 20.7, 20.8, 20.9, 21.0 (10×q, 10×OC(O)CH_3), 22.9 (q, NC(O)CH_3), 50.7 (d, C-2a), 61.9 (t, C-6a), 62.2 (t, C-6c), 65.7 (d, C-4c), 66.5 (d, C-4b), 66.9 (t, C-6b), 68.3 (d, C-2b), 68.8 (d, C-5c), 69.0 (d, C-3c), 69.2 (d, C-2c), 70.4 (d, C-5a), 70.5 (d, C-3a), 70.7 (d, C-3b), 72.8 (d, C-5b), 73.6 (d, C-4a), 90.6 (d, ^{1}J(C,H)=181 Hz; C-1a), 97.3 (d, ^{1}J(C,H)=160 Hz C-1b), 97.4 (d, ^{1}J(C,H)=174 Hz; C-1c), 168.8, 169.7, 169.7, 169.9, 170.1, 170.3, 170.5, 170.6, 171.4 ppm (9×s, 11×C=O); IR (KBr): $\tilde{\nu}$=3384 (br, NH), 1750, 1683 cm^{-1} (s, C=O); HRMS (ESI): *m/z*: calcd for $C_{40}H_{55}NNaO_{26}$: 988.2905; found 988.2896 $[M+Na]^+$.

2-Methyl-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-acetyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano]-[2,1-*d*]-oxazoline (19): Peracetate **18** (50.0 mg, 51.8 μmol) was dissolved in dry DCE (10 mL) and transferred via cannula to a flame-dried round-bottomed flask. TMSBr (103 μL, 0.777 mmol), $BF_3\cdot OEt_2$ (98 μL, 0.777 mmol) and 2,4,6-collidine (35 μL, 0.259 μmol) were added and the solution heated to 40°C, under an atmosphere of argon. After 22 h, TLC (ethyl acetate) indicated formation of a major product (R_f=0.45) and complete consumption of starting material (R_f=0.25). The reaction mixture was washed with $NaHCO_3$ (2×10 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate/Et_3N 400:1) to give acetylated oxazoline **19** (38 mg, 81%) as a white amorphous solid. $[\alpha]_D^{19}$=+26 (c=0.1 in $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6): δ=1.76, 1.78, 1.81, 1.82, 1.91, 1.94, 2.01, 2.07 (8×s, 30H; 9×OC(O)CH_3, NC(O)CH_3), 3.67 (brd, $^{3}J_{4a,5a}$=8.8 Hz, 1H; H-4a), 3.73 (dd, $^{3}J_{5b,6b}$=3.3, $^{2}J_{6b,6'b}$=10.7 Hz, 1H; H-6b), 3.80 (ddd, $^{3}J_{5a,6a}$=3.1, $^{3}J_{5a,6'a}$=6.3 Hz, 1H; H-5a), 3.91 (ddd, $^{3}J_{4b,5b}$=9.8, $^{3}J_{5b,6'b}$=6.2 Hz, 1H; H-5b), 4.11 (dd, 1H; H-6′b), 4.21–4.22 (m, 1H; H-2a), 4.34 (dd, $^{2}J_{6a,6'a}$=11.9 Hz, 1H; H-6a), 4.36 (dd, $^{3}J_{5c,6c}$=2.2, $^{2}J_{6c,6'c}$=12.3 Hz, 1H; H-6c), 4.43 (dd, 1H; H-6′a), 4.48 (ddd, $^{3}J_{4c,5c}$=10.0, $^{3}J_{5c,6'c}$=4.2 Hz, 1H; H-5c), 4.73 (dd, 1H; H-6′c), 4.80 (s, 1H; H-1b), 4.92 (s, 1H; H-1c), 5.42 (dd, $^{3}J_{2b,3b}$=3.3, $^{3}J_{3b,4b}$=10.0 Hz, 1H; H-3b), 5.70 (at, ^{3}J=10.0 Hz, 1H; H-4b), 5.76 (dd, $^{3}J_{1c,2c}$=1.7, $^{3}J_{2c,3c}$=

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3.3 Hz, 1H; H-2c), 5.79–5.83 (m, 3H; H-1a, H-2b, H-3c), 5.90 (at, ^3J = 10.1 Hz, 1H; H-4c), 6.11 ppm (br d, $^3J_{2a,3a}$ = 2.5 Hz, 1H; H-3a); ^{13}C NMR (125.8 MHz, C_6D_6): δ = 13.3 (q, NC(O)CH_3), 20.2, 20.2, 20.3, 20.4, 20.4, 20.5, 20.5, 20.9 (8×q, 9×OC(O)CH_3), 62.4 (t, C-6c), 64.7 (t, C-6a), 65.1 (d, C-2a), 66.3 (d, C-4c), 67.4 (d, C-4b), 67.5 (t, C-6b), 68.3 (d, C-5a), 69.3 (d, C-5c), 69.4 (d, C-2b), 69.7 (d, C-3a), 69.9 (d, C-3c), 70.0 (d, C-2c), 71.4 (d, C-3b), 73.3 (d, C-5b), 78.3 (d, C-4a), 98.2 (d, ^1J(C,H) = 175 Hz; C-1c), 99.4 (d, ^1J(C,H) = 184 Hz; C-1a), 99.8 (d, ^1J(C,H) = 158 Hz; C-1b), 165.9 (s, C=N), 169.3, 169.5, 169.6, 169.7, 170.1, 170.3, 170.3 ppm (7×s, 9×C=O); IR (KBr): $\tilde{\nu}$ = 1748, 1675 cm^{-1} (s, C=O, C=N); HRMS (ESI): m/z: calcd for $C_{38}H_{52}NO_{24}$: 906.2874; found 906.2879 [M+H]$^+$.

2-Methyl-[α-D-mannopyranosyl-(1→6)-β-D-mannopyranosyl-(1→4)-1,2-dideoxy-α-D-glucopyrano]-[2,1-*d*]-oxazoline (3): Acetylated oxazoline **19** (14.4 mg, 15.9 μmol) was dissolved in dry methanol (5 mL). Methanolic sodium methoxide (73.1 μL of a 10 mg mL^{-1} solution, 31.8 μmol) was added and the solution stirred at room temperature, under an atmosphere of argon. After 13 h, mass spectrometry indicated one product. The solution was concentrated in vacuo to yield deprotected oxazoline **3** (10.0 mg, quant.) as a white amorphous solid. ^{1}H NMR (500 MHz, D_2O): δ = 1.98 (d, $^5J_{2a,CH_3}$ = 1.7 Hz, 3H; CH_3), 3.34 (ddd, $^3J_{4a,5a}$ = 8.7, $^3J_{5a,6a}$ = 6.3, $^3J_{5a,6'a}$ = 2.5 Hz, 1H; H-5a), 3.44–3.48 (m, 1H; H-5b), 3.54–3.71 (m, 8H; H-3b, H-4a, H-4b, H-4c, H-5c, H-6a, H-6c, H-6′a), 3.76 (dd, $^3J_{5b,6b}$ = 2.0, $^2J_{6b,6'b}$ = 11.4 Hz, 1H; H-6b), 3.79 (dd, $^3J_{2c,3c}$ = 3.5, $^3J_{3c,4c}$ = 9.3 Hz, 1H; H-3c), 3.84 (dd, $^3J_{5c,6'c}$ = 1.8, $^2J_{6c,6'c}$ = 11.6 Hz, 1H; H-6′c), 3.85 (dd, $^3J_{5b,6'b}$ = 6.1 Hz, 1H; H-6′b), 3.90 (br d, J = 1.7 Hz, H-2b), 3.92 (dd, $^3J_{1c,2c}$ = 1.6 Hz, 1H; H-2c), 4.10–4.12 (m, 1H; H-2a), 4.30 (dd, ^3J = 1.7, ^3J = 3.0 Hz, H-3a), 4.64 (s, 1H; H-1b), 4.87 (d, 1H; H-1c), 6.01 ppm (d, $^3J_{1a,2a}$ = 7.3 Hz, 1H; H-1a); ^{13}C NMR (125.8 MHz, D_2O): δ = 12.9 (q, CH_3), 60.9 (t, C-6c), 61.7 (t, C-6a), 65.1 (d, C-2a), 65.9 (t, C-6b), 66.7, 66.8 (2×d, C-4b, C-4c), 69.2 (d, C-3a), 69.8 (d, C-2c), 70.4 (d, C-3c), 70.5 (d, C-2b), 70.8 (d, C-5a), 72.7 (d, C-5c), 72.8 (d, C-3b), 74.5 (d, C-5b), 77.8 (d, C-4a), 99.6 (d, ^1J(C,H) = 174 Hz; C-1c), 99.9 (d, ^1J(C,H) = 186 Hz; C-1a), 101.5 (d, ^1J(C,H) = 160 Hz; C-1b), 168.6 ppm (s, C=N); IR (KBr): $\tilde{\nu}$ = 3426 (br, OH), 1668 cm^{-1} (br s, C=N); HRMS (ESI): m/z: calcd for $C_{20}H_{33}NNaO_{15}$: 505.1742; found 505.1742 [M+Na]$^+$.

***p*-Methoxyphenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)]-2-*O*-acetyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (21)**: Diol **20** (233 mg, 183 μmol) and **14** (128 mg, 201 μmol) were dissolved in dry CH_2Cl_2 (10 mL) and transferred via cannula to a flame-dried round-bottomed flask containing activated 4 Å molecular sieves (100 mg). The solution was cooled to −60 °C and stirred under an atmosphere of argon. TMSOTf (3.31 μL, 18.3 μmol) was added and the temperature allowed to rise to 0 °C after 3 h. After 5 h, TLC (petrol/ethyl acetate 1:1) indicated formation of a major product (R_f = 0.3) and complete consumption of diol **20** (R_f = 0.05). Triethylamine (50 μL) was added and the solution stirred for a further 10 min. The reaction mixture was then filtered through Celite and the filtrate concentrated in vacuo. The residue was purified by flash column chromatography (petrol/ethyl acetate 1:1) to give tetrasaccharide **21** (243 mg, 76%) as a white foam. $[\alpha]_D^{22}$ = +39 (c = 0.25 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.00, 2.06, 2.12 (3×s, 9H; 3×OC(O)CH_3), 3.07 (dat, $^3J_{4b,5b}$ = 9.6, ^3J = 2.7 Hz, 1H; H-5b), 3.50 (brs, 1H; OH), 3.56 (dd, $^3J_{2b,3b}$ = 3.2, $^3J_{3b,4b}$ = 9.7 Hz, 1H; H-3b), 3.58–3.60 (m, 1H; H-5a), 3.65–3.78 (m, 11H; H-5d, H-6a, H-6b, H-6c, H-6d, H-6′a, H-6′c, H-6′d, OCH_3), 3.82 (at, ^3J = 9.5 Hz, 1H; H-4d), 3.82 (dd, $^3J_{2d,3d}$ = 2.3, $^3J_{3d,4d}$ = 9.3 Hz, 1H; H-3d), 3.86–3.87 (m, 2H; H-3c, H-5c), 3.91–3.98 (m, 3H; H-4b, H-4c, H-6′b), 4.10 (at, ^3J = 9.4 Hz, 1H; H-4a), 4.20, 4.41 (ABq, ^2J = 11.1 Hz, 2H; $PhCH_2$), 4.25 (dd, $^3J_{2a,3a}$ = 10.6, $^3J_{3a,4a}$ = 8.5 Hz, 1H; H-3a), 4.34 (dd, $^3J_{1a,2a}$ = 8.5 Hz, 1H; H-2a), 4.44, 4.77 (ABq, ^2J = 10.6 Hz, 2H; $PhCH_2$), 4.45–4.53 (m, 6H; 6×PhCH), 4.64–4.69 (m, 5H; H-1b, 4×PhCH), 4.83 (d, $^3J_{1d,2d}$ = 1.7 Hz, 1H; H-1d), 4.85 (d, ^2J = 11.2 Hz, 1H; PhCH), 4.86 (d, ^2J = 12.8 Hz, 1H; PhCH), 5.20 (d, $^3J_{1c,2c}$ = 1.2 Hz, 1H; H-1c), 5.30 (dd, 1H; H-2d), 5.35 (br d, 1H; H-2b), 5.41 (m, 1H; H-2c), 5.56 (d, 1H; H-1a), 6.67–6.69 (m, 2H; 2×Ar-H), 6.74–6.79 (m, 5H; 5×Ar-H), 6.97–6.98 (m, 2H; 2×Ar-H), 7.10–7.11 (m, 2H; 2×Ar-H), 7.14–7.16 (m, 2H; 2×Ar-H), 7.19–7.36 (m, 31H; 31×Ar-H), 7.64–7.81 ppm (m, 4H; 4×Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 20.9, 21.0, 21.1 (3×q, 3×OC(O)CH_3), 55.5 (q, OCH_3), 55.6 (d, C-2a), 66.1 (t, C-6b), 66.8 (d, C-4b), 68.1 (t, C-6a/c/d), 68.4 (d, C-2d), 68.7 (t, C-6a/c/d), 68.9 (d, C-2c), 68.9 (t, C-6a/c/d), 71.0 (d, C-2b), 71.5 (t, $PhCH_2$), 71.8 (d, C-4d), 71.8 (t, $PhCH_2$), 71.9 (d, C-4c), 73.3, 73.3, 73.4 (3×t, 3×$PhCH_2$), 74.1 (d, H-5c), 74.3 (d, H-5d), 74.5 (t, $PhCH_2$), 74.6 (2×d, C-5a, C-5b), 74.7, 75.3 (2×t, 2×$PhCH_2$), 76.8 (d, C-3a), 77.7 (d, C-3c), 77.9 (d, C-3b), 78.2 (d, C-3d), 78.8 (d, C-4a), 97.5 (d, ^1J(C,H) = 167 Hz; C-1a), 97.9 (d, ^1J(C,H) = 173 Hz; C-1d), 99.1 (d, ^1J(C,H) = 160 Hz; C-1b), 99.3 (d, ^1J(C,H) = 174 Hz; C-1c), 114.3, 118.5, 123.2, 127.2, 127.4, 127.6, 127.6, 127.7, 127.8, 127.8, 127.9, 128.0, 128.0, 128.0, 128.1, 128.2, 128.2, 128.3, 128.3, 128.4, 128.5 (21×d, 46×Ar-C), 131.6 (s, 2×Ar-C), 133.6 (d, 2×Ar-C), 137.8, 137.8, 137.9, 138.0, 138.0, 138.2, 138.5, 138.5, 150.8, 155.3 (10×s, 10×Ar-C), 170.0, 170.4, 170.5 ppm (3×s, 5×C=O); IR (KBr): $\tilde{\nu}$ = 3459 (br, OH), 1777, 1746, 1716 cm^{-1} (s, C=O); MS (ESI): species observed: [M+NH_4]$^+$, [M+Na]$^+$ (major); peaks observed: m/z (%): 1770.7 (84), 1771.7 (100), 1772.7 (51), 1773.7 (16), 1774.7 (5), 1775.7 (1); calcd for: 1770.7 (89), 1771.7 (100), 1772.7 (60), 1773.7 (26), 1774.7 (9), 1775.7 (2).

***p*-Methoxyphenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-mannopyranosyl-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (22)**: Phthalimide protected tetrasaccharide **21** (220 mg, 126 μmol) was dissolved in methanol (6 mL) and ethylene diamine (3.36 mL, 50.3 mmol) and the solution was refluxed at 65 °C. After 41 h, the reaction mixture was concentrated in vacuo, and the residue dissolved in pyridine (8 mL). The solution was cooled to 0 °C, acetic anhydride (7 mL) added and the reaction mixture stirred and allowed to warm to room temperature. After 1 d, TLC (petrol/ethyl acetate 1:1) indicated formation of a major product (R_f = 0.15) and complete consumption of starting material (R_f = 0.3). The reaction mixture was poured onto ice/water (20 mL) and extracted with CH_2Cl_2 (2×10 mL). The organic layers were washed with hydrochloric acid (3×30 mL of a 1 M solution), $NaHCO_3$ (2×20 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (petrol/ethyl acetate 2:3) to afford acetamide **22** (198 mg, 92%) as a white amorphous foam. $[\alpha]_D^{22}$ = +6 (c = 0.25 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ ? = 1.54, 1.89, 2.11, 2.14, 2.17 (5×s, 15H; 5×C(O)CH_3), 2.93 (br d, $^2J_{6d,6'd}$ = 10.6 Hz, 1H; H-6d), 3.25 (dat, $^3J_{2a,3a}$ = 9.2, ^3J = 7.8 Hz, 1H; H-2a), 3.37–3.41 (m, 2H; H-5b, H-6b), 3.47 (dd, $^3J_{5d,6'd}$ = 2.8 Hz, 1H; H-6′d), 3.56 (dat, $^3J_{4a,5a}$ = 8.9, ^3J = 2.5 Hz, 1H; H-5a), 3.64–3.69 (m, 3H; H-6a, H-6c, H-6′a), 3.73–3.82 (m, 8H; H-3b, H-3c, H-5d, H-6′b, H-6′c, OCH_3), 3.85–3.87 (m, 1H; H-5c), 3.90 (at, ^3J = 9.6 Hz, 1H; H-4c), 3.93 (dd, $^3J_{2d,3d}$ = 3.0, $^3J_{3d,4d}$ = 10.0 Hz, 1H; H-3d), 3.98 (at, ^3J = 9.5 Hz, 1H; H-4d), 4.13 (at, ^3J = 8.8 Hz, 1H; H-4a), 4.21 (at, ^3J = 9.0 Hz, 1H; H-3a), 4.28, 4.57 (ABq, ^2J = 12.1 Hz, 2H; $PhCH_2$), 4.37–4.50 (m, 7H; 7×PhCH), 4.52, 4.60 (ABq, ^2J = 11.6 Hz, 2H; $PhCH_2$), 4.62–4.67 (m, 2H; 2×PhCH), 4.71 (s, 1H; H-1b), 4.81–4.84 (m, 2H; 2×PhCH), 4.85 (d, $^3J_{1d,2d}$ = 1.4 Hz, 1H; H-1d), 4.85 (d, ^2J = 10.9 Hz, 1H; PhCH), 4.93 (d, $^3J_{2a,NH}$ = 7.2 Hz, 1H; NH), 4.97 (d, $^3J_{1c,2c}$ = 1.2 Hz, 1H; H-1c), 5.12 (m, 1H; H-2c), 5.12 (at, ^3J = 9.9 Hz, 1H; H-4b), 5.33 (dd, 1H; H-2d), 5.39–5.40 (m, 1H; H-2b), 5.41 (d, $^3J_{1a,2a}$ = 7.9 Hz, 1H; H-1a), 6.78–6.81 (m, 2H; 2×Ar-H), 6.88–6.92 (m, 2H; 2×Ar-H), 7.17–7.35 ppm (m, 40H; 40×Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 20.7, 20.8, 21.1, 21.1 (4×q, 4×OC(O)CH_3), 23.3 (q, NC(O)CH_3), 55.6 (q, OCH_3), 57.3 (d, C-2a), 66.3 (t, C-6b), 68.3 (t, C-6d), 68.6 (t, C-6a), 68.7 (t, C-6c), 68.9, 69.1 (2×d, C-2c, C-4b), 69.3 (d, C-2d), 70.6 (d, C-2b), 71.3 (d, C-5d), 71.7 (t, $PhCH_2$), 72.0 (d, C-5c), 72.2 (t, $PhCH_2$), 73.2 (d, C-5b), 73.3, 73.3, 73.4 (3×t, 3×$PhCH_2$), 73.8 (d, H-4c), 74.2 (d, H-5a), 74.5, 74.7 (2×t, 2×$PhCH_2$), 74.8 (d, C-4d), 75.4 (d, C-4a), 75.6 (t, $PhCH_2$), 76.9 (d, C-3b), 77.2 (d, C-3c), 77.2 (d, C-3a), 79.0 (d, C-3d), 96.8 (d, ^1J(C,H) = 161 Hz; C-1b), 97.4 (d, ^1J(C,H) = 172 Hz; C-1d), 98.6 (d, ^1J(C,H) = 167 Hz; C-1a), 100.0 (d, ^1J(C,H) = 173 Hz; C-1c), 114.4, 118.5, 127.4, 127.4, 127.5, 127.5, 127.6, 127.6, 127.7, 127.7, 127.7, 127.8, 127.9, 128.0, 128.2, 128.2, 128.3, 128.4, 128.4, 128.5, 128.6 (21×d, 44×Ar-C), 137.8, 138.0, 138.0, 138.2, 138.5, 138.5, 138.9, 138.9, 151.6, 155.1 (10×s, 10×Ar-C), 169.8, 170.3, 170.4, 170.5, 170.6 ppm (3×s, 5×C=O); IR (KBr): $\tilde{\nu}$ = 3419 (br, NH), 1747 cm^{-1} (s, C=O); MS (ESI): species observed: [M+Na]$^+$, [M+MeCN/NH_4]$^+$ (major); peaks observed: m/z (%): 1724.7 (87), 1725.7 (100), 1726.7 (48), 1727.7 (17), 1728.7 (5), 1729.7 (1); calcd for: 1724.7 (93), 1725.7 (100), 1726.7 (58), 1727.7 (24), 1728.7 (8), 1729.7 (2).

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***p*-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-acetamido-2-deoxy-β-D-glucopyranoside (23)**: Benzyl ether **22** (185 mg, 109 μmol) was dissolved in ethyl acetate (7 mL) and ethanol (7 mL). Palladium (10% on carbon, 65 mg) was added and the reaction mixture stirred at room temperature under an atmosphere of hydrogen. After 20 h, TLC (petrol/ethyl acetate 1:1) indicated formation of a major product (R_f=0) and complete consumption of starting material (R_f=0.15). The reaction mixture was poured onto Celite, washed with ethyl acetate (2×20 mL), ethanol (5×20 mL), filtered and concentrated in vacuo. The residue was dissolved in pyridine (7 mL), the solution cooled to 0°C and acetic anhydride (6 mL) added. The reaction mixture was stirred and allowed to warm to room temperature. After 19 h, TLC (ethyl acetate) indicated formation of a major product (R_f=0.4) and complete consumption of intermediate material (R_f=0). The reaction mixture was poured onto ice/water (10 mL) and extracted with CH_2Cl_2 (2×10 mL). The organic layers were washed with hydrochloric acid (2×20 mL of a 1 M solution), $NaHCO_3$ (2×20 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate) to give acetate **23** (117 mg, 82%) as a white amorphous foam. $[\alpha]_D^{24}$=+1 (*c*=0.2 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.97, 2.00, 2.06, 2.09, 2.11, 2.13, 2.14, 2.15, 2.15, 2.17, 2.20 (11×s, 39H; 13×C(O)CH$_3$), 3.57–3.59 (m, 1H; H-5b), 3.61 (dd, $^3J_{5b,6b}$=3.3, $^2J_{6b,6'b}$=11.2 Hz, 1H; H-6b), 3.76 (s, 3H; OCH$_3$), 3.80 (ddd, $^3J_{4a,5a}$=9.4, $^3J_{5a,6a}$=4.6, $^3J_{5a,6'a}$=2.4 Hz, 1H; H-5a), 3.85 (dd, $^3J_{5b,6'b}$=6.8 Hz, 1H; H-6′b), 3.92 (dd, $^3J_{2b,3b}$=4.3, $^3J_{3b,4b}$=9.1 Hz, 1H; H-3b), 3.93 (at, ^3J=9.1 Hz, 1H; H-4a), 4.04–4.14 (m, 3H; H-2a, H-5c, H-5d), 4.16 (dd, $^3J_{5c,6c}$=2.1, $^2J_{6c,6'c}$=12.4 Hz, 1H; H-6c), 4.21 (dd, $^3J_{5d,6d}$=2.1, $^2J_{6d,6'd}$=12.5 Hz, 1H; H-6d), 4.28 (dd, $^3J_{5c,6'c}$=4.4 Hz, 1H; H-6′c), 4.31–4.36 (m, 2H; H-6a, H-6′d), 4.39 (dd, $^2J_{6a,6'a}$=11.8 Hz, 1H; H-6′a), 4.72 (s, 1H; H-1b), 4.85 (s, 1H; H-1d), 5.00–5.01 (m, 2H; H-1c, H-2c), 5.03 (d, $^3J_{1a,2a}$=8.1 Hz, 1H; H-1a), 5.10 (at, ^3J=9.0 Hz, 1H; H-4b), 5.16 (dd, $^3J_{2c,3c}$=3.3, $^3J_{3c,4c}$=10.1 Hz, 1H; H-3c), 5.25–5.29 (m, 1H; H-3a), 5.29 (m, 2H; H-2d, H-3d), 5.31 (at, ^3J=9.9 Hz, 1H; H-4c), 5.37 (brs, 1H; H-2b), 5.37 (at, ^3J=10.0 Hz, 1H; H-4d), 5.95 (d, $^3J_{2a,NH}$=9.1 Hz, 1H; NH), 6.78–6.81 (m, 2H; 2×Ar-H), 6.91–6.94 ppm (m, 2H; 2×Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ=20.6, 20.6, 20.7, 20.7, 20.7, 20.7, 20.8, 20.8, 20.9, 21.0 (10×q, 12×OC(O)*C*H$_3$), 23.0 (q, NC(O)*C*H$_3$), 54.0 (d, C-2a), 55.6 (q, OCH$_3$), 62.2 (t, C-6d), 62.2 (t, C-6c), 62.5 (t, C-6a), 65.6 (d, C-4d), 65.6 (d, C-4c), 67.0 (t, C-6b), 68.2 (d, C-3c), 68.3 (d, C-4b), 68.8 (d, C-5d), 69.2, 69.3, 69.3 (3×d, C-2b, C-2d, C-3d), 69.4 (d, C-5c), 69.7 (d, C-2c), 71.9 (d, C-3a), 72.5 (d, C-5a), 72.8 (d, C-5b), 74.3 (d, C-4a), 75.5 (d, C-3b), 96.8 (d, ^1J(C,H)=160 Hz; C-1b), 97.2 (d, ^1J(C,H)=174 Hz; C-1d), 98.6 (d, ^1J(C,H)=175 Hz; C-1c), 100.1 (d, ^1J(C,H)=163 Hz; C-1a), 114.4, 118.3 (2×d, 4×Ar-C), 151.1, 155.4 (2×s, 2×Ar-C), 169.6, 169.8, 169.9, 170.0, 170.1, 170.2, 170.3, 170.5, 170.6, 170.6, 170.8, 170.8 ppm (12×s, 13×C=O); IR (KBr): $\tilde{\nu}$=3379 (br, NH), 1747, 1679 cm^{-1} (s, C=O); MS (ESI): species observed: [*M*+MeCN/NH$_4$]$^+$ (major), [*M*+Na]$^+$; peaks observed: *m/z* (%): 1340.4 (100), 1341.4 (62), 1342.4 (24), 1343.4 (6); calcd for: 1340.4 (100), 1341.4 (64), 1342.4 (27), 1343.4 (9).

2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-mannopyranosyl-(1→4)-2-acetamido-1,3,6-tri-*O*-acetyl-2-deoxy-D-glucopyranose (24): PMP-glycoside **23** (100 mg, 75.9 μmol) was dissolved in water (5 mL) and acetonitrile (10 mL). Ceric ammonium nitrate (125 mg, 228 μmol) was added and the solution stirred at room temperature. After 3 d, the reaction mixture was extracted with CH_2Cl_2 (2×20 mL). The organic portions were combined and washed with $NaHCO_3$ (2×20 mL of a saturated solution), sodium thiosulfate (2×10 mL of a 10% w/v solution), EDTA (2×30 mL of a 0.05 M solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate to ethyl acetate/methanol 9:1) and the product dissolved in pyridine (7 mL), the solution cooled to 0°C and acetic anhydride (5 mL) added. The reaction mixture was stirred and allowed to warm to room temperature. After 18 h, TLC (ethyl acetate) indicated formation of a major product (R_f=0.25) and complete consumption of starting material (R_f=0.4). The reaction mixture was poured onto ice/water (10 mL) and extracted with CH_2Cl_2 (2×10 mL). The organic layers were washed with hydrochloric acid (3×10 mL of a 1 M solution), $NaHCO_3$ (3×10 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate) to give peracetate **24** (65 mg, 70%) as a white foam and only the α anomer detected. ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.93, 1.98, 2.00, 2.05, 2.06, 2.07, 2.10, 2.11, 2.13, 2.17, 2.16, 2.20 (12×s, 42H; 14×C(O)CH$_3$), 3.61–3.66 (m, 1H; H-5b), 3.70 (dd, $^3J_{5b,6b}$=4.7, $^2J_{6b,6'b}$=10.7 Hz, 1H; H-6b), 3.93 (at, ^3J=9.3 Hz, 1H; H-4a), 3.93–4.01 (m, 4H; H-3b, H-5a, H-5d, H-6′b), 4.10–4.14 (m, 2H; H-5c, H-6c), 4.23 (dd, $^3J_{5d,6d}$=2.4, $^2J_{6d,6'd}$=12.4 Hz, 1H; H-6d), 4.25–4.39 (m, 5H; H-2a, H-6a, H-6′a, H-6′c, H-6′d), 4.80 (brs, 1H; H-1b), 4.84 (dd, $^3J_{1d,2d}$=1.2 Hz, 1H; H-1d), 5.00 (brs, 1H; H-1c), 5.02 (dd, $^3J_{1c,2c}$=1.8, $^3J_{2c,3c}$=3.3 Hz, 1H; H-2c), 5.08 (at, ^3J=7.4 Hz, 1H; H-4b), 5.12 (dd, $^3J_{3c,4c}$=10.2 Hz, 1H; H-3c), 5.27–5.39 (m, 6H; H-2b, H-2d, H-3a, H-3d, H-4c, H-4d), 5.87 (d, $^3J_{2a,NH}$=7.1 Hz, 1H; NH), 6.08 ppm (d, $^3J_{1a,2a}$=3.5 Hz, 1H; H-1a); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ=20.6, 20.7, 20.8, 20.8, 20.8, 20.9, 20.9, 21.1, 21.1 (9×q, 13×OC(O)*C*H$_3$), 23.0 (q, NC(O)*C*H$_3$), 50.8 (d, C-2a), 61.9, 62.2 (3×t, C-6a, C-6c, C-6d), 65.5 (d, C-4c), 66.0 (d, C-4d), 66.9 (t, C-6b), 68.4 (d, C-4b), 68.5 (d, C-3c), 68.7 (d, C-5d), 68.9 (d, C-2b), 69.1 (d, C-3d), 69.4 (2×d, C-2d, C-5c), 69.4 (d, C-2c), 70.3 (d, C-5a), 71.1 (d, C-3a), 72.7 (d, C-5b), 74.5 (2×d, C-3b, C-4a), 90.8 (d, ^1J(C,H)=181 Hz; C-1a), 97.1 (d, ^1J(C,H)=175 Hz; C-1d), 97.5 (d, ^1J(C,H)=163 Hz; C-1b), 98.0 (d, ^1J(C,H)=175 Hz; C-1c), 169.2, 169.8, 169.8, 169.9, 170.0, 170.1, 170.1, 170.3, 170.4, 170.6, 170.7, 170.8, 171.2, 171.3 ppm (14×s, 14×C=O); IR (KBr): $\tilde{\nu}$=3376 (br, NH), 1748, 1686 cm^{-1} (s, C=O); MS (ESI): species observed: [*M*+MeCN/NH$_4$]$^+$ (major), [*M*+Na]$^+$; peaks observed: *m/z* (%): 1276.4 (100), 1277.4 (57), 1278.4 (19), 1279.4 (4), 1280.4 (1); calcd for: 1276.4 (100), 1277.4 (59), 1278.4 (24), 1279.4 (7), 1280.4 (2).

2-Methyl-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano]-[2,1-*d*]-oxazoline (25): Peracetate **24** (50 mg, 39.9 μmol) was dissolved in dry DCE (10 mL) and transferred via cannula to a flame-dried round-bottomed flask. TMSBr (78.9 μL, 598 μmol), BF_3·OEt_2 (75.8 μL, 598 μmol) and 2,4,6-collidine (26.3 μL, 199 μmol) were added and the solution heated to 40°C, under an atmosphere of argon. After 26 h, TLC (ethyl acetate) indicated formation of a major product (R_f=0.45) and complete consumption of starting material (R_f=0.25). The reaction mixture was washed with $NaHCO_3$ (2×10 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate/Et_3N 400:1) to give protected oxazoline **25** (34.2 mg, 72%) as a white amorphous solid. $[\alpha]_D^{19}$=+16 (*c*=0.1 in $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6): δ=1.73, 1.73, 1.76, 1.77, 1.79, 1.82, 1.82, 1.96, 2.05, 2.09, 2.27 (11×s, 39H; 12×OC(O)CH$_3$, NC(O)CH$_3$), 3.77 (dd, $^3J_{5b,6b}$=3.5, $^2J_{6b,6'b}$=10.7 Hz, 1H; H-6b), 3.85 (ddd, $^3J_{4a,5a}$=8.6, $^3J_{5a,6a}$=2.7, $^3J_{5a,6'a}$=5.7 Hz, 1H; H-5a), 3.89–3.94 (m, 2H; H-4a, H-5b), 4.02 (dd, $^3J_{2b,3b}$=3.5, $^3J_{3b,4b}$=9.6 Hz, 1H; H-3b), 4.19 (dd, $^3J_{5b,6'b}$=6.8 Hz, 1H; H-6′b), 4.26–4.28 (m, 1H; H-2a), 4.35 (dd, $^3J_{5d,6d}$=2.3, $^2J_{6d,6'd}$=12.4 Hz, 1H; H-6d), 4.44 (dd, $^2J_{6a,6'a}$=11.8 Hz, 1H; H-6a), 4.47 (ddd, $^3J_{4d,5d}$=10.1, $^3J_{5d,6'd}$=4.3 Hz, 1H; H-5d), 4.63 (dd, 1H; H-6′a), 4.63 (dd, $^3J_{5c,6c}$=2.8, $^2J_{6c,6'c}$=11.6 Hz, 1H; H-6c), 4.66 (ddd, $^3J_{4c,5c}$=9.9, $^3J_{5c,6'c}$=6.8 Hz, 1H; H-5c), 4.72–4.77 (m, 2H; H-6′c, H-6′d), 4.90 (d, $^3J_{1d,2d}$=1.3 Hz, 1H; H-1d), 5.05 (s, 1H; H-1b), 5.34 (d, $^3J_{1c,2c}$=1.6 Hz, 1H; H-1c), 5.51 (dd, $^3J_{2c,3c}$=3.3 Hz, 1H; H-2c), 5.67 (at, ^3J=9.6 Hz, 1H; H-4b), 5.73 (dd, $^3J_{2d,3d}$=3.3 Hz, 1H; H-2d), 5.78 (dd, $^3J_{3c,4c}$=10.2 Hz, 1H; H-3c), 5.81–5.85 (m, 2H; H-1a, H-3d), 5.88 (brd, 1H; H-2b), 5.90 (at, ^3J=10.0 Hz, 1H; H-4d), 5.93 (at, ^3J=10.0 Hz, 1H; H-4c), 6.13 ppm (brd, $^3J_{2a,3a}$=2.4 Hz, 1H; H-3a); ^{13}C NMR (125.8 MHz, C_6D_6): δ=13.4 (q, NC(O)*C*H$_3$), 20.2, 20.2, 20.3, 20.3, 20.4, 20.5, 20.5, 20.5, 20.6, 20.9 (10×q, 12×OC(O)*C*H$_3$), 62.4 (t, C-6c), 62.7 (t, C-6d), 64.3 (t, C-6a), 65.2 (d, C-2a), 66.3 (d, C-4d), 66.7 (d, C-4c), 67.7 (t, C-6b), 68.5 (d, C-5a), 68.9 (d, C-3c), 69.2 (d, C-4b), 69.4 (d, C-5d), 70.0, 70.0, 70.1 (3×d, C-2d, C-3a, C-3d), 70.4 (d, C-5c), 70.5 (d, C-2b), 70.9 (d, C-2c), 73.4 (d, C-5b), 76.7 (d, C-3b), 78.0 (d, C-4a), 98.1 (d, ^1J(C,H)=174 Hz; C-1d), 99.3 (d, ^1J(C,H)=174 Hz; C-1c), 99.6 (d, ^1J(C,H)=184 Hz; C-1a), 99.9 (d, ^1J(C,H)=159 Hz; C-1b), 166.1 (s, C=N), 169.2, 169.3, 169.7, 169.7, 169.7, 169.8, 170.0, 170.1, 170.3, 170.3, 170.4, 170.9 ppm (12×s, 12×C=O); IR (KBr): $\tilde{\nu}$=1748, 1676 cm^{-1} (s, C=O, C=N); MS (ESI): species observed: [*M*+MeCN/NH$_4$]$^+$ (major), [*M*+Na]$^+$; peaks observed: *m/z* (%): 1216.3

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(100), 1217.3 (57), 1218.4 (21), 1219.4 (4), 1220.4 (1); calcd for: 1216.4 (100), 1217.4 (56), 1218.4 (22), 1219.4 (7), 1220.4 (2).

2-Methyl-[α-D-mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→6)]-β-D-mannopyranosyl-(1→4)-α-D-glucopyrano]-[2,1-*d*]-oxazoline (4): Acetylated oxazoline **25** (26 mg, 21.8 μmol) was dissolved in dry methanol (5 mL). Methanolic sodium methoxide (100 μL of a 10 mg mL^{-1} solution, 43.5 μmol) was added and the solution stirred at room temperature, under an atmosphere of argon. After 13 h, mass spectrometry indicated one product. The solution was concentrated in vacuo to yield deprotected oxazoline **4** (17.3 mg, quant.) as a white amorphous solid. ^{1}H NMR (500 MHz, D_2O): δ = 1.98 (d, $^{5}J_{2a,CH_3}$ = 1.7 Hz, 3H; CH_3), 3.32 (ddd, $^{3}J_{4a,5a}$ = 8.8, $^{3}J_{5a,6a}$ = 6.3, $^{3}J_{5a,6'a}$ = 2.5 Hz, 1H; H-5a), 3.50 (ddd, $^{3}J_{4b,5b}$ = 9.6, $^{3}J_{5b,6b}$ = 1.6, $^{3}J_{5b,6'b}$ = 5.5 Hz, 1H; H-5b), 3.53–3.72 (m, 11H; H-3b, H-4a, H-4b, H-4c, H-4d, H-5c, H-5d, H-6a, H-6c, H-6d, H-6′a), 3.74 (dd, $^{2}J_{6b,6'b}$ = 11.1 Hz, 1H; H-6b), 3.78 (dd, $^{3}J_{2d,3d}$ = 3.4, $^{3}J_{3d,4d}$ = 9.2 Hz, 1H; H-3d), 3.80–3.82 (m, 2H; H-3c, H-6′c), 3.83 (dd, $^{3}J_{5d,6'd}$ = 1.7, $^{2}J_{6d,6'd}$ = 11.8 Hz, 1H; H-6′d), 3.88 (dd, 1H; H-6′b), 3.93 (dd, $^{3}J_{1d,2d}$ = 1.5 Hz, 1H; H-2d), 3.98 (dd, $^{3}J_{1c,2c}$ = 1.4, $^{3}J_{2c,3c}$ = 3.2 Hz, 1H; H-2c), 4.07 (br d, J = 2.9 Hz, 1H; H-2b), 4.10–4.12 (m, 1H; H-2a), 4.30 (dd, ^{3}J = 1.6, ^{3}J = 3.0 Hz, 1H; H-3a), 4.65 (s, 1H; H-1b), 4.86 (d, 1H; H-1d), 5.01 (d, 1H; H-1c), 6.01 ppm (d, $^{3}J_{1a,2a}$ = 7.3 Hz, 1H; H-1a); ^{13}C NMR (125.8 MHz, D_2O): δ = 12.9 (q, CH_3), 60.9 (t, C-6d), 61.1 (t, C-6c), 61.7 (t, C-6a), 65.1 (d, C-2a), 65.6 (t, C-6b), 65.7 (d, C-4b), 66.8 (d, C-4d), 66.8 (d, C-4c), 69.0 (d, C-3a), 69.8 (d, C-2d), 70.0 (d, C-2c), 70.2 (d, C-2b), 70.3 (d, C-3c), 70.5 (d, C-3d), 70.9 (d, C-5a), 72.7 (d, C-5d), 73.3 (d, C-5c), 74.3 (d, C-5b), 77.8 (d, C-4a), 80.6 (d, C-3b), 99.5 (d, ^{1}J(C,H) = 174 Hz; C-1d), 99.9 (d, ^{1}J(C,H) = 186 Hz; C-1a), 101.3 ppm (d, ^{1}J(C,H) = 160 Hz; C-1b), 102.5 (d, ^{1}J(C,H) = 174 Hz; C-1c), 168.6 (s, C=N); IR (KBr): $\tilde{\nu}$ = 3423 (br, OH), 1668 cm^{-1} (br s, C=N); HRMS (ESI): m/z: calcd for $C_{26}H_{43}NNaO_{20}$: 712.2271; found 712.2268 $[M+Na]^+$.

***p*-Methoxyphenyl 2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidine-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (27)**: Alcohol **26** (575 mg, 614 μmol) was dissolved in pyridine (8 mL) and the solution cooled to 0 °C. Acetic anhydride (10 mL) was added and the reaction mixture stirred and allowed to warm up to room temperature. After 15 h, TLC (ethyl acetate/petrol 1:1) indicated formation of a major product (R_f = 0.55) and full consumption of starting material (R_f = 0.45). The reaction mixture was added to water (20 mL) and extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were washed with hydrochloric acid (20 mL of a 1 M solution), $NaHCO_3$ (2 × 20 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was crystallised (ethyl acetate/petrol) to give acetate **27** (521 mg, 87 %) as white crystals. M.p. 111–113 °C (ethyl acetate/petrol); $[\alpha]_D^{19}$ = +38 (c = 0.5 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.99 (s, 3H; OC(O)CH_3), 3.25 (dat, ^{3}J = 4.9, ^{3}J = 9.7, ^{3}J = 9.7 Hz, 1H; H-5b), 3.50 (at, J = 10.3 Hz, 1H; H-6b), 3.58 (at, ^{3}J = 9.2 Hz, 1H; H-3b), 3.61 (dat, $^{3}J_{4a,5a}$ = 10.0, ^{3}J = 2.6 Hz, 1H; H-5a), 3.67 (at, ^{3}J = 9.3 Hz, 1H; H-4b), 3.71 (s, 3H; OCH_3), 3.78 (br d, J = 2.4 Hz, 2H; H-6a, H-6′a), 4.12 (at, ^{3}J = 8.8 Hz, 1H; H-4a), 4.27–4.32 (m, 2H; H-3a, H-6′b), 4.39 (dd, $^{3}J_{1a,2a}$ = 8.5, $^{3}J_{2a,3a}$ = 10.8 Hz, 1H; H-2a), 4.45, 4.78 (ABq, ^{2}J = 12.7 Hz, 2H; $PhCH_2$), 4.48, 4.77 (ABq, ^{2}J = 12.1 Hz, 2H; $PhCH_2$), 4.60 (d, $^{3}J_{1b,2b}$ = 8.1 Hz, 1H; H-1b), 4.65, 4.88 (ABq, ^{2}J = 12.1 Hz, 2H; $PhCH_2$), 5.00 (dd, $^{3}J_{2b,3b}$ = 9.0 Hz, 1H; H-2b), 5.49 (s, 1H; PhCH(O)), 5.61 (d, 1H; H-1a), 6.68–6.70 (m, 2H; 2 × Ar-H), 6.80–6.82 (m, 2H; 2 × Ar-H), 6.88–6.93 (m, 3H; 3 × Ar-H), 7.02–7.04 (m, 2H; 2 × Ar-H), 7.28–7.50 (m, 15H; 15 × Ar-H), 7.63–7.82 ppm (m, 4H; 4 × Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 20.9 (q, OC(O)CH_3), 55.5 (q, OCH_3), 55.5 (d, C-2a), 65.9 (d, C-5b), 67.5 (t, C-6a), 68.6 (t, C-6b), 73.3 (d, C-2b), 73.6, 74.1, 74.7 (3 × t, 3 × $PhCH_2$), 75.1 (d, C-5a), 76.7 (d, C-3a), 78.0 (d, C-4a), 78.5 (d, C-3b), 81.7 (d, C-4b), 97.6 (d, ^{1}J(C,H) = 166 Hz; C-1a), 100.8 (d, ^{1}J(C,H) = 165 Hz; C-1b), 101.2 (d, PhCH(O)), 114.3, 118.7, 123.3, 126.0, 127.1, 127.6, 127.7, 127.8, 127.9, 127.9, 128.0, 128.3, 128.3, 128.5, 129.0, (15 × d, 26 × Ar-C), 131.6 (s, 2 × Ar-C), 133.7 (d, 2 × Ar-C), 137.2, 137.8, 138.3, 138.3, 150.8, 155.3 (6 × s, 6 × Ar-C), 169.1 ppm (s, 3 × C=O); IR (KBr): $\tilde{\nu}$ = 1777, 1753, 1716 cm^{-1} (s, C=O); HRMS (ESI): m/z: calcd for $C_{57}H_{59}N_2O_{14}$: 995.3961; found 995.3925 $[M+NH_4]^+$.

***p*-Methoxyphenyl 2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (28)**: Benzylidene acetal **27** (50 mg, 51.1 μmol) was added to a flask containing activated 4 Å molecular sieves and anhydrous CH_2Cl_2 (2 mL) added. The solution was stirred for 30 min at room temperature and then cooled to −78 °C. Et_3SiH (24.5 μL, 153 μmol) and $PhBCl_2$ (22.6 μL, 174 μmol) were added successively. After 1 h, TLC (ethyl acetate/petrol 2:1) indicated formation of a major product (R_f = 0.65) and full consumption of starting material (R_f = 0.75). Triethylamine (100 μL) and methanol (100 μL) were added successively and the reaction mixture diluted with CH_2Cl_2 (5 mL) and washed with $NaHCO_3$ (2 × 5 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate/petrol 1:1) to yield alcohol **28** (49.7 mg, quant.) as a white amorphous solid. $[\alpha]_D^{19}$ = +43 (c = 0.5 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.94 (s, 3H; OC(O)CH_3), 3.26 (ddd, $^{3}J_{4b,5b}$ = 8.7, $^{3}J_{5b,6b}$ = 5.5, $^{3}J_{5b,6'b}$ = 2.4 Hz, 1H; H-5b), 3.41 (dd, $^{2}J_{6b,6'b}$ = 12.1 Hz, 1H; H-6b), 3.52 (at, ^{3}J = 8.6 Hz, 1H; H-4b), 3.55 (at, ^{3}J 8.7 Hz, 1H; H-3b), 3.63 (dat, $^{3}J_{4a,5a}$ = 10.0, ^{3}J = 2.5 Hz, 1H; H-5a), 3.70–3.74 (s, 4H; H-6′b, OCH_3), 3.78 (br d, J = 2.5 Hz, 2H; H-6a, H-6′a), 4.09 (at, ^{3}J = 9.3 Hz, 1H; H-4a), 4.32 (dd, $^{3}J_{2a,3a}$ = 10.8, $^{3}J_{3a,4a}$ = 8.6 Hz, 1H; H-3a), 4.41 (dd, $^{3}J_{1a,2a}$ = 8.4 Hz, 1H; H-2a), 4.48, 4.84 (ABq, ^{2}J = 12.3 Hz, 2H; $PhCH_2$), 4.51, 4.75 (ABq, ^{2}J = 12.0 Hz, 2H; $PhCH_2$), 4.56 (d, $^{3}J_{1b,2b}$ = 8.2 Hz, 1H; H-1b), 4.58, 4.77 (ABq, ^{2}J = 11.2 Hz, 2H; $PhCH_2$), 4.64, 4.80 (ABq, ^{2}J = 11.4 Hz, 2H; $PhCH_2$), 4.97 (at, ^{3}J = 8.6 Hz, 1H; H-2b), 5.62 (d, 1H; H-1a), 6.68–6.70 (m, 2H; 2 × Ar-H), 6.80–6.82 (m, 2H; 2 × Ar-H), 6.94–6.98 (m, 3H; 3 × Ar-H), 7.05–7.06 (m, 2H; 2 × Ar-H), 7.26–7.36 (m, 15H; 15 × Ar-H), 7.64–7.77 ppm (m, 4H; 4 × Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 20.9 (q, OC(O)CH_3), 55.5 (d, C-2a), 55.6 (q, OCH_3), 61.8 (t, C-6b), 67.5 (t, C-6a), 73.5 (d, C-2b), 73.7, 74.5, 74.9 (3 × t, 3 × $PhCH_2$), 75.1 (d, C-5a), 75.1 (t, $PhCH_2$), 75.3 (d, C-5b), 76.6 (d, C-3a), 77.8 (d, C-4a), 78.0 (d, C-4b), 82.8 (d, C-3b), 97.6 (d, ^{1}J(C,H) = 167 Hz; C-1a), 100.2 (d, ^{1}J(C,H) = 163 Hz; C-1b), 114.3, 118.7, 123.4, 127.3, 127.4, 127.6, 127.7, 127.9, 127.9, 128.0, 128.0, 128.1, 128.4, 128.5, 128.5 (15 × d, 26 × Ar-C), 131.2 (s, 2 × Ar-C), 133.8 (d, 2 × Ar-C), 137.7, 137.8, 138.1, 138.2, 150.8, 155.3 (6 × s, 6 × Ar-C), 169.3 ppm (s, 3 × C=O); IR (KBr): $\tilde{\nu}$ = 3476 (br, OH), 1776, 1749, 1716 cm^{-1} (s, C=O); HRMS (ESI): m/z: calcd for $C_{57}H_{61}N_2O_{14}$: 997.4117; found 997.4081 $[M+NH_4]^+$.

***p*-Methoxyphenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)-2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (29)**: Alcohol **28** (335 mg, 342 μmol) and **14** (239 mg, 376 μmol) were dissolved in dry CH_2Cl_2 (10 mL) and transferred via cannula to a flame-dried round-bottomed flask containing activated 4 Å molecular sieves (100 mg). The solution was cooled to −60 °C and stirred under an atmosphere of argon. TMSOTf (6.19 μL, 34.2 μmol) was added and the temperature allowed to rise to 0 °C after 3 h. After 14 h, TLC (petrol/ethyl acetate 1:1) indicated formation of a major product (R_f = 0.5) and complete consumption of acceptor **28** (R_f = 0.35). Triethylamine (50 μL) was added and the solution stirred for a further 10 min. The reaction mixture was then filtered through Celite and the filtrate concentrated in vacuo. The residue was purified by flash column chromatography (petrol/ethyl acetate 1:1) to give trisaccharide **29** (490 mg, 99 %) as a white foam. $[\alpha]_D^{19}$ = +47 (c = 0.5 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.90, 1.98 (2 × s, 6H; 2 × OC(O)CH_3), 3.36 (dat, $^{3}J_{4b,5b}$ = 9.7, ^{3}J = 2.3 Hz, 1H; H-5b), 3.51–3.55 (m, 1H; H-6c), 3.53 (at, ^{3}J = 9.2 Hz, 1H; H-3b), 3.59–3.63 (m, 2H; H-4b, H-5a), 3.65 (dd, $^{3}J_{5c,6'c}$ = 4.3, $^{2}J_{6c,6'c}$ = 10.8 Hz, 1H; H-6′c), 3.67–3.70 (m, 4H; H-5c, OCH_3), 3.76–3.85 (m, 5H; H-4c, H-6a, H-6b, H-6′a, H-6′b), 3.86 (dd, $^{3}J_{2c,3c}$ = 3.1, $^{3}J_{3c,4c}$ = 9.3 Hz, 1H; H-3c), 4.10 (dd, $^{3}J_{3a,4a}$ = 8.4, $^{3}J_{4a,5a}$ = 9.7 Hz, 1H; H-4a), 4.24 (dd, $^{3}J_{2a,3a}$ = 10.6 Hz, 1H; H-3a), 4.32–4.36 (m, 2H; H-2a, PhCH), 4.41, 4.58 (ABq, ^{2}J = 11.9 Hz, 2H; $PhCH_2$), 4.45, 4.82 (ABq, ^{2}J = 11.1 Hz, 2H; $PhCH_2$), 4.50 (d, ^{2}J = 11.2 Hz, 1H; PhCH), 4.50, 4.79 (ABq, ^{2}J = 11.1 Hz, 2H; $PhCH_2$), 4.52, 4.74 (ABq, ^{2}J = 12.1 Hz, 2H; $PhCH_2$), 4.55, 4.75 (ABq, ^{2}J = 12.8 Hz, 2H; $PhCH_2$), 4.58 (d, $^{3}J_{1b,2b}$ = 8.5 Hz, 1H; H-1b), 4.64, 4.75 (ABq, ^{2}J = 11.2 Hz, 2H; $PhCH_2$), 4.89 (d, $^{3}J_{1c,2c}$ = 1.7 Hz, 1H; H-1c), 5.04 (dd, $^{3}J_{2b,3b}$ = 9.4 Hz, 1H; H-2b), 5.24 (dd, 1H; H-2c), 5.57 (d, $^{3}J_{1a,2a}$ = 8.5 Hz, 1H; H-1a), 6.65–6.67 (m, 2H; 2 × Ar-H), 6.72–6.73 (m, 3H; 3 × Ar-H), 6.77–6.79 (m, 2H; 2 × Ar-H), 6.98–7.00 (m, 2H; 2 × Ar-H), 7.12–7.36 (m, 30H; 30 × Ar-H), 7.47–7.74 ppm (m, 4H; 4 × Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 20.8, 20.9 (2 × q, 2 × C(O)CH_3), 55.5 (q, OCH_3), 55.6 (d, C-2a), 66.2 (t, C-6b), 67.7 (t, C-6a), 68.2 (d, C-2c), 68.8 (t, C-6c), 71.5 (t, $PhCH_2$), 71.8 (d, C-5c), 73.3, 73.6

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(2×t, 2×PhCH$_2$), 73.6 (d, C-2b), 74.1 (d, C-4c), 74.3 (d, C-5b), 74.4, 74.7, 74.9, 75.1 (4×t, 4×PhCH$_2$), 75.2 (d, C-5a), 76.0 (d, C-3a), 77.5 (d, C-4b), 77.6 (d, C-3c), 78.4 (d, C-4a), 83.2 (d, C-3b), 97.5 (d, ^1J(C,H)=166 Hz; C-1a), 98.2 (d, ^1J(C,H)=174 Hz; C-1c), 100.5 (d, ^1J(C,H)=163 Hz; C-1b), 114.3, 118.6, 123.2, 127.0, 127.3, 127.4, 127.6, 127.7, 127.7, 127.8, 127.9, 127.9, 128.1, 128.1, 128.2, 128.2, 128.3, 128.4, 128.5, 128.5, 128.6 (21×d, 41×Ar-C), 131.6 (s, 2×Ar-C), 133.5 (d, 2×Ar-C), 137.8, 138.0, 138.0, 138.1, 138.2, 138.3, 138.6, 150.8, 155.2 (9×s, 9×Ar-C), 169.3, 169.9 ppm (2×s, 4×C=O); IR (KBr): $\tilde{\nu}$=1749, 1716 cm^{-1} (s, C=O); MS (ESI): species observed: [*M*+MeCN/NH$_4$]$^+$ (major), [*M*+Na]$^+$; peaks observed: *m*/*z* (%): 1476.6 (100), 1477.6 (94), 1478.6 (41), 1479.6 (11), 1480.6 (3); calcd for: 1476.6 (100), 1477.6 (95), 1478.6 (49), 1479.6 (18), 1480.6 (5).

***p*-Methoxyphenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)-2-*O*-acetyl-3,4-di-*O*-benzyl-β-D-glucopyranosyl-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (30)**: Phthalimide protected trisaccharide **29** (465 mg, 320 μmol) was dissolved in methanol (10 mL), ethylene diamine (8.55 mL, 128 mmol) added and the solution refluxed at 65 °C. After 19 h, TLC (petrol/ethyl acetate 1:1) indicated formation of a major product (R_f=0) and complete consumption of starting material (R_f=0.5). The reaction mixture was concentrated in vacuo, and the residue dissolved in pyridine (7 mL). The solution was cooled to 0 °C, acetic anhydride (6 mL) added and the reaction mixture stirred and allowed to warm to room temperature. After 18 h, TLC (petrol/ethyl acetate 1:1) indicated formation of a major product (R_f=0.2) and complete consumption of starting material (R_f=0.5). The reaction mixture was poured onto ice/water (10 mL) and extracted with CH_2Cl_2 (2×10 mL). The organic layers were washed with hydrochloric acid (2×10 mL of a 1 M solution), $NaHCO_3$ (2×10 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (petrol/ethyl acetate 1:1) to afford acetamide **30** (367 mg, 84 %) as a white foam. $[\alpha]_D^{19}$=−8 (*c*=0.5 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.88, 1.96, 2.09 (3×s, 9H; C(O)CH$_3$), 3.40 (ddd, $^3J_{4b,5b}$=9.7, $^3J_{5b,6b}$=1.5, $^3J_{5b,6'b}$=4.6 Hz, 1H; H-5b), 3.45 (dd, $^3J_{5c,6c}$=1.3, $^2J_{6c,6'c}$=10.8 Hz, 1H; H-6c), 3.56 (at, ^3J=9.3 Hz, 1H; H-4b), 3.62 (dd, $^3J_{5c,6'c}$=4.1 Hz, 1H; H-6′c), 3.65 (at, ^3J=9.1 Hz, 1H; H-3b), 3.69 (dd, $^2J_{6b,6'b}$=11.3 Hz, 1H; H-6b), 3.72 (dd, $^3J_{5a,6a}$=5.2, $^2J_{6a,6'a}$=10.2 Hz, 1H; H-6a), 3.74–3.78 (m, 5H; H-5a, H-5c, OCH$_3$), 3.80 (dd, 1H; H-6′b), 3.85–3.94 (m, 4H; H-3a, H-3c, H-4c, H-6′a), 4.04 (m, 1H; H-4a), 4.12–4.16 (m, 1H; H-2a), 4.35 (d, ^2J=11.8 Hz, 1H; PhCH), 4.38, 4.60 (ABq, ^2J=12.1 Hz, 2H; PhCH$_2$), 4.42–4.45 (m, 4H; H-1b, 3×PhCH), 4.52, 4.82 (ABq, ^2J=11.2 Hz, 2H; PhCH$_2$), 4.60 (d, ^2J=11.0 Hz, 1H; PhCH), 4.65, 4.74 (ABq, ^2J=11.7 Hz, 2H; PhCH$_2$), 4.67, 4.78 (ABq, ^2J=11.5 Hz, 2H; PhCH$_2$), 4.84 (d, ^2J=10.8 Hz, 1H; PhCH), 4.92 (d, $^3J_{1c,2c}$=1.6 Hz, 1H; H-1c), 4.99 (dd, $^3J_{1b,2b}$=8.3, $^3J_{2b,3b}$=9.3 Hz, 1H; H-2b), 5.23 (d, $^3J_{1a,2a}$=4.6 Hz, 1H; H-1a), 5.38 (dd, $^3J_{2c,3c}$=2.8 Hz, 1H; H-2c), 5.99 (d, $^3J_{2a,NH}$=8.6 Hz, 1H; NH), 6.77–6.78 (m, 2H; 2×Ar-H), 6.90–6.92 (m, 2H; 2×Ar-H), 7.12–7.14 (m, 2H; 2×Ar-H), 7.19–7.35 ppm (m, 33H; 33×Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ=21.0, 21.0 (2×q, 2×OC(O)*C*H$_3$), 23.2 (q, NC(O)*C*H$_3$), 50.6 (d, C-2a), 55.6 (q, OCH$_3$), 66.0 (t, C-6b), 68.5 (d, C-2c), 68.7 (t, C-6c), 69.6 (t, C-6a), 71.6 (d, C-5c), 71.7, 72.5, 73.3, 73.4 (4×t, 4×PhCH$_2$), 73.6 (d, C-2b), 73.8 (d, C-4a), 74.3 (d, C-4c), 74.3 (d, C-5b), 74.4 (d, C-5a), 74.9, 75.2, 75.3 (3×t, 3×PhCH$_2$), 76.0 (d, C-3a), 77.6 (d, C-4b), 77.9 (d, C-3c), 82.8 (d, C-3b), 98.1 (d, ^1J(C,H)=174 Hz; C-1c), 98.6 (d, ^1J(C,H)=168 Hz; C-1a), 99.1 (d, ^1J(C,H)=160 Hz; C-1b), 114.4, 117.7, 127.5, 127.5, 127.6, 127.7, 127.8, 127.8, 127.9, 127.9, 127.9, 128.2, 128.2, 128.3, 128.4, 128.4, 128.5, (17×d, 39×Ar-C), 137.7, 137.7, 137.9, 138.0, 138.2, 138.5, 138.6, 151.3, 154.8 (9×s, 9×Ar-C), 170.2, 170.3, 170.3 ppm (3×s, 3×C=O); IR (KBr): $\tilde{\nu}$=3406 (br, NH), 1748, 1676 cm^{-1} (s, C=O); MS (ESI): species observed: [*M*+MeCN/NH$_4$]$^+$ (major), [*M*+Na]$^+$; peaks observed: *m*/*z* (%): 1388.5 (100), 1389.5 (84), 1390.5 (34), 1391.6 (10); calcd for: 1388.6 (100), 1389.6 (89), 1390.6 (43), 1391.6 (15).

***p*-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranoside (31)**: Benzyl ether **30** (340 mg, 249 μmol) was dissolved in ethyl acetate (15 mL) and ethanol (15 mL). Palladium (10 % on carbon, 105 mg) was added and the reaction mixture stirred at room temperature under an atmosphere of hydrogen. After 16 h, TLC (ethyl acetate) indicated formation of a major product (R_f=0) and complete consumption of starting material (R_f=0.75). The reaction mixture was poured onto Celite, washed with ethyl acetate (3×20 mL) and ethanol (5×20 mL), filtered and concentrated in vacuo. The residue was dissolved in pyridine (8 mL), the solution cooled to 0 °C and acetic anhydride (7 mL) added. The reaction mixture was stirred and allowed to warm to room temperature. After 4.5 h, TLC (ethyl acetate) indicated formation of a major product (R_f=0.3) and complete consumption of intermediate material (R_f=0). The reaction mixture was poured onto ice/water (10 mL) and extracted with CH_2Cl_2 (2×10 mL). The organic layers were washed with hydrochloric acid (2×20 mL of a 1 M solution), $NaHCO_3$ (2×20 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate) to give acetate **31** (229 mg, 89 %) as a white amorphous foam. $[\alpha]_D^{19}$=+32 (*c*=0.5 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.83, 1.92, 2.03, 2.04, 2.08, 2.09, 2.10, 2.11, 2.17 (9×s, 30H; 10×C(O)CH$_3$), 3.36 (dd, $^3J_{5b,6b}$=1.6, $^2J_{6b,6'b}$=11.0 Hz, 1H; H-6b), 3.74 (dd, $^3J_{5b,6'b}$=2.8 Hz, 1H; H-6′b), 3.76 (s, 3H; OCH$_3$), 3.76–3.79 (m, 1H; H-5c), 3.86 (dat, $^3J_{4b,5b}$=10.9, ^3J=2.0 Hz, 1H; H-5b), 3.91 (at, ^3J=8.8 Hz, 1H; H-4a), 4.07 (dd, $^3J_{5c,6c}$=2.4, $^2J_{6c,6'c}$=12.2 Hz, 1H; H-6c), 4.15 (ddd, $^3J_{4a,5a}$=9.3, $^3J_{5a,6a}$=2.0, $^3J_{5a,6'a}$=4.5 Hz, 1H; H-5a), 4.27 (dd, $^3J_{5c,6'c}$=5.8 Hz, 1H; H-6′c), 4.33–4.38 (m, 2H; H-2a, H-6a), 4.52 (dd, $^2J_{6a,6'a}$=11.9 Hz, 1H; H-6′a), 4.76 (at, ^3J=3.5 Hz, 1H; H-2b), 4.86 (br d, $^3J_{1c,2c}$=1.2 Hz, 1H; H-1c), 4.93 (d, $^3J_{1b,2b}$=3.9 Hz, 1H; H-1b), 5.06 (dd, $^3J_{2b,3b}$=3.0, $^3J_{3b,4b}$=8.3 Hz, 1H; H-3b), 5.13 (dd, $^3J_{2a,3a}$=10.0, $^3J_{3a,4a}$=8.6 Hz, 1H; H-3a), 5.21 (dd, $^3J_{2c,3c}$=3.3, $^3J_{3c,4c}$=10.2 Hz, 1H; H-3c), 5.23 (d, $^3J_{1a,2a}$=8.1 Hz, 1H; H-1a), 5.28 (at, ^3J=10.0 Hz, 1H; H-4c), 5.67 (dd, 1H; H-4b), 5.72 (dd, 1H; H-2c), 6.31 (d, $^3J_{2a,NH}$=9.9 Hz, 1H; NH), 6.79–6.80 (m, 2H; 2×Ar-H), 6.98–7.00 ppm (m, 2H; 2×Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ=20.7, 20.7, 20.7, 20.7, 20.8, 21.0 (6×q, 9×OC(O)*C*H$_3$), 23.0 (q, NC(O)*C*H$_3$), 53.2 (d, C-2a), 55.7 (q, OCH$_3$), 62.5 (t, C-6a), 62.6 (t, C-6c), 65.4 (d, C-4c), 66.4 (t, C-6b), 67.6 (d, C-4b), 68.8 (d, C-5c), 69.1 (d, C-2c), 69.9 (d, C-3c), 70.7 (d, C-5b), 71.7 (d, C-5a), 72.7 (d, C-2b), 73.4 (d, C-3b), 74.9 (d, C-3a), 75.3 (d, C-4a), 98.0 (d, ^1J(C,H)=171 Hz; C-1b), 98.5 (d, ^1J(C,H)=176 Hz; C-1c), 99.4 (d, ^1J(C,H)=164 Hz; C-1a), 114.3, 117.7 (2×d, 4×Ar-C), 151.5, 155.0 (2×s, 2×Ar-C), 169.2, 169.3, 169.8, 170.3, 170.5, 170.5, 170.6, 170.8, 171.0 ppm (9×s, 10×C=O); IR (KBr): $\tilde{\nu}$=3387 (br, NH), 1749, 1672 cm^{-1} (s, C=O); MS (ESI): species observed: [*M*+MeCN/NH$_4$]$^+$ (major), [*M*+Na]$^+$; peaks observed: *m*/*z* (%): 1052.3 (100), 1053.3 (49), 1054.3 (12), 1055.3 (2); calcd for: 1052.3 (100), 1053.3 (51), 1054.3 (18), 1055.3 (5).

2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2-acetamido-1,3,6-tri-*O*-acetyl-2-deoxy-D-glucopyranose (32): PMP glycoside **31** (203 mg, 197 μmol) was dissolved in water (5 mL) and acetonitrile (10 mL). Ceric ammonium nitrate (324 mg, 591 μmol) was added and the solution stirred at room temperature. After 3 d, the reaction mixture was extracted with CH_2Cl_2 (2×20 mL). The organic portions were combined and washed with $NaHCO_3$ (2×20 mL of a saturated solution), sodium thiosulfate (2×10 mL of a 10 % w/v solution), EDTA (2×30 mL of a 0.05 M solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate to ethyl acetate/methanol 9:1) and the product dissolved in pyridine (7 mL), the solution cooled to 0 °C and acetic anhydride (5 mL) added. The reaction mixture was stirred and allowed to warm to room temperature. After 19 h, TLC (ethyl acetate) indicated formation of a major product (R_f=0.3) and complete consumption of starting material (R_f=0.45). The reaction mixture was poured onto ice/water (15 mL) and extracted with CH_2Cl_2 (2×10 mL). The organic layers were washed with hydrochloric acid (3×30 mL of a 1 M solution), $NaHCO_3$ (2×10 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate) to give peracetate **32** (168 mg, 88 %) as a white foam and only the α anomer detected. ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.91, 2.01, 2.01, 2.05, 2.06, 2.07, 2.12, 2.13, 2.17, 2.18 (10×s, 33H; 11×C(O)CH$_3$), 3.62 (dd, $^3J_{5b,6b}$=3.2, $^2J_{6b,6'b}$=11.1 Hz, 1H; H-6b), 3.69 (ddd, $^3J_{4b,5b}$=9.6, $^3J_{5b,6'b}$=5.2 Hz, 1H; H-5b), 3.78 (dd, 1H; H-6′b), 3.89–3.95 (m, 3H; H-4a, H-5a, H-5c), 4.12 (dd, $^3J_{5c,6c}$=2.6, $^2J_{6c,6'c}$=12.4 Hz, 1H; H-6c), 4.15 (dd, $^3J_{5a,6a}$=4.0, $^2J_{6a,6'a}$=12.2 Hz, 1H; H-6a), 4.27 (dd, $^3J_{5c,6'c}$=5.1 Hz, 1H; H-6′c), 4.34 (ddd, $^3J_{1a,2a}$=3.6, $^3J_{2a,3a}$=11.0, $^3J_{2a,NH}$=9.0 Hz, 1H; H-2a), 4.43 (dd, $^3J_{5a,6'a}$=1.2 Hz, 1H; H-6′a), 4.61 (d, $^3J_{1b,2b}$=7.7 Hz,

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1H; H-1b), 4.85 (d, $^3J_{1c,2c}$=1.4 Hz, 1H; H-1c), 4.93 (dd, $^3J_{2b,3b}$=8.6 Hz, 1H; H-2b), 5.10 (at, ^3J=9.5 Hz, 1H; H-4b), 5.17 (at, ^3J=9.1 Hz, 1H; H-3b), 5.19–5.24 (m, 2H; H-2c, H-3a), 5.29–5.33 (m, 2H; H-3c, H-4c), 5.72 (d, 1H; NH), 6.10 ppm (d, 1H; H-1a); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ=20.5, 20.6, 20.7, 20.7, 20.8, 20.9, 20.9 (7×q, 10×OC(O)CH_3), 22.9 (q, NC(O)CH_3), 51.1 (d, C-2a), 61.5 (t, C-6a), 62.4 (t, C-6c), 65.9 (d, C-4c), 66.7 (t, C-6b), 68.7 (d, C-3c), 68.9 (d, C-5c), 69.1 (d, C-4b), 69.4 (d, C-2c), 70.5 (d, C-5a), 70.8 (d, C-3a), 71.7 (2×d, C-2b, C-5b), 72.9 (d, C-3b), 75.4 (d, C-4a), 90.5 (d, ^1J(C,H)=180 Hz; C-1a), 97.2 (d, ^1J(C,H)=174 Hz; C-1c), 100.5 (d, ^1J(C,H)=163 Hz; C-1b), 168.8, 169.2, 169.5, 169.7, 169.8, 170.1, 170.1, 170.2, 170.4, 170.6, 171.4 ppm (11×s, 11×C=O); IR (KBr): $\tilde{\nu}$=3374 (br, NH), 1750, 1681 cm^{-1} (s, C=O); HRMS (ESI): m/z: calcd for $C_{40}H_{56}NO_{26}$: 966.3085; found 966.3077 [M+H]$^+$.

2-Methyl-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano]-[2,1-*d*]-oxazoline (33): Peracetate **32** (100 mg, 104 μmol) was dissolved in dry DCE (10 mL) and transferred via cannula to a flame-dried round-bottomed flask. TMSBr (205 μL, 1.55 mmol), BF_3·OEt_2 (196 μL, 1.55 mmol) and 2,4,6-collidine (68.5 μL, 518 μmol) were added and the solution heated to 40°C, under an atmosphere of argon. After 21 h, TLC (ethyl acetate) indicated formation of a major product (R_f=0.45) and complete consumption of starting material (R_f=0.3). The reaction mixture was washed with $NaHCO_3$ (2×10 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate/Et_3N 400:1) to give protected oxazoline **33** (70.2 mg, 75%) as a white amorphous solid. $[\alpha]_D^{24}$=+32 (c=0.1 in $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6): δ=1.73, 1.75, 1.77, 1.82, 1.84, 1.94, 2.09, 2.13 (8×s, 30H; 9×OC(O)CH_3, NC(O)CH_3), 3.55 (dd, $^3J_{5b,6b}$=2.8, $^2J_{6b,6'b}$=10.6 Hz, 1H; H-6b), 3.79 (brd, $^3J_{4a,5a}$=8.6 Hz, 1H; H-4a), 3.89 (ddd, $^3J_{4a,5a}$=8.6, $^3J_{5a,6a}$=6.7, $^3J_{5a,6'a}$=2.0 Hz, 1H; H-5a), 4.00 (dd, $^3J_{5b,6'b}$=7.5 Hz, 1H; H-6'b), 4.09 (ddd, $^3J_{4b,5b}$=10.1 Hz, 1H; H-5b), 4.30 (dd, $^2J_{6a,6'a}$=12.0 Hz, 1H; H-6a), 4.37–4.39 (m, 1H; H-2a), 4.43 (dd, $^3J_{5c,6c}$=2.0, $^2J_{6c,6'c}$=12.4 Hz, 1H; H-6c), 4.48 (dd, 1H; H-6'a), 4.52 (ddd, $^3J_{4c,5c}$=10.1, $^3J_{5c,6'c}$=4.3 Hz, 1H; H-5c), 4.82 (dd, $^3J_{1c,2c}$=1.5 Hz, 1H; H-1c), 4.82 (dd, 1H; H-6'c), 5.00 (d, 1H; $^3J_{1b,2b}$=8.3 Hz, 1H; H-1b), 5.09 (at, ^3J=9.7 Hz, 1H; H-4b), 5.36 (dd, $^3J_{2b,3b}$=9.5 Hz, 1H; H-2b), 5.59 (at, ^3J=9.4 Hz, 1H; H-3b), 5.69 (dd, $^3J_{2c,3c}$=3.5 Hz, 1H; H-2c), 5.76 (dd, $^3J_{3c,4c}$=10.2 Hz, 1H; H-3c), 5.86 (d, $^3J_{1a,2a}$=7.4 Hz, 1H; H-1a), 5.90 (at, ^3J=10.3 Hz, 1H; H-4c), 6.27 ppm (brd, $^3J_{2a,3a}$=2.6 Hz, 1H; H-3a); ^{13}C NMR (125.8 MHz, C_6D_6): δ=13.3 (q, N=C(O)CH_3), 20.2, 20.2, 20.3, 20.4, 20.4, 20.5, 20.9 (7×q, 9×OC(O)CH_3), 62.3 (t, C-6c), 64.6 (t, C-6a), 65.1 (d, C-2a), 66.3 (d, C-4c), 67.6 (t, C-6b), 68.2 (d, C-5a), 69.4 (d, C-5c), 69.5 (d, C-3a), 70.0 (d, C-2c), 70.0 (d, C-3c), 70.1 (d, C-4b), 72.0 (d, C-2b), 72.8 (d, C-5b), 73.5 (d, C-3b), 79.3 (d, C-4a), 98.0 (d, ^1J(C,H)=173 Hz; C-1c), 99.4 (d, ^1J(C,H)=185 Hz; C-1a), 102.2 (d, ^1J(C,H)=162 Hz; C-1b), 166.1 (s, C=N), 169.2, 169.3, 169.4, 169.7, 169.8, 169.9, 170.2, 170.3 ppm (8×s, 9×C=O); IR (KBr): $\tilde{\nu}$=1751, 1674 cm^{-1} (s, C=O, C=N); HRMS (ESI): m/z: calcd for $C_{38}H_{52}NO_{24}$: 906.2874; found 906.2872 [M+H]$^+$.

2-Methyl-[α-D-mannopyranosyl-(1→6)-β-D-glucopyranosyl-(1→4)-1,2-dideoxy-α-D-glucopyrano]-[2,1-*d*]-oxazoline (8): Protected oxazoline **33** (59.5 mg, 65.7 μmol) was dissolved in dry methanol (5 mL). Methanolic sodium methoxide (300 μL of a 10 mg mL^{-1} solution, 131 μmol) was added and the solution stirred at room temperature, under an atmosphere of argon. After 13 h, mass spectrometry indicated one product. The solution was concentrated in vacuo to yield deprotected oxazoline **8** (41.5 mg, quant.) as a white amorphous solid. ^{1}H NMR (500 MHz, D_2O): δ=1.98 (d, $^5J_{2a,CH_3}$=1.7 Hz, 3H; CH_3), 3.17–3.21 (m, 1H; H-2b), 3.34–3.40 (m, 2H; H-3b, H-4b), 3.36 (ddd, $^3J_{4a,5a}$=8.9, $^3J_{5a,6a}$=6.3, $^3J_{5a,6'a}$=2.3 Hz, 1H; H-5a), 3.53–3.55 (m, 1H; H-5b), 3.57–3.61 (m, 3H; H-4c, H-5c, H-6a), 3.63 (brd, 1H; H-4a), 3.68 (dd, $^3J_{5c,6c}$=5.5, $^2J_{6c,6'c}$=12.0 Hz, 1H; H-6c), 3.72–3.75 (m, 1H; H-6b), 3.73 (dd, $^2J_{6a,6'a}$=12.6 Hz, 1H; H-6'a), 3.76 (dd, $^3J_{2c,3c}$=3.3, $^3J_{3c,4c}$=9.3 Hz, 1H; H-3c), 3.82 (dd, $^3J_{5c,6'c}$=1.5 Hz, 1H; H-6'c), 3.86 (dd, $^3J_{5b,6'b}$=5.3, $^2J_{6b,6'b}$=11.2 Hz, 1H; H-6'b), 3.92 (dd, $^3J_{1c,2c}$=1.6 Hz, 1H; H-2c), 4.10–4.12 (m, 1H; H-2a), 4.30 (dd, ^3J=1.6, ^3J=2.9 Hz, 1H; H-3a), 4.41 (d, $^3J_{1b,2b}$=7.9 Hz, 1H; H-1b), 4.84 (d, 1H; H-1c), 6.01 ppm (d, $^3J_{1a,2a}$=7.3 Hz, 1H; H-1a); ^{13}C NMR (125.8 MHz, D_2O): δ=12.9 (q, CH_3), 60.9 (t, C-6c), 61.7 (t, C-6a), 65.2 (d, C-2a), 65.5 (t, C-6b), 66.7 (d, C-4c), 69.0 (d, C-3a), 69.5 (d, C-4b), 69.8 (d, C-2c), 70.5 (d, C-3c), 70.8 (d, C-5a), 72.8 (d, C-5c), 73.0 (d, C-2b), 74.2 (d, C-5b), 75.7 (d, C-3b), 78.8 (d, C-4a), 99.7 (d, ^1J(C,H)=174 Hz; C-1c), 99.8 (d, ^1J(C,H)=186 Hz; C-1a), 104.5 (d, ^1J(C,H)=163 Hz; C-1b), 168.3 ppm (s, C=N); IR (KBr): $\tilde{\nu}$=3431 (br, OH), 1673 cm^{-1} (brs, C=N); HRMS (ESI): m/z: calcd for $C_{20}H_{33}NNaO_{15}$: 505.1742; found 505.1736 [M+Na]$^+$.

***p*-Methoxyphenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-2-*O*-levulinoyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (35)**: Benzylidene acetal **34** (400 mg, 282 μmol) was dissolved in an aqueous solution of acetic acid (80%, 50 mL). The reaction mixture was stirred and heated at 50°C. After 16 h, TLC (petrol/ethyl acetate 1:2) indicated formation of a major product (R_f=0.25) and full consumption of starting material (R_f=0.75). The reaction mixture was added to water (50 mL) and extracted with CH_2Cl_2 (2×50 mL). The combined organic layers were washed with $NaHCO_3$ (2×50 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (petrol/ethyl acetate 1:2) to give diol **35** (320 mg, 86%) as a white foam. $[\alpha]_D^{19}$=+43 (c=0.5 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.14 (s, 3H; OC(O)CH_3), 2.16 (s, 3H; $CH_2C(O)CH_3$), 2.46–2.52 (m, 1H; CH_2CHH'), 2.59–2.64 (m, 1H; CH_2CHH'), 2.67–2.80 (m, 2H; CH_2CHH'), 3.05 (ddd, $^3J_{4b,5b}$=9.3, $^3J_{5b,6b}$=5.7, $^3J_{5b,6'b}$=3.2 Hz, 1H; H-5b), 3.30 (dd, $^2J_{6b,6'b}$=11.9 Hz, 1H; H-6b), 3.51 (dd, 1H; H-6'b), 3.53–3.58 (m, 2H; H-4c, H-6c), 3.61 (at, ^3J=9.8 Hz, 1H; H-3b), 3.67–3.72 (m, 5H; H-4b, H-5a, OCH_3), 3.79–3.83 (m, 2H; H-6a, H-6'c), 3.89 (dd, $^3J_{5a,6'a}$=3.5, $^2J_{6a,6'a}$=11.0 Hz, 1H; H-6'a), 3.93 (dd, $^3J_{2c,3c}$=3.2, $^3J_{3c,4c}$=9.2 Hz, 1H; H-3c), 4.07 (at, ^3J=9.2 Hz, 1H; H-4a), 4.10–4.14 (m, 1H; H-5c), 4.29 (dd, $^3J_{2a,3a}$=10.8, $^3J_{3a,4a}$=8.6 Hz, 1H; H-3a), 4.39 (dd, $^3J_{1a,2a}$=8.5 Hz, 1H; H-2a), 4.41, 4.80 (ABq, ^2J=12.3 Hz, 2H; $PhCH_2$), 4.45, 4.86 (ABq, ^2J=11.1 Hz, 2H; $PhCH_2$), 4.48, 4.51 (ABq, ^2J=11.8 Hz, 2H; $PhCH_2$), 4.54, 4.76 (ABq, ^2J=11.1 Hz, 2H; $PhCH_2$), 4.54, 4.73 (ABq, ^2J=11.6 Hz, 2H; $PhCH_2$), 4.55–4.57 (m, 1H; H-1b), 4.90 (dd, $^3J_{1b,2b}$=8.0, $^3J_{2b,3b}$=10.1 Hz, 1H; H-2b), 5.19 (dd, $^3J_{1c,2c}$=1.8 Hz, 1H; H-2c), 5.22 (brs, 1H; H-1c), 5.60 (d, 1H; H-1a), 6.68–6.71 (m, 2H; 2×Ar-H), 6.80–6.83 (m, 2H; 2×Ar-H), 6.89–6.96 (m, 3H; 3×Ar-H), 7.03–7.06 (m, 2H; 2×Ar-H), 7.17–7.18 (m, 2H; 2×Ar-H), 7.28–7.36 (m, 18H; 18×Ar-H), 7.67–7.83 ppm (m, 4H; 4×Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ=21.2 (q, OC(O)CH_3), 27.7 (t, $CH_2CH_2C(O)CH_3$), 29.8 (q, $CH_2C(O)CH_3$), 37.6 (t, $CH_2CH_2C(O)CH_3$), 55.6 (q, OCH_3), 55.6 (d, C-2a), 62.3 (t, C-6b), 67.7 (t, C-6a), 69.0 (d, C-4b), 69.0 (d, C-2c), 69.8 (t, C-6c), 70.5 (d, C-2b), 71.6 (d, C-5c), 71.9 (t, $PhCH_2$), 73.6 (t, $PhCH_2$), 73.8 (t, $PhCH_2$), 74.5 (2×C-4c), 74.7 (t, $PhCH_2$), 75.0 (t, $PhCH_2$), 75.1 (d, C-5a), 75.6 (d, C-5b), 76.9 (d, C-3a), 78.2 (d, C-3c), 78.3 (d, C-4a), 81.0 (d, C-3b), 94.9 (d, ^1J(C,H)=172 Hz; C-1c), 97.6 (d, ^1J(C,H)=165 Hz; C-1a), 100.3 (d, ^1J(C,H)=163 Hz; C-1b), 114.4, 118.7, 123.4, 127.3, 127.5, 127.7, 127.7, 127.8, 127.9, 128.1, 128.1, 128.2, 128.3, 128.4, 128.4, 128.6, 128.6, 133.8 (18×d, 33×Ar-C), 137.2, 137.9, 138.1, 138.3, 138.4, 150.9, 155.4 (7×s, 9×Ar-C), 169.8, 171.6, 206.4 ppm (3×s, 5×C=O); IR (KBr): $\tilde{\nu}$=3459 (br, OH), 1777, 1748, 1716 cm^{-1} (s, C=O); MS (ESI): species observed: [M+NH$_4$]$^+$, [M+Na]$^+$ (major); peaks observed: m/z (%): 1352.5 (100), 1353.5 (76), 1354.5 (19), 1355.5 (2); calcd for: 1352.5 (100), 1353.5 (83), 1354.5 (39), 1355.5 (13).

***p*-Methoxyphenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)]-2-*O*-levulinoyl-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (36)**: Diol **35** (700 mg, 526 μmol) and **14** (369 mg, 579 μmol) were dissolved in dry CH_2Cl_2 (100 mL) and transferred via cannula to a flame-dried round-bottomed flask containing activated 4 Å molecular sieves (400 mg). The solution was cooled to −60°C and stirred under an atmosphere of argon. TMSOTf (5.71 μL, 31.6 μmol) was added and the temperature allowed to rise to 0°C after 3 h. After 16 h, TLC (petrol/ethyl acetate 1:1) indicated formation of a major product (R_f=0.25) and complete consumption of acceptor **35** (R_f=0). Triethylamine (100 μL) was added and the solution stirred for a further 10 min. The reaction mixture was then filtered through Celite and the filtrate concentrated in vacuo. The residue was purified by flash column chromatography (petrol/ethyl acetate 1:1) to give tetrasaccharide **36** (743 mg, 84%) as a white foam. $[\alpha]_D^{19}$=+37 (c=0.5 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.01, 2.02, 2.10 (3×s, 9H; 3×C(O)CH_3), 2.42–2.48, 2.53–2.57, 2.70–2.76 (m, 4H; 2×CH_2), 3.12 (dat, $^3J_{4b,5b}$=9.7, ^3J=

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2.8 Hz, 1H; H-5b), 3.65–3.91 (m, 20H; H-3b, H-3c, H-3d, H-4b, H-4c, H-4d, H-5a, H-5c, H-5d, H-6a, H-6b, H-6c, H-6d, H-6′a, H-6′b, H-6′c, H-6′d, OCH_3), 4.10 (at, $^{3}J=9.1$ Hz, 1H; H-4a), 4.23 (dd, $^{3}J_{2a,3a}=10.7$, $^{3}J_{3a,4a}=8.3$ Hz, 1H; H-3a), 4.15, 4.31 (ABq, $^{2}J=11.0$ Hz, 2H; $PhCH_2$), 4.33 (dd, $^{3}J_{1a,2a}=8.5$ Hz, 1H; H-2a), 4.43–4.54 (m, 8H; H-1b, 7×PhCH), 4.61 (d, $^{2}J=12.0$ Hz, 1H; PhCH), 4.66 (d, $^{2}J=12.3$ Hz, 1H; PhCH), 4.69 (d, $^{2}J=11.5$ Hz, 1H; PhCH), 4.72 (d, $^{2}J=12.1$ Hz, 1H; PhCH), 4.76 (d, $^{3}J_{1d,2d}=1.5$ Hz, 1H; H-1d), 4.78 (d, $^{2}J=10.9$ Hz, 1H; PhCH), 4.82 (d, $^{2}J=12.9$ Hz, 1H; PhCH), 4.83 (d, $^{2}J=10.9$ Hz, 1H; PhCH), 4.93 (dd, $^{3}J_{1b,2b}=8.1$, $^{3}J_{2b,3b}=9.9$ Hz, 1H; H-2b), 5.17 (dd, $^{3}J_{1d,2d}=1.9$, $^{3}J_{2d,3d}=3.0$ Hz, 1H; H-2d), 5.36 (dd, $^{3}J_{1c,2c}=1.7$, $^{3}J_{2c,3c}=3.0$ Hz, 1H; H-2c), 5.44 (d, 1H; H-1c), 5.59 (d, 1H; H-1a), 6.67–6.74 (m, 4H; 4×Ar-H), 6.78–6.80 (m, 2H; 2×Ar-H), 6.99–7.01 (m, 2H; 2×Ar-H), 7.11–7.14 (m, 6H; 6×Ar-H), 7.21–7.34 (m, 30H; 30×Ar-H), 7.49–7.74 ppm (m, 4H; 4×Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta=21.0$, 21.2 (2×q, $OC(O)CH_3$), 27.8 (t, CH_2CH_2), 29.7 (q, $CC(O)CH_3$), 37.6 (t, CH_2CH_2), 55.6 (q, OCH_3), 55.7 (d, C-2a), 66.0 (t, C-6b), 67.9 (t, C-6a), 68.5 (d, C-2d), 68.7 (d, C-2c), 68.8, 69.2 (2×t, C-6c, C-6d), 70.1 (d, C-4b), 71.6 (t, $PhCH_2$), 71.7 (2×d, C-4c, C-4d), 71.8 (t, $PhCH_2$), 71.8 (d, C-2b), 73.4 (t, $PhCH_2$), 73.5 (t, $PhCH_2$), 73.6 (t, $PhCH_2$), 74.2, 74.3 (3×d, H-5b, H-5c, H-5d), 74.8 (t, $PhCH_2$), 75.0 (t, $PhCH_2$), 75.1 (d, C-5a), 75.3 (t, $PhCH_2$), 76.7 (d, C-3a), 78.0 (d, C-3d), 78.1 (d, C-3c), 78.2 (d, C-4a), 78.4 (d, C-3b), 96.6 (d, ^{1}J(C,H)=175 Hz; C-1c), 97.5 (d, ^{1}J(C,H)=166 Hz; C-1a), 97.7 (d, ^{1}J(C,H)=175 Hz; C-1d), 100.4 (d, ^{1}J(C,H)=164 Hz; C-1b), 114.4, 118.6, 123.3, 127.1, 127.6, 127.7, 127.7, 127.7, 127.8, 127.9, 127.9, 128.0, 128.0, 128.1, 128.2, 128.2, 128.3, 128.4, 128.4, 128.5, 128.5 (21×d, 46×Ar-C), 131.6 (s, 2×Ar-C), 133.5 (d, 2×Ar-C), 137.8, 137.9, 138.0, 138.1, 138.1, 138.1, 138.6, 138.6, 150.9, 155.3 (10×s, 10×Ar-C), 170.0, 170.3, 171.5, 206.4 ppm (4×s, 6×C=O); IR (KBr): $\tilde{\nu}=3442$ (br, OH), 1716, 1643 cm^{-1} (s, C=O); MS (ESI): species observed: $[M+Na]^+$ (major); peaks observed: m/z (%): 1826.7 (68), 1827.7 (100), 1828.7 (68), 1829.7 (24), 1830.7 (3); calcd for: 1826.7 (87), 1827.7 (100), 1828.7 (62), 1829.7 (27), 1830.7 (9).

***p*-Methoxyphenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)-[2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (37)**: Phthalimide protected tetrasaccharide **36** (50.0 mg, 27.7 μmol) was dissolved in methanol (1 mL) and ethylene diamine (741 μL, 11.1 mmol) and the solution was refluxed at 65 °C. After 21 h, the reaction mixture was concentrated in vacuo, and the residue dissolved in pyridine (1.1 mL). The solution was cooled to 0 °C, acetic anhydride (1 mL) added and the reaction mixture stirred and allowed to warm to room temperature. After 1 d, TLC (petrol/ethyl acetate 1:1) indicated formation of a major product ($R_f=0.15$) and complete consumption of starting material ($R_f=0.3$). The reaction mixture was poured onto ice/water (10 mL) and extracted with CH_2Cl_2 (2×5 mL). The organic layers were washed with hydrochloric acid (10 mL of a 1 M solution), $NaHCO_3$ (2×10 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (petrol/ethyl acetate 1:1) to afford acetamide **37** (43.1 mg, 95 %). $[\alpha]_D^{19}=+11$ ($c=0.5$ in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): 1.79, 2.01, 2.11, 2.14, 2.14 (5×s, 15H; 5×$C(O)CH_3$), 3.43–3.49 (m, 3H; H-5b, H-6b, H-6c), 3.60 (br d, $^{2}J_{6d,6'd}=9.1$ Hz, 1H; H-6d), 3.67 (dd, $^{3}J_{5c,6'c}=4.2$, $^{2}J_{6c,6'c}=10.8$ Hz, 1H; H-6′c), 3.70–3.80 (m, 10H; H-3b, H-4c, H-4d, H-5a, H-6a, H-6′b, H-6′d, OCH_3), 3.85 (dd, $^{3}J_{5a,6'a}=5.4$, $^{2}J_{6a,6'a}=10.2$ Hz, 1H; H-6′a), 3.88–3.91 (m, 2H; H-3d, H-5d), 3.93–3.98 (m, 4H; H-2a, H-3c, H-4a, H-5c), 4.03 (m, 1H; H-3a), 4.35 (d, $^{2}J=11.8$ Hz, 1H; PhCH), 4.41–4.51 (m, 8H; H-1b, 7×PhCH), 4.57 (d, $^{2}J=11.0$ Hz, 1H; PhCH), 4.60–4.67 (m, 5H; 5×PhCH), 4.82 (d, $^{2}J=11.1$ Hz, 1H; PhCH), 4.84 (d, $^{2}J=11.0$ Hz, 1H; PhCH), 4.86 (d, $^{3}J_{1c,2c}=1.4$ Hz, 1H; H-1c), 4.93 (dd, $^{3}J_{1b,2b}=8.4$, $^{3}J_{2b,3b}=9.2$ Hz, 1H; H-2b), 4.96 (d, $^{3}J_{1d,2d}=1.7$ Hz, 1H; H-1d), 5.04 (at, $^{3}J=9.6$ Hz, 1H; H-4b), 5.12 (at, $^{3}J=2.5$ Hz, 1H; H-2d), 5.28 (d, $^{3}J_{1a,2a}=5.2$ Hz, 1H; H-1a), 5.35 (dd, $^{3}J_{2c,3c}=2.9$ Hz, 1H; H-2c), 5.69 (d, $^{3}J_{2a,NH}=8.2$ Hz, 1H; NH), 6.77–6.79 (m, 2H; 2×Ar-H), 6.79–6.91 (m, 2H; 2×Ar-H), 7.11–7.12 (m, 2H; 2×Ar-H), 7.16–7.17 (m, 2H; 2×Ar-H), 7.20–7.35 ppm (m, 26H; 26×Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta=20.7$, 20.9, 20.9, 20.9, 23.0 (5×q, $OC(O)CH_3$), 51.7 (d, C-2a), 55.4 (q, OCH_3), 66.1 (t, C-6b), 68.2 (t, C-6d), 68.6 (t, C-6c), 68.7 (d, C-2c), 68.8 (d, C-2d), 69.1 (t, C-6a), 70.5 (d, C-4b), 71.4 (d, C-4c), 71.9 (t, $PhCH_2$), 72.1 (d, C-2b), 72.2 (d, C-4d), 72.4 (d, H-5b), 72.8 (t, $PhCH_2$), 73.2 (t, $PhCH_2$), 73.3 (t, $PhCH_2$), 73.4 (d, C-4a), 74.1 (d, H-5a), 74.1 (d, C-3a), 74.2 (d, C-5d), 74.7 (t, $PhCH_2$), 75.0 (t, $PhCH_2$), 75.8 (d, C-5c), 77.4 (d, C-3d), 78.2 (d, C-3c), 79.5 (d, C-3b), 97.6 (d, ^{1}J(C,H)=173 Hz; C-1c), 98.3 (d, ^{1}J(C,H)=169 Hz; C-1a), 98.8 (d, ^{1}J(C,H)=162 Hz; C-1b), 99.3 (d, ^{1}J(C,H)=172 Hz; C-1d), 114.2, 117.7, 127.2, 127.3, 127.4, 127.4, 127.5, 127.5, 127.6, 127.6, 127.8, 127.8, 127.8, 127.9, 128.0, 128.0, 128.1, 128.2, 128.2, (10×d, 44×Ar-C), 137.9, 138.0, 138.1, 138.3, 138.5, 138.7, 151.4, 154.9 (8×s, 10×Ar-C), 169.5, 169.9, 170.3, 170.4, 170.5 ppm (5×s, 5×C=O); IR (KBr): $\tilde{\nu}=3399$ (br, NH), 1752, 1674 cm^{-1} (s, C=O); MS (ESI): species observed: $[M+2Na]^{2+}$ (major); peaks observed: m/z (%): 873.9 (86), 874.4 (100), 874.9 (43), 875.4 (13), 875.9 (3); calcd for: 873.8 (93), 874.3 (100), 874.8 (58), 875.3 (24), 875.8 (8).

***p*-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-acetamido-2-deoxy-β-D-glucopyranoside (38)**: Benzyl ether **37** (400 mg, 235 μmol) was dissolved in ethyl acetate (6 mL) and ethanol (7 mL). Palladium (10 % on carbon, 170 mg) was added and the reaction mixture stirred at room temperature under an atmosphere of hydrogen. After 19 h, TLC (ethyl acetate) indicated formation of a major product ($R_f=0$) and complete consumption of starting material ($R_f=0.15$). The reaction mixture was poured onto Celite, washed with ethanol (3×50 mL), ethyl acetate (3×50 mL), filtered and concentrated in vacuo. The residue was dissolved in pyridine (12 mL), the solution cooled to 0 °C and acetic anhydride (10 mL) added. The reaction mixture was stirred and allowed to warm to room temperature. After 20 h, TLC (ethyl acetate) indicated formation of a major product ($R_f=0.3$) and complete consumption of intermediate material ($R_f=0$). The reaction mixture was poured onto ice/water (100 mL) and extracted with CH_2Cl_2 (100 mL). The organic layers were washed with hydrochloric acid (10 mL of a 1 M solution), $NaHCO_3$ (2×10 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate) to give acetate **38** (280 mg, 91 %) as a white amorphous foam. $[\alpha]_D^{24}=+17$ ($c=0.5$ in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.88$, 1.95, 1.98, 2.04, 2.07, 2.09, 2.11, 2.12, 2.12, 2.14, 2.15, 2.17 (12×s, 39H; 13×$C(O)CH_3$), 3.44 (dd, $^{3}J_{5b,6b}=2.0$, $^{2}J_{6b,6'b}=11.0$ Hz, 1H; H-6b), 3.69 (dat, $^{3}J_{4b,5b}=10.0$, $^{3}J=3.0$ Hz, 1H; H-5b), 3.74 (dd, $^{3}J_{5b,6'b}=4.2$ Hz, 1H; H-6′b), 3.76 (s, 3H; OCH_3), 3.81 (dd, $^{3}J_{2b,3b}=5.7$, $^{3}J_{3b,4b}=8.9$ Hz, 1H; H-3b), 3.87 (at, $^{3}J=8.2$ Hz, 1H; H-4a), 3.92 (ddd, $^{3}J_{4d,5d}=8.7$, $^{3}J=2.7$, $^{3}J=5.8$ Hz, 1H; H-5d), 4.00–4.03 (m, 1H; H-5a), 4.08–4.12 (m, 3H; H-5c, H-6c, H-6d), 4.27–4.34 (m, 3H; H-2a, H-6′c, H-6′d), 4.41 (dd, $^{3}J_{5a,6a}=2.4$, $^{2}J_{6a,6'a}=11.9$ Hz, 1H; H-6a), 4.46 (dd, $^{3}J_{5a,6a}=4.6$ Hz, 1H; H-6′a), 4.69 (d, $^{3}J_{1b,2b}=5.2$ Hz, 1H; H-1b), 4.85 (s, 1H; H-1d), 4.92 (d, $^{3}J_{1c,2c}=1.7$ Hz, 1H; H-1c), 5.00 (at, $^{3}J=5.4$ Hz, 1H; H-2b), 5.10 (dd, $^{3}J_{2c,3c}=3.2$ Hz, 1H; H-2c), 5.14 (at, $^{3}J=8.4$ Hz, 1H; H-3a), 5.17 (d, $^{3}J_{1a,2a}=7.3$ Hz, 1H; H-1a), 5.22 (dd, $^{3}J_{3c,4c}=10.1$ Hz, 1H; H-3c), 5.26 (dd, $^{3}J_{2d,3d}=2.9$, $^{3}J_{3d,4d}=10.2$ Hz, 1H; H-3d), 5.31 (at, $^{3}J=9.9$ Hz, 1H; H-4d), 5.35 (at, $^{3}J=10.1$ Hz, 1H; H-4c), 5.43 (at, $^{3}J=9.5$ Hz, 1H; H-4b), 5.56 (dd, $^{3}J_{1d,2d}=1.3$ Hz, 1H; H-2d), 6.25 (d, $^{3}J_{2a,NH}=9.5$ Hz, 1H; NH), 6.79–6.80 (m, 2H; 2×Ar-H), 6.96–6.98 ppm (m, 2H; 2×Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta=20.6$, 20.7, 20.7, 20.8, 20.8, 20.9, 20.9 (7×q, 12×$OC(O)CH_3$), 23.0 (q, $NC(O)CH_3$), 52.9 (d, C-2a), 55.7 (q, OCH_3), 61.7 (t, C-6d), 62.4 (t, C-6a), 62.5 (t, C-6c), 65.2 (d, C-4c), 65.6 (d, C-4d), 66.7 (t, C-6b), 68.7 (d, C-3c), 68.8 (d, C-5d), 68.9 (d, C-4b), 69.2 (d, C-2d), 69.5, (d, C-5c), 69.6 (2×d, C-2c, C-3d), 71.9 (d, C-5b), 72.1 (d, C-5a), 73.4 (d, C-2b), 73.5 (d, C-3a), 75.0 (d, C-4a), 81.0 (d, C-3b), 98.2 (d, ^{1}J(C,H)=173 Hz; C-1d), 99.2 (d, ^{1}J(C,H)=167 Hz; C-1b), 99.4 (d, ^{1}J(C,H)=164 Hz; C-1a), 99.5 (d, ^{1}J(C,H)=173 Hz; C-1c), 114.4, 117.9 (2×d, 4×Ar-C), 151.3, 155.1 (2×s, 2×Ar-C), 169.3, 169.4, 169.6, 169.7, 169.9, 170.1, 170.2, 170.4, 170.6, 170.6 ppm (10×s, 13×C=O); IR (KBr): $\tilde{\nu}=3386$ (br, NH), 1742 cm^{-1} (s, C=O); MS (ESI): species observed: $[M+MeCN/NH_4]^+$ (major), $[M+Na]^+$; peaks observed: m/z (%): 1340.4 (100), 1341.4 (63), 1342.4 (24), 1343.4 (6), 1344.4 (1); calcd for: 1340.4 (100), 1341.4 (64), 1342.4 (27), 1343.4 (9), 1344.4 (2).

2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2-acetamido-1,3,6-tri-*O*-acetyl-2-deoxy-D-glucopyranose (39): PMP glycoside **38** (244 mg, 185 μmol) was dissolved in water (5 mL) and acetonitrile (10 mL). Ceric ammonium nitrate (305 mg, 555 μmol) was added and the solution stirred at room temperature. After 4 d, the reac-

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tion mixture was extracted with CH_2Cl_2 (2×20 mL). The organic portions were combined and washed with $NaHCO_3$ (2×20 mL of a saturated solution), sodium thiosulfate (2×10 mL of a 10% w/v solution), EDTA (2×30 mL of a 0.05 M solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate to ethyl acetate/methanol 9:1) and the product dissolved in pyridine (7 mL), the solution cooled to 0°C and acetic anhydride (5 mL) added. The reaction mixture was stirred and allowed to warm to room temperature. After 18 h, TLC (ethyl acetate) indicated formation of a major product (R_f=0.25) and complete consumption of starting material (R_f=0.3). The reaction mixture was poured onto ice/water (10 mL) and extracted with CH_2Cl_2 (2×10 mL). The organic layers were washed with hydrochloric acid (10 mL of a 1 M solution), $NaHCO_3$ (2×10 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate) to give peracetate **39** (196 mg, 84%) as a white foam (only the α anomer detected). ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.91, 1.97, 2.01, 2.04, 2.05, 2.07, 2.12, 2.13, 2.16, 2.16, 2.17, 2.19 (12×s, 42H; 14×C(O)CH_3), 3.57 (ddd, $^3J_{4b,5b}$=6.1, $^3J_{5b,6b}$=3.7, $^3J_{5b,6'b}$=6.1 Hz, 1H; H-5b), 3.61 (dd, $^2J_{6b,6'b}$=11.1 Hz, 1H; H-6b), 3.77 (dd, 1H; H-6′b), 3.81 (at, ^3J=9.0 Hz, 1H; H-3b), 3.87–3.89 (m, 1H; H-5a), 3.92 (at, ^3J=9.2 Hz, 1H; H-4a), 3.96–4.01 (m, 2H; H-5c, H-5d), 4.10–4.15 (m, 2H; H-6c, H-6d), 4.18 (dd, $^3J_{5a,6a}$=4.1, $^2J_{6a,6'a}$=12.2 Hz, 1H; H-6a), 4.21 (dd, $^3J_{5d,6'd}$=3.6, $^2J_{6d,6'd}$=12.8 Hz, 1H; H-6′d), 4.28 (dd, $^3J_{5c,6'c}$=4.7, $^2J_{6c,6'c}$=12.1 Hz, 1H; H-6′c), 4.32 (ddd, $^3J_{1a,2a}$=3.5, $^3J_{2a,3a}$=11.3, $^3J_{2a,NH}$=9.0 Hz, 1H; H-2a), 4.38 (dd, $^3J_{5a,6'a}$=1.6 Hz, 1H; H-6′a), 4.45 (d, $^3J_{1b,2b}$=7.6 Hz, 1H; H-1b), 4.85 (d, $^3J_{1c,2c}$=1.2 Hz, 1H; H-1c), 4.91 (d, $^3J_{1d,2d}$=1.9 Hz, 1H; H-1d), 4.97 (at, ^3J=8.3 Hz, 1H; H-2b), 5.02 (at, ^3J=9.2 Hz, 1H; H-4b), 5.09 (dd, $^3J_{2d,3d}$=3.2 Hz, 1H; H-2d), 5.12 (dd, $^3J_{3d,4d}$=10.0 Hz, 1H; H-3d), 5.20 (dd, $^3J_{3a,4a}$=8.6 Hz, 1H; H-3a), 5.22–5.33 (m, 1H; H-2c), 5.31–5.36 (m, 3H; H-3c, H-4c, H-4d), 5.71 (d, 1H; NH), 6.10 ppm (d, 1H; H-1a); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ=20.6, 20.7, 20.7, 20.8, 20.9, 20.9, 21.0, 21.0, 21.0, 22.9 (10×q, 14×C(O)CH_3), 51.1 (d, C-2a), 61.6 (t, C-6d), 61.6 (t, C-6a), 62.3 (t, C-6c), 65.1 (d, C-4d), 65.9 (d, C-4c), 67.0 (t, C-6b), 68.7 (d, C-3c), 68.8 (d, C-3d), 68.9 (d, C-5c), 69.3 (d, C-2d), 69.5 (d, C-2c), 69.8 (d, C-5d), 70.1 (d, C-4b), 70.6 (d, C-3a), 70.6 (d, C-5a), 71.9 (d, C-5b), 72.4 (d, C-2b), 75.1 (d, C-4a), 81.4 (d, C-3b), 90.5 (d, ^1J(C,H)=181 Hz; C-1a), 96.9 (d, ^1J(C,H)=173 Hz; C-1c), 99.8 (d, ^1J(C,H)=173 Hz; C-1d), 100.6 (d, ^1J(C,H)=161 Hz; C-1b), 168.9, 169.2, 169.6, 169.6, 169.7, 169.9, 169.9, 170.0, 170.1, 170.5, 170.6, 170.6, 171.2, 171.5 ppm (14×s, 14×C=O); IR (KBr): $\tilde{\nu}$=3379 (br, NH), 1746 cm^{-1} (s, C=O); MS (ESI): species observed: $[M+Na]^+$ (major); peaks observed: m/z (%): 1276.4 (100), 1277.4 (58), 1278.4 (22), 1279.4 (5), 1280.4 (1); calcd for: 1276.4 (100), 1277.4 (59), 1278.4 (24), 1279.4 (7), 1280.4 (2).

2-Methyl-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)]-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano]-[2,1-*d*]-oxazoline (40): PMP-glycoside **39** (100 mg, 79.7 μmol) was dissolved in dry DCE (10 mL) and transferred via cannula to a flame-dried round-bottomed flask. TMSBr (158 μL, 1.20 mmol), BF_3·OEt_2 (152 μL, 1.20 mmol) and 2,4,6-collidine (52.7 μL, 400 μmol) were added and the solution heated to 40°C, under an atmosphere of argon. After 14 h, TLC (ethyl acetate) indicated formation of a major product (R_f=0.45) and complete consumption of starting material (R_f=0.25). The reaction mixture was washed with $NaHCO_3$ (2×10 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate/Et_3N 400:1) to give protected oxazoline **40** (70.2 mg, 74%) as a white amorphous solid. $[\alpha]_D^{24}$=+44 (c=0.25 in $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6): δ=1.74, 1.74, 1.75, 1.76, 1.76, 1.77, 1.82 (7×s, 21H; 7×OC(O)CH_3), 1.83 (d, $^5J_{2a,CH_3}$=1.8 Hz, 3H; NC(O)CH_3), 1.96, 1.99, 2.17, 2.34, 2.45 (5×s, 15H; 5×OC(O)CH_3), 3.60 (at, ^3J=9.3 Hz, 1H; H-3b), 3.66 (dd, $^3J_{5b,6b}$=2.5, $^2J_{6b,6'b}$=10.5 Hz, 1H; H-6b), 3.90 (br d, $^3J_{4a,5a}$=8.8 Hz, 1H; H-4a), 3.95 (ddd, $^3J_{4a,5a}$=10.2, $^3J_{5a,6a}$=6.2, $^3J_{5a,6'a}$=2.3 Hz, 1H; H-5a), 4.04 (ddd, $^3J_{4b,5b}$=10.2, $^3J_{5b,6b}$=2.5, $^3J_{5b,6'b}$=7.8 Hz, 1H; H-5b), 4.14–4.18 (m, 2H; H-5c, H-6′b), 4.40 (dd, $^2J_{6a,6'a}$=12.2 Hz, 1H; H-6a), 4.43–4.48 (m, 3H; H-2a, H-6d, H-6′a), 4.53 (br d, J=2.6 Hz, 2H; H-6c, H-6′c), 4.63 (ddd, $^3J_{4d,5d}$=10.1, $^3J_{5d,6d}$=1.8, $^3J_{5d,6'd}$=4.5 Hz, 1H; H-5d), 4.87 (br s, 1H; H-1d), 4.88 (dd, $^2J_{6d,6'd}$=12.3 Hz, 1H; H-6′d), 4.97 (d, $^3J_{1c,2c}$=1.6 Hz, 1H; H-1c), 5.00 (d, $^3J_{1b,2b}$=8.2 Hz, 1H; H-1b), 5.04 (at, ^3J=9.7 Hz, 1H; H-4b), 5.27 (at, ^3J=8.8 Hz, 1H; H-2b), 5.51 (dd, $^3J_{2c,3c}$=3.4, $^3J_{3c,4c}$=9.9 Hz, 1H; H-3c), 5.53 (br at, ^3J=2.7 Hz, 1H; H-2c), 5.72 (dd, $^3J_{1d,2d}$ = 1.4, $^3J_{2d,3d}$ = 3.4 Hz, 1H; H-2d), 5.79 (dd, $^3J_{3d,4d}$=10.2 Hz, 1H; H-3d), 5.85 (at, ^3J=10.0 Hz, 1H; H-4c), 5.91 (d, $^3J_{1a,2a}$=7.1 Hz, 1H; H-1a), 5.92 (at, ^3J=10.2 Hz, 1H; H-4d), 6.35 ppm (br d, $^3J_{2a,3a}$=2.6 Hz, 1H; H-3a); ^{13}C NMR (125.8 MHz, C_6D_6): δ=13.4 (q, N=C(O)CH_3), 20.1, 20.2, 20.2, 20.3, 20.4, 20.5, 20.7, 21.0, 21.2 (9×q, 12×OC(O)CH_3), 61.7 (t, C-6c), 62.3 (t, C-6d), 64.5 (t, C-6a), 65.1 (d, C-2a), 65.4 (d, C-4c), 66.3 (d, C-4d), 67.8 (t, C-6b), 68.2 (d, C-5a), 69.4 (2×d, C-3a, C-5d), 69.8 (d, C-3c), 70.0 (d, C-2c), 70.1 (2×d, C-2d, C-3d), 70.1 (d, C-4b), 70.6 (d, C-5c), 72.8 (d, C-2b), 73.0 (d, C-5b), 79.0 (d, C-4a), 82.7 (d, C-3b), 98.0 (d, ^1J(C,H)=173 Hz; C-1d), 99.4 (d, ^1J(C,H)=183 Hz; C-1a), 100.4 (d, ^1J(C,H)=173 Hz; C-1c), 102.0 (d, ^1J(C,H)=161 Hz; C-1b), 166.1 (s, C=N), 169.2, 169.4, 169.4, 169.7, 169.7, 169.8, 170.0, 170.0, 170.1, 170.3, 170.4 ppm (11×s, 12×C=O); $\tilde{\nu}$=1751, 1675 cm^{-1} (s, C=O, C=N); MS (ESI): species observed: $[M+Na]^+$ (major); peaks observed: m/z (%): 1216.4 (100), 1217.4 (56), 1218.4 (21), 1219.4 (5), 1220.4 (1); calcd for: 1216.4 (100), 1217.4 (56), 1218.4 (22), 1219.4 (7), 1220.4 (2).

2-Methyl-[α-D-mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→6)]-β-D-glucopyranosyl-(1→4)-α-D-glucopyrano]-[2,1-*d*]-oxazoline (9): Protected oxazoline **40** (48.5 mg, 40.6 μmol) was dissolved in dry methanol (4.5 mL). Methanolic sodium methoxide (500 μL of a 2.8 mg mL^{-1} solution, 60.9 μmol) was added and the solution stirred at room temperature, under an atmosphere of argon. After 17 h, mass spectrometry indicated one product. The solution was concentrated in vacuo to yield deprotected oxazoline **9** (34.5 mg, quant.) as a pale yellow solid. ^{1}H NMR (500 MHz, D_2O): 1.98 (d, $^5J_{2a,CH_3}$=1.8 Hz, 3H; CH_3), 3.23–3.27 (m, 1H; H-2b), 3.35 (ddd, $^3J_{4a,5a}$=8.8, $^3J_{5a,6a}$=6.4, $^3J_{5a,6'a}$=2.3 Hz, 1H; H-5a), 3.53–3.78 (m, 15H; H-3b, H-3c, H-3d, H-4a, H-4b, H-4c, H-4d, H-5b, H-5d, H-6a, H-6b, H-6c, H-6d, H-6′a, H-6′c), 3.82 (dd, $^3J_{5d,6'd}$=1.1, $^2J_{6d,6'd}$=12.0 Hz, 1H; H-6′d), 3.86–3.91 (m, 2H; H-5c, H-6′b), 3.92 (dd, $^3J_{1d,2d}$=1.7, $^3J_{2d,3d}$=3.4 Hz, 1H; H-2d), 3.96 (dd, $^3J_{1c,2c}$=1.7, $^3J_{2c,3c}$=3.3 Hz, 1H; H-2c), 4.11–4.13 (m, 1H; H-2a), 4.32 (dd, ^3J=1.5, ^3J=2.9 Hz, 1H; H-3a), 4.44 (d, $^3J_{1b,2b}$=8.0 Hz, 1H; H-1b), 4.84 (d, 1H; H-1d), 5.12 (d, 1H; H-1c), 6.01 ppm (d, $^3J_{1a,2a}$=7.3 Hz, 1H; H-1a); ^{13}C NMR (125.8 MHz, D_2O): 12.9 (q, CH_3), 60.6 (t, C-6c), 60.9 (t, C-6d), 61.6 (t, C-6a), 65.1 (t, C-6b), 65.3 (d, C-2a), 66.4 (d, C-4c), 66.7 (d, C-4d), 68.8 (d, C-3a), 69.7, 69.8 (2×d, C-2d, C-4b), 70.2 (d, C-2c), 70.4 (d, C-3d), 70.5 (d, C-3c), 70.7 (d, C-5a), 71.8 (d, C-2b), 72.6 (d, C-5c), 72.7 (d, C-5d), 73.9 (d, C-5b), 78.9 (d, C-4a), 82.0 (d, C-3b), 99.7 (d, ^1J(C,H)=174 Hz; C-1d), 99.8 (d, ^1J(C,H)=185 Hz; C-1a), 101.0 (d, ^1J(C,H)=174 Hz; C-1c), 104.5 (d, ^1J(C,H)=160 Hz; C-1b), 168.3 ppm (s, C=N); IR (KBr): $\tilde{\nu}$=3406 (br, OH), 1664 cm^{-1} (br s, C=N); HRMS (ESI): m/z: calcd for $C_{26}H_{43}NNaO_{20}$: 712.2271; found 712.2272 $[M+Na]^+$.

***p*-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-benzoyl-α-D-mannopyranosyl-(1→6)-2-*O*-levulinoyl-[3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)]-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (42)**: Trisaccharide diol **35** (695 mg, 522 μmol) and trisaccharide trichloroacetimidate **41** (686 mg, 575 μmol) were dissolved in dry alcohol-free CH_2Cl_2 (100 mL) and added via cannula to a flame-dried round-bottomed flask containing activated 4 Å molecular sieves (1 g). The reaction mixture was stirred, cooled to −60°C and TMSOTf (5.67 μL, 31.4 μmol) added. After 15 h, TLC (petrol/ethyl acetate 1:2) indicated formation of a major product (R_f=0.3) and complete consumption of starting materials (R_f=0.4 and R_f=0.25). Triethylamine (1 mL) was added and the reaction mixture stirred for a further 10 min. The reaction mixture was filtered through Celite and concentrated in vacuo. The residue was filtered through Celite and the filtrate concentrated in vacuo. The residue was purified by flash column chromatography (petrol/ethyl acetate 1:2) to give hexasaccharide **42** (1.08 g, 88%) as an amorphous white foam. $[\alpha]_D^{22}$=+32 (c=0.6 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): 1.87, 1.89, 1.90, 2.02, 2.05, 2.08, 2.09, 2.10, 2.15, 2.17 (10×s, 30H; 10×$COCH_3$), 2.56–2.67, 2.75–2.83 (m, 4H; CH_2CH_2C(O)CH_3), 3.39 (ddd, $^3J_{4b,5b}$=8.8, $^3J_{5b,6b}$=2.0, $^3J_{5b,6'b}$=6.6 Hz, 1H; H-5b), 3.46 (dd, $^3J_{5d,6d}$=1.7, $^2J_{6d,6'd}$=10.4 Hz, 1H; H-6d), 3.70–3.80 (m, 9H; H-3b, H-4b, H-4c, H-5a, H-6b, H-6c, OCH_3), 3.83–3.95 (m, 6H; H-6a, H-6e, H-6′a, H-6′b, H-6′c, H-6′d), 3.97–4.04 (m, 3H; H-3c, H-5c, H-5e), 4.07–4.28 (m, 7H; H-3a, H-4a, H-5d, H-5f, H-6f, H-6′e, H-6′f), 4.38

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(dd, $^3J_{1a,2a}$=8.5, $^3J_{2a,3a}$=10.5 Hz, 1H; H-2a), 4.49–4.52 (m, 2H; H-3d, PhCH), 4.56–4.60 (m, 4H; 4×PhCH), 4.64 (d, $^3J_{1b,2b}$=8.2 Hz, 1H; H-1b), 4.67 (d, ^2J=11.7 Hz, 1H; PhCH), 4.72 (d, $^3J_{1f,2f}$=1.6 Hz, 1H; H-1f), 4.78 (d, ^2J=11.5 Hz, 1H; PhCH), 4.81 (d, ^2J=12.2 Hz, 1H; PhCH), 4.82 (d, ^2J=12.6 Hz, 1H; PhCH), 4.90 (d, ^2J=10.9 Hz, 1H; PhCH), 5.02 (dd, $^3J_{2b,3b}$=9.4 Hz, 1H; H-2b), 5.07 (m, 2H; H-1d, H-2e), 5.13–5.14 (m, 2H; H-3e, H-4e), 5.20 (d, $^3J_{1e,2e}$=1.6 Hz, 1H; H-1e), 5.22 (dd, $^3J_{2f,3f}$=3.3 Hz, 1H; H-2f), 5.31 (at, ^3J=10.2 Hz, 1H; H-4f), 5.41 (dd, $^3J_{1c,2c}$=1.6, $^3J_{2c,3c}$=3.0 Hz, 1H; H-2c), 5.44 (dd, $^3J_{3f,4f}$=10.2 Hz, 1H; H-3f), 5.47 (d, 1H; H-1c), 5.55 (dd, $^3J_{1d,2d}$=1.5, $^3J_{2d,3d}$=3.5 Hz, 1H; H-2d), 5.65 (d, 1H; H-1a), 5.66 (at, ^3J=10.0 Hz, 1H; H-4d), 6.72–6.78 (m, 5H; 5×Ar-H), 6.81–6.83 (m, 2H; 2×Ar-H), 7.02–7.03 (m, 2H; 2×Ar-H), 7.19–7.21 (m, 2H; 2×Ar-H), 7.32–7.46 (m, 19H; 19×Ar-H), 7.55–7.58 (m, 4H; 4×Ar-H), 7.63–7.67 (m, 5H; 5×Ar-H), 8.07–8.09 (m, 2H; 2×Ar-H), 8.16–8.17 ppm (m, 2H; 2×Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ=20.5, 20.5, 20.6, 20.5, 20.7, 20.8, 20.8, 21.1 (8×q, 10×OCOC*H*$_3$), 27.7 (t, *C*H$_2$CH$_2$C(O)CH$_3$), 29.7 (q, CH$_2$C(O)*C*H$_3$), 37.5 (t, CH$_2$*C*H$_2$C(O)CH$_3$), 55.5 (d, C-2a), 55.5 (q, OCH$_3$), 62.0 (t, C-6e), 62.2 (t, C-6f), 65.8 (d, C-4f), 65.9 (d, C-4e), 66.2 (t, C-6d), 67.2 (t, C-6b), 67.7 (t, C-6a), 68.5 (d, C-4d), 68.5 (d, C-5f), 68.7 (d, C-3e), 68.7 (d, C-2c), 69.1 (d, C-2e), 69.2 (d, C-3f), 69.2 (d, C-5e), 69.4 (d, C-5d), 69.5 (t, C-6c), 69.5 (d, C-2f), 70.4 (d, C-4b), 71.4 (d, C-2b), 71.6 (d, C-5c), 71.8 (t, PhCH$_2$), 72.0 (t, C-2d), 73.5 (t, PhCH$_2$), 73.6 (t, PhCH$_2$), 74.3 (d, C-4c), 74.5 (t, PhCH$_2$), 74.7 (d, C-5b), 74.9 (t, PhCH$_2$), 75.1 (d, C-5a), 76.4 (d, C-3a), 76.5 (d, C-3d), 77.9 (d, C-4a), 78.2 (d, C-3c), 79.0 (d, C-3b), 96.2 (d, ^1J(C,H)=173 Hz; C-1c), 96.9 (d, ^1J(C,H)=175 Hz; C-1f), 97.4 (d, ^1J(C,H)=175 Hz; C-1d), 97.4 (d, ^1J(C,H)=167 Hz; C-1a), 99.9 (d, ^1J(C,H)=175 Hz; C-1e), 100.1 (d, ^1J(C,H)=162 Hz; C-1b), 114.3, 118.5, 127.0, 127.5, 127.6, 127.7, 127.8, 127.9, 127.9, 128.0, 128.1, 128.2, 128.2, 128.3, 128.4, 128.4, 128.5, 128.7 (18×d, 37×Ar-C), 129.0, 129.2 (2×s, 2×Ar-C), 130.0, 130.0, 133.2, 133.4 (4×d, 6×Ar-C), 137.7, 138.0, 138.1, 138.4, 138.5, 150.9, 155.2 (7×s, 9×Ar-C), 165.6, 165.7, 169.1, 169.2, 169.6, 169.9, 169.9, 170.6, 170.6, 171.4, 206.3 ppm (11×s, 15×C=O); IR (KBr): $\tilde{\nu}$=3487 (br, OH), 1714, 1751 cm^{-1} (s, C=O); MS (ESI): species observed: [*M*+Na]$^+$ (major); peaks observed: *m/z* (%): 2382.9 (68), 2383.9 (100), 2384.9 (68), 2385.9 (24), 2386.9 (3); calcd for: 2382.8 (73), 2383.8 (100), 2384.8 (75), 2385.8 (40), 2386.8 (17).

***p*-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,4-di-*O*-acetyl-[3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→3)]-β-D-glucopyranosyl-(1→4)-2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranoside (43)**: Phthalimide protected hexasaccharide **42** (1.02 g, 430 μmol) was dissolved in methanol (20 mL) and ethylene diamine (11.5 mL, 172 mmol) added. The solution was refluxed at 65 °C. After 3 d, the reaction mixture was concentrated in vacuo and the residue dissolved in pyridine (15 mL). The solution was cooled to 0 °C and acetic anhydride (10 mL) added. After 1 d, TLC (petrol/ethyl acetate 1:3) indicated formation of a single product (R_f=0.3) and complete consumption of starting material (R_f=0.5). The reaction mixture was poured onto ice/water (50 mL) and extracted with CH_2Cl_2 (2×20 mL). The combined organic layers were washed with hydrochloric acid (2×20 mL of a 1 M solution), $NaHCO_3$ (2×20 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (petrol/ethyl acetate 1:3) to afford acetamide **43** (755 mg, 82 %) as an amorphous white foam. $[\alpha]_D^{23}$=+33 (*c*=0.5 in $CHCl_3$); ^{1}H NMR (700 MHz, $CDCl_3$): δ=1.93, 1.96, 1.96, 2.00, 2.02, 2.03, 2.05, 2.05, 2.10, 2.13, 2.14, 2.14, 2.15, 2.17 (14×s, 42H; 14×C(O)CH$_3$), 3.40 (dd, $^3J_{5b,6b}$=2.3, $^2J_{6b,6'b}$=10.7 Hz, 1H; H-6b), 3.43 (ddd, $^3J_{4b,5b}$=10.1, $^3J_{5b,6'b}$=4.8 Hz, 1H; H-5b), 3.53 (dd, $^3J_{5d,6d}$=2.2, $^2J_{6d,6'd}$=11.4 Hz, 1H; H-6d), 3.61 (br d, $^2J_{6c,6'c}$=8.9 Hz, 1H; H-6c), 3.68–3.85 (m, 12H; H-3b, H-5a, H-5c, H-5d, H-6a, H-6′a, H-6′b, H-6′c, H-6′d, OCH$_3$), 3.89 (dd, $^3J_{2c,3c}$=3.1, $^3J_{3c,4c}$=9.5 Hz, 1H; H-3c), 3.92–3.95 (m, 2H; H-3a, H-4c), 3.96–4.01 (m, 3H; H-2a, H-4a, H-6e), 4.02 (ddd, $^3J_{4e,5e}$=9.9, $^3J_{5e,6e}$=2.3, $^3J_{5e,6'e}$=4.8 Hz, 1H; H-5e), 4.07 (ddd, $^3J_{4f,5f}$=9.6, $^3J_{5f,6f}$=2.5, $^3J_{5f,6'f}$=4.8 Hz, 1H; H-5f), 4.11 (dd, $^2J_{6f,6'f}$=10.7 Hz, 1H; H-6f), 4.13 (dd, $^3J_{2d,3d}$=3.4, $^3J_{3d,4d}$=7.7 Hz, 1H; H-3d), 4.27 (dd, 1H; H-6′f), 4.28 (dd, $^2J_{6e,6'e}$=12.2 Hz, 1H; H-6′e), 4.34, 4.65 (ABq, ^2J=12.0 Hz, 2H; PhCH$_2$), 4.42 (d, $^3J_{1b,2b}$=8.2 Hz, 1H; H-1b), 4.44, 4.81 (ABq, ^2J=11.1 Hz, 2H; PhCH$_2$), 4.48, 4.50 (ABq, ^2J=12.1 Hz, 2H; PhCH$_2$), 4.50, 4.61 (ABq, ^2J=11.0 Hz, 2H; PhCH$_2$), 4.70, 4.76 (ABq, ^2J=11.7 Hz, 2H; PhCH$_2$), 4.78 (d, $^3J_{1d,2d}$=1.5 Hz, 1H; H-1d), 4.81 (d, $^3J_{1f,2f}$=1.2 Hz, 1H; H-1f), 4.94 (d, $^3J_{1e,2e}$=1.8 Hz, 1H; H-1e), 4.96 (dd, $^3J_{2b,3b}$=9.5 Hz, 1H; H-2b), 4.97 (d, $^3J_{1c,2c}$=2.1 Hz, 1H; H-1c), 5.08 (dd, $^3J_{2e,3e}$=3.3 Hz, 1H; H-2e), 5.12 (dd, $^3J_{2c,3c}$=3.0 Hz, 1H; H-2c), 5.13 (at, ^3J=9.6 Hz, 1H; H-4b), 5.18 (dd, $^3J_{3e,4e}$=10.1 Hz, 1H; H-3e), 5.22–5.30 (m, 7H; H-1a, H-2d, H-2f, H-3f, H-4d, H-4e, H-4f), 6.76–6.77 (m, 2H; 2×Ar-H), 6.88–6.89 (m, 2H; 2×Ar-H), 7.10–7.12 (m, 2H; 2×Ar-H), 7.21–7.36 ppm (m, 23H; 23×Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ=20.6, 20.7, 20.7, 20.8, 20.8, 20.9, 20.9, 21.1, 23.2 (9×q, 14×C(O)*C*H$_3$), 51.6 (d, C-2a), 55.6 (q, OCH$_3$), 62.0 (t, C-6e), 62.4 (t, C-6f), 65.6 (d, C-4e), 65.9 (d, C-4f), 65.9 (t, C-6d), 66.4 (t, C-6b), 67.5 (d, C-4d), 68.5 (t, C-6c), 68.6 (2×d, C-3e, C-5f), 69.0 (t, C-6a), 69.0 (t, C-2c), 69.0 (d, C-3f), 69.3 (d, C-5e), 69.4 (d, C-2d), 69.5 (d, C-5d), 69.7 (d, C-2e), 70.1 (d, C-4b), 70.6 (d, C-2f), 71.9 (t, PhCH$_2$), 72.1 (d, C-2b), 72.3 (d, C-5b), 72.3 (d, C-5c), 73.1, 73.4, 73.5 (3×t, 3×PhCH$_2$), 73.6 (d, C-4c), 74.3 (d, C-5a), 74.9 (t, PhCH$_2$), 75.1 (d, C-4a), 75.8 (d, C-3d), 76.0 (d, C-3a), 77.7 (d, C-3c), 79.4 (d, C-3b), 97.2 (d, ^1J(C,H)=174 Hz; C-1f), 97.4 (d, ^1J(C,H)=174 Hz; C-1d), 98.6 (d, ^1J(C,H)=168 Hz; C-1a), 99.2 (d, ^1J(C,H)=174 Hz; C-1e), 99.4 (d, ^1J(C,H)=174 Hz; C-1c), 99.5 (d, ^1J(C,H)=161 Hz; C-1b), 114.4, 117.8, 127.4, 127.5, 127.7, 127.7, 127.7, 127.8, 128.0, 128.1, 128.2, 128.3, 128.3, 128.3, 128.4, 128.4 (16×d, 29×Ar-C), 137.9, 137.9, 138.0, 138.3, 138.5, 151.2, 154.9 (7×s, 7×Ar-C), 169.4, 169.6, 169.7, 169.8, 169.8, 170.0, 170.0, 170.2, 170.3, 170.4, 170.5, 170.5, 170.7 ppm (13×s, 14×C=O); IR (KBr): $\tilde{\nu}$=3418 (br, NH), 1751 cm^{-1} (s, C=O); MS (ESI): species observed: [*M*+2Na]$^{2+}$ (major); peaks observed: *m/z* (%): 1089.9 (85), 1090.4 (100), 1090.9 (41), 1091.4 (28), 1091.9 (8); calcd for: 1089.9 (86), 1090.4 (100), 1090.9 (67), 1091.4 (32), 1091.9 (14).

***p*-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,4-di-*O*-acetyl-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)]-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-acetamido-2-deoxy-β-D-glucopyranoside (44)**: Benzyl ether **43** (55 mg, 25.8 μmol) was dissolved in ethanol (5 mL) and ethyl acetate (5 mL). Palladium (10 % on carbon, 20 mg) was added and the reaction mixture stirred at room temperature under an atmosphere of hydrogen. After 21 h, TLC (ethyl acetate/methanol 8:2) indicated formation of a major product (R_f=0.45) and complete consumption of starting material (R_f=0.8). The reaction mixture was poured onto Celite, washed with ethanol (3×10 mL) and ethyl acetate (3×10 mL), filtered and concentrated in vacuo. The residue was dissolved in pyridine (2.5 mL), the solution cooled to 0 °C and acetic anhydride (2 mL) added. After 25 h, TLC (ethyl acetate) indicated formation of a single product (R_f=0.3) and complete consumption of starting material (R_f=0.65). The reaction mixture was poured onto ice/water (5 mL) and extracted with CH_2Cl_2 (2×5 mL). The combined organic layers were washed with hydrochloric acid (2×10 mL of a 1 M solution), $NaHCO_3$ (2×10 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate) to afford acetate **44** (45.0 mg, 92 %) as a white amorphous solid. $[\alpha]_D^{23}$=+22 (*c*=0.2 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.01, 2.03, 2.04, 2.08, 2.10, 2.10, 2.13, 2.15, 2.17, 2.18, 2.19, 2.21, 2.21, 2.22, 2.27 (15×s, 57H; 19×C(O)CH$_3$), 3.51 (br d, $^2J_{6d,6'd}$=9.2 Hz, 1H; H-6d), 3.58 (dd, $^3J_{5b,6b}$=1.8, $^2J_{6b,6'b}$=11.6 Hz, 1H; H-6b), 3.61 (dat, $^3J_{4b,5b}$=9.8, ^3J=2.9 Hz, 1H; H-5b), 3.82 (s, 3H; OCH$_3$), 3.83–3.92 (m, 6H; H-3b, H-4a, H-5a, H-5d, H-6′b, H-6′d), 4.07 (dat, $^3J_{4e,5e}$=10.2, ^3J=2.7 Hz, 1H; H-5e), 4.09–4.18 (m, 4H; H-5c, H-5f, H-6c, H-6e), 4.20 (dd, $^3J_{5f,6f}$=2.2, $^2J_{6f,6'f}$=12.3 Hz, 1H; H-6f), 4.26–4.35 (m, 5H; H-2a, H-3d, H-6a, H-6′e, H-6′f), 4.36 (dd, $^3J_{5c,6'c}$=4.7, $^2J_{6c,6'c}$=12.2 Hz, 1H; H-6′c), 4.50 (dd, $^3J_{5a,6'a}$=3.1, $^2J_{6a,6'a}$=11.8 Hz, 1H; H-6′a), 4.50 (d, $^3J_{1b,2b}$=8.0 Hz, 1H; H-1b), 4.84 (d, $^3J_{1d,2d}$=0.6 Hz, 1H; H-1d), 4.89 (d, $^3J_{1f,2f}$=1.0 Hz, 1H; H-1f), 4.96 (d, $^3J_{1c,2c}$=1.7 Hz, 1H; H-1c), 5.06 (dd, $^3J_{2b,3b}$=9.4 Hz, 1H; H-2b), 5.07 (d, $^3J_{1a,2a}$=6.4 Hz, 1H; H-1a), 5.14 (m, 3H; H-1e, H-2c, H-2e), 5.17 (dd, $^3J_{2e,3e}$=3.2, $^3J_{3e,4e}$=10.1 Hz, 1H; H-3e), 5.21 (dd, $^3J_{2a,3a}$=9.3, $^3J_{3a,4a}$=10.2 Hz, 1H; H-3a), 5.23–5.36 (m, 8H; H-2d, H-2f, H-3c, H-3f, H-4b, H-4c, H-4d, H-4f), 5.38 (at, ^3J=10.0 Hz, 1H; H-4e), 6.13 (d, $^3J_{2a,NH}$=9.4 Hz, 1H; NH), 6.84–6.86 (m, 2H; 2×Ar-H), 6.96–6.98 ppm (m, 2H; 2×Ar-H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ=20.6, 20.6, 20.7, 20.7, 20.7, 20.8, 20.8, 20.9, 20.9, 20.9, 21.0 (11×q, 18×OC(O)*C*H$_3$), 23.2 (q, NC(O)*C*H$_3$), 52.4 (d, C-2a), 55.6 (q, OCH$_3$), 61.6 (t, C-6e), 62.2 (t, C-6c), 62.3 (t, C-6f), 62.7 (t, C-6a), 65.1 (d, C-4e), 65.8 (2×

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d, C-4c, C-4f), 66.3 (t, C-6b), 66.4 (t, C-6d), 67.7 (d, C-3c), 68.5 (d, C-4d), 68.6 (d, C-5f), 68.8 (d, C-3e), 68.8 (d, C-4b), 69.1 (d, C-3f), 69.3 (d, C-5c), 69.4 (d, C-2f), 69.6 (2×d, C-5d, C-5e), 69.7, 69.7 (2×d, C-2c, C-2e), 70.6 (d, C-2d), 71.8 (d, C-3a), 72.3 (d, C-2b), 72.6 (d, C-5a), 72.7 (d, C-5b), 74.8 (d, C-4a), 75.3 (d, C-3d), 81.3 (d, C-3b), 97.2 (d, ^1J(C,H)=174 Hz; C-1f), 97.7 (d, ^1J(C,H)=174 Hz; C-1d), 99.1 (d, ^1J(C,H)=174 Hz; C-1e), 99.6 (d, ^1J(C,H)=174 Hz; C-1c), 99.6 (d, ^1J(C,H)=164 Hz; C-1a), 100.3 (d, ^1J(C,H)=161 Hz; C-1b), 114.5, 118.2 (2×d, 4×Ar-C), 150.9, 155.3 (2×s, 2×Ar-C), 169.5, 169.5, 169.6, 169.6, 169.8, 169.8, 170.0, 170.1, 170.1, 170.2, 170.3, 170.4, 170.4, 170.6, 170.7 ppm (15×s, 19×C=O); IR (KBr): $\tilde{\nu}$=3424 (br, NH), 1747 cm^{-1} (s, C=O); MS (ESI): species observed: [M+Na]$^+$ (major); peaks observed: m/z (%): 1916.6 (100), 1917.6 (80), 1918.6 (24), 1919.6 (4); calcd for: 1916.6 (100), 1917.6 (91), 1918.6 (51), 1919.6 (22).

2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,4-di-*O*-acetyl-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)]-α-D-glucopyranosyl-(1→4)-1,3,6-tri-*O*-acetyl-2-acetamido-2-deoxy-D-glucopyranose (45): PMP glycoside **44** (400 mg, 211 μmol) was dissolved in water (10 mL) and acetonitrile (20 mL). Ceric ammonium nitrate (347 mg, 633 μmol) was added and the solution allowed to stir. After 3 d, TLC (ethyl acetate) indicated formation of a product (R_f=0) and complete consumption of starting material (R_f=0.3). The reaction mixture was concentrated and filtered through a silica plug (ethyl acetate/methanol 8:2) and the filtrate was concentrated in vacuo. The residue was dissolved in pyridine (15 mL), the solution cooled to 0 °C and acetic anhydride (10 mL) added. After 20 h, TLC (ethyl acetate) indicated formation of a single product (R_f=0.2). The reaction mixture was poured onto ice/water (50 mL) and extracted with CH_2Cl_2 (2×25 mL). The combined organic layers were washed with hydrochloric acid (2×10 mL of a 1 M solution), $NaHCO_3$ (2×10 mL of a saturated solution), sodium thiosulfate (20 mL of a 10% w/v solution), EDTA (20 mL of a 0.05 M solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate) to afford peracetate **45** (316 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.92, 1.96, 1.99, 2.00, 2.04, 2.06, 2.08, 2.09, 2.11, 2.12, 2.12, 2.13, 2.15, 2.15, 2.16, 2.17, 2.21 (17×s, 60H; 20×C(O)CH$_3$), 3.41 (brd, $^2J_{6d,6'd}$=9.6 Hz, 1H; H-6d), 3.54 (brd, $^2J_{6b,6'b}$=11.6 Hz, 1H; H-6b), 3.57 (dat, $^3J_{4b,5b}$=9.8, ^3J=3.1 Hz, 1H; H-5b), 3.72–3.86 (m, 6H; H-3b, H-4a, H-5a, H-5d, H-6′b, H-6′d), 4.02–4.17 (m, 7H; H-5c, H-5e, H-5f, H-6a, H-6c, H-6e, H-6f), 4.20–4.37 (m, 6H; H-2a, H-3d, H-6′a, H-6′c, H-6′e, H-6′f), 4.40 (d, $^3J_{1b,2b}$=7.9 Hz, 1H; H-1b), 4.74 (s, 1H; H-1d), 4.83 (s, 1H; H-1f), 4.88 (s, 1H; H-1c), 4.97–5.01 (m, 1H; H-2b), 5.08–5.10 (m, 3H; H-2c, H-2e, H-3e), 5.11 (s, 1H; H-1e), 5.13–5.35 (m, 10H; H-2d, H-2f, H-3a, H-3c, H-3f, H-4b, H-4c, H-4d, H-4e, H-4f), 5.73 (d, $^3J_{2a,NH}$=9.1 Hz, 1H; NH), 6.08 ppm (d, $^3J_{1a,2a}$=3.5 Hz, 1H; H-1a); ^{13}C NMR (125.8 MHz, $CDCl_3$): 20.7, 20.7, 20.7, 20.7, 20.8, 20.8, 20.8, 20.9, 21.0, 21.1 (10×q, 19×OC(O)*C*H$_3$), 23.0 (q, NC(O)*C*H$_3$), 50.9 (d, C-2a), 61.5 (t, C-6a), 61.6, 62.2 (3×t, C-6c, C-6e, C-6f), 65.0 (d, C-4e), 65.7, 65.8 (2×d, C-4c, C-4f), 65.8 (t, C-6b), 66.2 (t, C-6d), 67.7 (d, C-3c), 67.9 (d, C-4b), 68.4 (d, C-4d), 68.7 (d, C-5f), 68.9 (d, C-3e), 68.9 (d, C-3f), 69.2 (d, C-5c), 69.3 (d, C-2e), 69.5 (d, C-2f), 69.5 (d, C-5d), 69.6 (d, C-5e), 69.7 (d, C-2c), 70.4 (d, C-5a), 70.7 (d, C-2d), 70.8 (d, C-3a), 72.3 (d, C-2b), 72.6 (d, C-5b), 75.3 (d, C-3d), 75.5 (d, C-4a), 82.0 (d, C-3b), 90.4 (d, ^1J(C,H)=181 Hz; C-1a), 97.0 (d, ^1J(C,H)=175 Hz; C-1f), 97.8 (d, ^1J(C,H)=173 Hz; C-1d), 99.3 (d, ^1J(C,H)=175 Hz; C-1e), 99.9 (d, ^1J(C,H)=172 Hz; C-1c), 101.2 (d, ^1J(C,H)=161 Hz; C-1b), 168.8, 169.0, 169.3, 169.3, 169.5, 169.6, 169.6, 169.8, 169.8, 170.0, 170.1, 170.2, 170.2, 170.3, 170.4, 170.4, 170.6, 170.7, 170.7, 171.3 ppm (20×s, 20×C=O); IR (KBr): $\tilde{\nu}$=3402 (br, NH), 1751 cm^{-1} (s, C=O); MS (ESI): species observed: [M+Na]$^+$ (major); peaks observed: m/z (%): 1852.5 (100), 1853.5 (84), 1854.5 (44), 1855.5 (15), 1856.6 (3); calcd for: 1852.5 (100), 1853.5 (86), 1854.6 (47), 1855.6 (19), 1856.6 (6).

2-Methyl-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-mannopyranosyl-(1→6)-2,4-di-*O*-acetyl-[2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl-(1→3)]-α-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano]-[2,1-*d*]-oxazoline (46): Peracetate **45** (100 mg, 54.6 μmol) was dissolved in dry DCE (10 mL) and transferred via cannula to a flame-dried round-bottomed flask. TMSBr (108 μL, 819 μmol), BF_3·OEt$_2$ (104 μL, 819 μmol) and 2,4,6-collidine (36.1 μL, 273 μmol) were added and the solution heated to 40 °C, under an atmosphere of argon. After 1 d, TLC (ethyl acetate) indicated formation of a major product (R_f=0.45) and complete consumption of starting material (R_f=0.2). The reaction mixture was washed with $NaHCO_3$ (2×10 mL of a saturated solution), dried ($MgSO_4$), filtered and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate/Et$_3$N 400:1) to give protected oxazoline **46** (78 mg, 81%) as a white amorphous solid. ^{1}H NMR (500 MHz, C_6D_6): δ=1.58, 1.60, 1.61, 1.62, 1.62, 1.72, 1.78, 1.80, 1.81, 1.86, 1.89 (11×s, 42H; 14×OC(O)CH$_3$), 1.92 (d, $^5J_{2a,CH_3}$=1.7 Hz, 3H; N=C(CH$_3$)), 2.04, 2.14, 2.20, 2.23 (4×s, 12H; 4×OC(O)CH$_3$), 3.59 (at, ^3J=9.2 Hz, 1H; H-3b), 3.66 (dd, $^3J_{5b,6b}$=1.7, $^2J_{6b,6'b}$=10.7 Hz, 1H; H-6b), 3.79 (dd, $^3J_{5d,6d}$=2.1, $^2J_{6d,6'd}$=11.1 Hz, 1H; H-6d), 3.82 (m, 2H; H-4a, H-5a), 3.87–3.93 (m, 1H; H-5b), 4.02 (dd, $^3J_{5d,6'd}$=7.2 Hz, 1H; H-6′d), 4.14–4.18 (m, 2H; H-5e, H-6′b), 4.19–4.21 (m, 1H; H-2a), 4.27 (dd, $^3J_{5c,6c}$=2.1, $^2J_{6c,6'c}$=11.9 Hz, 1H; H-6c), 4.28–4.30 (m, 1H; H-6a), 4.32–4.42 (m, 6H; H-5c, H-5d, H-6e, H-6f, H-6′a, H-6′c), 4.45 (dd, $^3J_{5e,6'e}$=3.3, $^2J_{6e,6'e}$=12.8 Hz, 1H; H-6′e), 4.58–4.63 (m, 3H; H-3d, H-5f, H-6′f), 4.81 (d, $^3J_{1b,2b}$=8.3 Hz, 1H; H-1b), 4.88 (brs, 1H; H-1d), 4.89 (brs, 1H; H-1e), 5.07 (d, $^3J_{1c,2c}$=1.6 Hz, 1H; H-1c), 5.32 (d, $^3J_{1f,2f}$=1.5 Hz, 1H; H-1f), 5.38 (dd, $^3J_{2b,3b}$=8.9 Hz, 1H; H-2b), 5.39–5.43 (m, 4H; H-2e, H-2f, H-3e, H-4b), 5.66 (dd, $^3J_{2c,3c}$=2.7 Hz, 1H; H-2c), 5.68–5.78 (m, 7H; H-2d, H-3c, H-3f, H-4c, H-4d, H-4e, H-4f), 5.83 (d, $^3J_{1a,2a}$=7.3 Hz, 1H; H-1a), 6.05 ppm (brd, J=2.6 Hz, 1H; H-3a); ^{13}C NMR (125.8 MHz, C_6D_6): δ=13.5 (q, C=N(CH$_3$)), 20.2, 20.3, 20.3, 20.4, 20.4, 20.4, 20.5, 20.5, 20.7, 20.8, 20.8, 21.2 (12×q, 18×OC(O)*C*H$_3$), 61.7, 62.5, 62.6 (3×t, C-6c, C-6e, C-6f), 64.3 (t, C-6a), 65.2 (d, C-2a), 65.4, 66.5 (2×d, C-4c, C-4e, C-4f), 67.0 (t, C-6d), 67.2 (t, C-6b), 68.0 (d, C-5a), 68.9, 69.0 (2×d, C-3f, C-4d), 69.3 (d, C-4b), 69.6 (d, C-5c), 69.8 (d, C-3e), 69.9 (d, C-5d), 70.0 (d, C-3a), 70.0 (d, C-3c), 70.1 (2×d, C-2c, C-2e), 70.2 (d, C-5f), 70.4 (d, C-5e), 71.1 (d, C-2f), 71.3 (d, C-2d), 72.7 (d, C-2b), 73.3 (d, C-5b), 76.2 (d, C-3d), 78.5 (d, C-4a), 82.8 (d, C-3b), 97.5 (d, ^1J(C,H)=174 Hz; C-1c), 97.9 (d, ^1J(C,H)=174 Hz; C-1d), 99.5 (d, ^1J(C,H)=185 Hz; C-1a), 99.7 (d, ^1J(C,H)=174 Hz; C-1f), 100.1 (d, ^1J(C,H)=173 Hz; C-1e), 102.0 (d, ^1J(C,H)=161 Hz; C-1b), 166.6, 169.3, 169.3, 169.4, 169.4, 169.5, 169.6, 169.7, 169.7, 169.8, 170.0, 170.0, 170.1, 170.1, 170.2, 170.2, 170.3 ppm (18×s, 18×C=O, C=N); IR (KBr): $\tilde{\nu}$=1748 (s, C=O), 1674 cm^{-1} (s, C=N); MS (ESI): species observed: [M+Na]$^+$ (major); peaks observed: m/z (%): 1792.5 (100), 1793.5 (78), 1794.5 (36), 1795.5 (13), 1796.5 (4), 1797.5 (1); calcd for: 1792.5 (100), 1793.5 (83), 1794.5 (44), 1795.5 (18), 1796.5 (6), 1797.5 (2).

2-Methyl-[α-D-mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→6)]-α-D-mannopyranosyl-(1→6)-[α-D-mannopyranosyl-(1→3)]-β-D-glucopyranosyl-(1→4)-1,2-dideoxy-α-D-glucopyrano]-[2,1-*d*]-oxazoline (10): Protected oxazoline **46** (50 mg, 28.2 μmol) was dissolved in dry methanol (10 mL). Methanolic sodium methoxide (1.5 μL of a 1.3 mg mL^{-1} solution, 84.6 μmol) was added and the solution stirred at room temperature, under an atmosphere of argon. After 18 h, mass spectrometry indicated one product. The solution was concentrated in vacuo to yield deprotected oxazoline **10** (33.1 mg, quant.) as a white amorphous solid. ^{1}H NMR (500 MHz, D_2O): δ=2.00 (d, $^5J_{2a,CH_3}$=1.5 Hz, 3H; CH$_3$), 3.27 (at, ^3J=8.4 Hz, 1H; H-2b), 3.37 (ddd, $^3J_{4a,5a}$=8.7, $^3J_{5a,6a}$=6.4, $^3J_{5a,6'a}$=2.2 Hz, 1H; H-5a), 3.54–3.95 (m, 29H; H-2f, H-3b, H-3c, H-3d, H-3e, H-3f, H-4a, H-4b, H-4c, H-4d, H-4e, H-4f, H-5b, H-5c, H-5d, H-5e, H-5f, H-6a, H-6b, H-6c, H-6d, H-6e, H-6f, H-6′a, H-6′b, H-6′c, H-6′d, H-6′e, H-6′f), 4.00 (m, 2H; H-2c, H-2e), 4.10 (dd, $^3J_{1d,2d}$=1.6, $^3J_{2d,3d}$=2.8 Hz, 1H; H-2d), 4.14–4.15 (m, 1H; H-2a), 4.31 (dd, ^3J=1.6, ^3J=2.7 Hz, 1H; H-3a), 4.46 (d, $^3J_{1b,2b}$=8.0 Hz, 1H; H-1b), 4.83 (d, 1H; H-1d), 4.86 (d, $^3J_{1f,2f}$=1.3 Hz, 1H; H-1f), 5.08 (d, $^3J_{1e,2e}$=1.3 Hz, 1H; H-1e), 5.14 (d, $^3J_{1c,2c}$=1.3 Hz, 1H; H-1c), 6.03 ppm (d, $^3J_{1a,2a}$=7.3 Hz, 1H; H-1a); ^{13}C NMR (125.8 MHz, D_2O): δ=12.9 (q, CH$_3$), 60.5, 60.9, 61.0 (3×t, C-6c, C-6e, C-6f), 61.6 (t, C-6a), 65.1 (d, C-2a), 65.4 (t, C-6d), 65.5 (t, C-6b), 65.7 (d, C-4f), 66.4 (d, C-4c), 66.7, 66.7 (2×d, C-4d, C-4e), 69.0 (d, C-3a), 69.4 (d, C-2d), 69.7 (d, C-4b), 69.9 (d, C-2f), 70.0, 70.2 (2×d, C-2c, C-2e), 70.3, 70.4, 70.6 (3×d, C-3c, C-3e, C-3f), 70.7 (d, C-5a), 71.8 (d, C-2b), 72.6 (d, C-5c), 72.7 (2×d, C-5d, C-5f), 73.3 (d, C-5e), 73.8 (d, C-5b), 78.3 (d, C-3d), 78.9 (d, C-4a), 81.9 (d, C-3b), 99.2 (d, ^1J(C,H)=173 Hz; C-1f), 99.8 (d, ^1J(C,H)=185 Hz; C-1a), 99.8 (d, ^1J(C,H)=173 Hz; C-1d), 101.0 (d, ^1J(C,H)=173 Hz; C-1c), 102.3 (d, ^1J(C,H)=173 Hz; C-1e), 104.5 (d, ^1J(C,H)=

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161 Hz; C-1b), 168.4 ppm (s, C=N); IR (KBr): $\tilde{\nu}$ = 3418 (br, OH), 1662 cm^{-1} (s, C=N); MS (ESI): species observed: [M+MeCN/NH$_4$]$^+$ (major), [M+Na]$^+$; peaks observed: m/z (%): 1036.3 (100%), 1037.3 (39), 1038.3 (12), 1039.3 (3); calcd for: 1036.3 (100), 1037.3 (43), 1038.3 (15), 1039.3 (4).

N^4-β-D-Mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-N^2-(benzyloxycarbonyl)-L-asparagine methyl ester (47): *manno*-Disaccharide oxazoline **1** (250 µg, 684 nmol) and glycosyl amino acid **11** (110 µg, 228 nmol) were dissolved in sodium phosphate buffer (50 µL of a 100 mM solution, pH 6.0). Endo M (10 mU) was added and the temperature maintained at 23 °C. The reaction was analysed by HPLC and UV integration analysis indicated 95% consumption of **11** to give **47** after 3 h. The product was isolated and characterised by NMR and HRMS. ^{1}H NMR (500 MHz, D$_2$O): δ = 1.85, 1.96 (2×s, 6H; 2×C(O)CH$_3$), 2.70 (dd, $^3J_{H\text{-}\alpha,H\text{-}\beta'}$ = 7.3, $^2J_{H\text{-}\beta,H\text{-}\beta'}$ = 15.6 Hz, 1H; H-β′), 2.76 (dd, $^3J_{H\text{-}\alpha,H\text{-}\beta}$ = 5.3 Hz, 1H; H-β), 3.32 (ddd, $^3J_{4c,5c}$ = 9.2, $^3J_{5c,6c}$ = 6.7, $^3J_{5c,6'c}$ = 1.9 Hz, 1H; H-5c), 3.45–3.75 (m, 17H; CO$_2$CH$_3$, H-2a, H-2b, H-3a, H-3b, H-3c, H-4a, H-4b, H-4c, H-5a, H-5b, H-6a, H-6b, H-6c, H-6′a), 3.80 (dd, $^3J_{5b,6'b}$ = 1.7, $^2J_{6b,6'b}$ = 12.8 Hz, 1H; H-6′b), 3.83 (dd, $^2J_{6c,6'c}$ = 12.4 Hz, 1H; H-6′c), 3.96 (br d, J = 3.0 Hz, H-2c), 4.50–4.51 (m, 1H; H-α), 4.51 (d, $^3J_{1b,2b}$ = 7.63 Hz, 1H; H-1b), 4.67 (s, 1H; H-1c), 4.94 (d, $^3J_{1a,2a}$ = 10.0 Hz, 1H; H-1a), 5.04 (s, 2H; PhCH$_2$), 7.31–7.37 ppm (m, 5H; 5×Ar-H); HRMS (ESI): m/z: calcd for $C_{35}H_{52}N_4NaO_{20}$: 871.3067; found 871.3062 [M+Na]$^+$.

N^4-α-D-Mannopyranosyl-(1→3)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-N^2-(benzyloxycarbonyl)-L-asparagine methyl ester (48): *manno*-(1→3)-Linked trisaccharide oxazoline **2** (350 µg, 664 nmol) and glycosyl amino acid **11** (106 µg, 221 nmol) were dissolved in sodium phosphate buffer (50 µL of a 100 mM solution, pH 6.0). Endo M (10 mU) was added and the temperature maintained at 23 °C. The reaction was analysed by HPLC and UV integration analysis indicated 65% consumption of **11** to give **48** after 90 min. The product was isolated and characterised by NMR and HRMS. ^{1}H NMR (500 MHz, D$_2$O): δ = 1.85, 1.96 (2×s, 6H; 2×C(O)CH$_3$), 2.70 (dd, $^3J_{H\text{-}\alpha,H\text{-}\beta'}$ = 7.4, $^2J_{H\text{-}\beta,H\text{-}\beta'}$ = 16.0 Hz, 1H; H-β′), 2.76 (dd, $^3J_{H\text{-}\alpha,H\text{-}\beta}$ = 4.9 Hz, 1H; H-β), 3.36 (ddd, $^3J_{4c,5c}$ = 9.7, $^3J_{5c,6c}$ = 6.5, $^3J_{5c,6'c}$ = 2.0 Hz, 1H; H-5c), 3.46–3.84 (m, 24H; CO$_2$CH$_3$, H-2a, H-2b, H-3a, H-3b, H-3c, H-3d, H-4a, H-4b, H-4c, H-4d, H-5a, H-5b, H-5d, H-6a, H-6b, H-6c, H-6d, H-6′a, H-6′b, H-6′c, H-6′d), 3.97 (dd, $^3J_{1d,2d}$ = 1.6, $^3J_{2d,3d}$ = 3.2 Hz, 1H; H-2d), 4.13 (br d, J = 3.0 Hz, 1H; H-2c), 4.50–4.52 (m, 2H; H-1b, H-α), 4.70 (br s, 1H; H-1c), 4.94 (d, $^3J_{1a,2a}$ = 9.7 Hz, 1H; H-1a), 5.01 (br s, 1H; H-1d), 5.04 (s, 2H; PhCH$_2$), 7.31–7.37 ppm (m, 5H; 5×Ar-H); MS (ESI): species observed: [M+Na]$^+$ (major) [2M+Na]$^+$; peaks observed: m/z (%): 1033.4 (100%), 1034.4 (42), 1035.48 (10), 1036.4 (3); calcd for: 1033.4 (100), 1034.4 (48), 1035.4 (16), 1036.4 (4).

N^4-α-D-Mannopyranosyl-(1→6)-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-N^2-(benzyloxycarbonyl)-L-asparagine methyl ester (49): (1→6)-Mannosylated *manno*-trisaccharide oxazoline **3** (350 µg, 664 nmol) and glycosyl amino acid **11** (106 µg, 221 nmol) were dissolved in sodium phosphate buffer (50 µL of a 100 mM solution, pH 6.0). Endo M (10 mU) was added and the temperature maintained at 23 °C. The reaction was analysed by HPLC and UV integration analysis indicated 89% consumption of **11** to give **49** after 3 h. The product was isolated and characterised by NMR and HRMS. ^{1}H NMR (500 MHz, D$_2$O): 1.85, 1.98 (2×s, 6H; 2×C(O)CH$_3$), 2.70 (dd, $^3J_{H\text{-}\alpha,H\text{-}\beta'}$ = 7.4, $^2J_{H\text{-}\beta,H\text{-}\beta'}$ = 15.7 Hz, 1H; H-β′), 2.76 (dd, $^3J_{H\text{-}\alpha,H\text{-}\beta}$ = 5.0 Hz, 1H; H-β), 3.45–3.81 (m, 25H; CO$_2$CH$_3$, H-2a, H-2b, H-3a, H-3b, H-3c, H-3d, H-4a, H-4b, H-4c, H-4d, H-5a, H-5b, H-5c, H-5d, H-6a, H-6b, H-6c, H-6d, H-6′a, H-6′b, H-6′c, H-6′d), 3.87 (dd, $^3J_{1d,2d}$ = 1.7, $^3J_{2d,3d}$ = 3.3 Hz, 1H; H-2d), 3.98 (br d, J = 2.6 Hz, 1H; H-2c), 4.49–4.55 (m, 1H; H-α), 4.51 (d, $^3J_{1b,2b}$ = 7.9 Hz, 1H; H-1b), 4.67 (s, 1H; H-1c), 4.82 (s, 1H; H-1d), 4.94 (d, $^3J_{1a,2a}$ = 9.4 Hz, 1H; H-1a), 5.05 (s, 2H; PhCH$_2$), 7.29–7.37 ppm (m, 5H; 5×Ar-H); MS (ESI): species observed: [M+Na]$^+$ (major), [2M+Na]$^+$; peaks observed: m/z (%): 1033.4 (100%), 1034.4 (44), 1035.4 (12), 1036.4 (2); calcd for: 1033.4 (100), 1034.4 (48), 1035.4 (16), 1036.4 (4).

N^4-α-D-Mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→6)]-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-N^2-(benzyloxycarbonyl)-L-asparagine methyl ester (50): *manno*-Tetrasaccharide oxazoline **4** (500 µg, 725 nmol) and glycosyl amino acid **11** (117 µg, 242 nmol) were dissolved in sodium phosphate buffer (50 µL of a 100 mM solution, pH 6.0). Endo M (10 mU) was added and the temperature maintained at 23 °C. The reaction was analysed by HPLC and UV integration analysis indicated 36% consumption of **11** to give **50** after 60 min. The product was isolated and characterised by NMR and HRMS. ^{1}H NMR (500 MHz, D$_2$O): δ = 1.85, 1.98 (2×s, 6H; 2×C(O)CH$_3$), 2.66–2.79 (m, 2H; H-β, H-β′), 3.46–3.84 (m, 30H; CO$_2$CH$_3$, H-2a, H-2b, H-3a, H-3b, H-3c, H-3d, H-3e, H-4a, H-4b, H-4c, H-4d, H-4e, H-5a, H-5b, H-5c, H-5d, H-5e, H-6a, H-6b, H-6c, H-6d, H-6e, H-6′a, H-6′b, H-6′c, H-6′d, H-6′e), 3.88 (dd, $^3J_{1e,2e}$ = 1.4, $^3J_{2e,3e}$ = 3.2 Hz, 1H; H-2e), 3.97 (dd, $^3J_{1d,2d}$ = 1.2, $^3J_{2d,3d}$ = 3.3 Hz, 1H; H-2d), 4.16 (br d, J = 1.0 Hz, 1H; H-2c), 4.49–4.54 (m, 1H; H-α), 4.52 (d, $^3J_{1b,2b}$ = 7.7 Hz, 1H; H-1b), 4.69 (s, 1H; H-1c), 4.82 (d, 1H; H-1e), 4.94 (d, $^3J_{1a,2a}$ = 9.7 Hz, 1H; H-1a), 5.01 (d, 1H; H-1d), 5.05 (s, 2H; PhCH$_2$), 7.31–7.38 ppm (m, 5H; 5×Ar-H); MS (ESI): species observed: [M+Na]$^+$ (major), [2M+Na]$^+$; peaks observed: 1195.4 (100), 1196.4 (50), 1197.4 (18), 1198.4 (5), 1199.4 (1); calcd for: 1195.4 (100), 1196.4 (54), 1197.4 (21), 1198.4 (6), 1199.4 (1).

N^4-α-D-Mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→6)]-α-D-mannopyranosyl-(1→6)-[α-D-mannopyranosyl-(1→3)]-β-D-mannopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-N^2-(benzyloxycarbonyl)-L-asparagine methyl ester (51): *manno*-Hexasaccharide oxazoline **5** (629 µg, 621 nmol) and glycosyl amino acid **11** (100 µg, 207 nmol) were dissolved in sodium phosphate buffer (50 µL of a 100 mM solution, pH 6.0). Endo M (10 mU) was added and the temperature maintained at 23 °C. The reaction was analysed by HPLC and UV integration analysis indicated 24% consumption of **11** to give **51** after 3 h. The product was isolated and characterised by NMR and HRMS. ^{1}H NMR (500 MHz, D$_2$O): δ = 1.85, 1.97 (2×s, 6H; 2×C(O)CH$_3$), 2.67–2.76 (m, 2H; H-β, H-β′), 3.44–3.91 (m, 41H; CO$_2$CH$_3$, H-2a, H-2b, H-2e, H-3a, H-3b, H-3c, H-3d, H-3e, H-3f, H-3 g, H-4a, H-4b, H-4c, H-4d, H-4e, H-4f, H-4 g, H-5a, H-5b, H-5c, H-5d, H-5e, H-5f, H-5 g, H-6a, H-6b, H-6c, H-6d, H-6e, H-6f, H-6 g, H-6′a, H-6′b, H-6′c, H-6′d, H-6′e, H-6′f, H-6′g), 3.97–3.98 (m, 2H; H-2d, H-2f), 4.05 (s, 1H; H-2 g), 4.16 (br d, J = 1.2 Hz, 1H; H-2c), 4.50–4.53 (m, 2H; H-1b, H-α), 4.69 (s, 1H; H-1c), 4.78 (s, 1H; H-1 g), 4.81 (s, 1H; H-1e), 4.94 (d, $^3J_{1a,2a}$ = 9.3 Hz, 1H; H-1a), 5.00 (br s, 2H; H-1d, H-1f), 5.05 (s, 2H; PhCH$_2$), 7.31–7.38 ppm (m, 5H; 5×Ar-H); MS (ESI): species observed: [M+Na]$^+$ (major), [2M+Na]$^+$; peaks observed: m/z (%): 1519.5 (100), 1520.5 (58), 1521.5 (17), 1522.5 (4); calcd for: 1519.5 (100), 1520.5 (68), 1521.5 (31), 1522.5 (11).

N^4-β-D-Glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl)-N^2-(benzyloxycarbonyl)-L-asparagine methyl ester (52): *gluco*-Disaccharide **6** (250 µg, 684 nmol) and glycosyl amino acid **11** (110 µg, 228 nmol) were dissolved in sodium phosphate buffer (50 µL of a 100 mM solution, pH 6.0). Endo M (10 mU) was added and the temperature maintained at 23 °C. The reaction was analysed by HPLC and UV integration analysis indicated 4% consumption of **11** to give **52** after 3 h. The product was isolated and characterised by NMR and HRMS. ^{1}H NMR (500 MHz, D$_2$O): δ = 1.85, 1.96 (2×s, 6H; 2×C(O)CH$_3$), 2.71 (dd, $^3J_{H\text{-}\alpha,H\text{-}\beta'}$ = 7.3, $^2J_{H\text{-}\beta,H\text{-}\beta'}$ = 16.2 Hz, 1H; H-β′), 2.77 (dd, $^3J_{H\text{-}\alpha,H\text{-}\beta}$ = 4.9 Hz, 1H; H-β), 3.21 (dd, $^3J_{1c,2c}$ = 8.0, $^3J_{2c,3c}$ = 9.3 Hz, 1H; H-2c), 3.31 (at, ^3J = 9.4 Hz, 1H; H-4c), 3.37–3.43 (m, 2H; H-3c, H-5c), 3.45–3.48 (m, 1H; H-5a), 3.52–3.76 (m, 14H; CO$_2$CH$_3$, H-2a, H-2b, H-3a, H-3b, H-4a, H-4b, H-5b, H-6a, H-6b, H-6c, H-6′a), 3.81 (dd, $^3J_{5c,6'c}$ = 1.8, $^2J_{6c,6'c}$ = 12.3 Hz, 1H; H-6′c), 3.89 (dd, $^3J_{5b,6'b}$ = 1.8, $^2J_{6b,6'b}$ = 12.3 Hz, 1H; H-6′b), 4.43 (d, 1H; H-1c), 4.50–4.53 (m, 1H; H-α), 4.51 (d, $^3J_{1b,2b}$ = 8.3 Hz, 1H; H-1b), 4.94 (d, $^3J_{1a,2a}$ = 9.6 Hz, 1H; H-1a), 5.05 (s, 2H; PhCH$_2$), 7.31–7.37 ppm (m, 5H; 5×Ar-H); HRMS (ESI): m/z: calcd for $C_{35}H_{52}N_4NaO_{20}$: 871.3067; found 871.3061 [M+Na]$^+$.

N^4-α-D-Mannopyranosyl-(1→3)-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-N^2-(benzyloxycarbonyl)-L-asparagine methyl ester (53): (1→3)-Mannosylated *gluco*-trisaccharide oxazoline **7** (350 µg, 664 nmol) and glycosyl amino acid **11** (106 µg, 221 nmol) were dissolved in sodium phosphate buffer (50 µL of a 100 mM solution, pH 6.0). Endo M (10 mU) was

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added and the temperature maintained at 23 °C. The reaction was analysed by HPLC and UV integration analysis indicated 88 % consumption of **11** to give **53** after 3 h. The product was isolated and characterised by NMR and HRMS. ^{1}H NMR (500 MHz, D_2O): δ = 1.85, 1.96 (2 × s, 6 H; 2 × C(O)CH_3), 2.70 (dd, $^{3}J_{H\text{-}\alpha,H\text{-}\beta'}$ = 7.5, $^{2}J_{H\text{-}\beta,H\text{-}\beta'}$ = 15.9 Hz, 1 H; H-β′), 2.76 (dd, $^{3}J_{H\text{-}\alpha,H\text{-}\beta}$ = 5.0 Hz, 1 H; H-β), 3.27 (at, ^{3}J = 8.7 Hz, 1 H; H-2c), 3.40 (ddd, $^{3}J_{4c,5c}$ = 9.9, ^{3}J = 2.0, ^{3}J = 5.4 Hz, 1 H; H-5c), 3.43–3.47 (m, 2 H; H-4c, H-5a), 3.52–3.76 (m, 19 H; CO_2CH_3, H-2a, H-2b, H-3a, H-3b, H-3c, H-3d, H-4a, H-4b, H-4d, H-5b, H-6a, H-6b, H-6c, H-6d, H-6′a, H-6′d), 3.80 (br d, J = 11.0 Hz, 1 H; H-6′c), 3.86 (ddd, $^{3}J_{4d,5d}$ = 10.3, ^{3}J = 2.4, ^{3}J = 4.6 Hz, 1 H; H-5d), 3.88 (br d, $^{2}J_{6b,6'b}$ = 10.9 Hz, 1 H; H-6′b), 3.95 (dd, $^{3}J_{1d,2d}$ = 1.7, $^{3}J_{2d,3d}$ = 2.7 Hz, 1 H; H-2d), 4.45 (d, $^{3}J_{1c,2c}$ = 8.0 Hz, 1 H; H-1c), 4.50–4.51 (m, 1 H; H-α), 4.51 (d, $^{3}J_{1b,2b}$ = 8.2 Hz, 1 H; H-1b), 4.94 (d, $^{3}J_{1a,2a}$ = 9.6 Hz, 1 H; H-1a), 5.04 (s, 2 H; PhCH_2), 5.12 (s, 1 H; H-1d), 7.31–7.37 ppm (m, 5 H; 5 × Ar-H); MS (ESI): species observed: $[M+Na]^+$, $[M+MeCN/NH_4]^+$ (major); peaks observed: m/z (%): 1033.2 (100), 1034.2 (29), 1035.2 (14), 1036.2 (8); calcd for: 1033.4 (100), 1034.4 (48), 1035.4 (16), 1036.4 (4).

N^4-α-D-Mannopyranosyl-(1→6)-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-N^2-(benzyloxycarbonyl)-L-asparagine methyl ester (54): (1→6)-Mannosylated *gluco*-trisaccharide oxazoline **8** (350 µg, 664 nmol) and glycosyl amino acid **11** (106 µg, 221 nmol) were dissolved in sodium phosphate buffer (50 µL of a 100 mM solution, pH 6.0). Endo M (10 mU) was added and the temperature maintained at 23 °C. The reaction was analysed by HPLC and UV integration analysis indicated 4 % consumption of **11** to give **54** after 3 h. The product was isolated and characterised by NMR and HRMS. ^{1}H NMR (500 MHz, D_2O): δ = 1.85, 1.97 (2 × s, 6 H; 2 × C(O)CH_3), 2.70 (dd, $^{3}J_{H\text{-}\alpha,H\text{-}\beta'}$ = 7.5, $^{2}J_{H\text{-}\beta?H\text{-}\beta'}$ = 15.4 Hz, 1 H; H-β′), 2.76 (dd, $^{3}J_{H\text{-}\alpha,H\text{-}\beta}$ = 5.8 Hz, 1 H; H-β), 3.22 (at, ^{3}J = 8.6 Hz, 1 H; H-2c), 3.36 (at, ^{3}J = 9.3 Hz, 1 H; H-4c), 3.41 (at, ^{3}J = 9.2 Hz, 1 H; H-3c), 3.47 (ddd, $^{3}J_{4a,5a}$ = 9.3, ^{3}J = 2.4, ^{3}J = 4.4 Hz, 1 H; H-5a), 3.52–3.83 (m, 22 H; CO_2CH_3, H-2a, H-2b, H-3a, H-3b, H-3d, H-4a, H-4b, H-4d, H-5b, H-5c, H-5d, H-6a, H-6b, H-6c, H-6d, H-6′a, H-6′b, H-6′c, H-6′d), 3.87 (br d, $^{3}J_{2d,3d}$ = 1.8 Hz, 1 H; H-2d), 4.43 (d, $^{3}J_{1c,2c}$ = 8.1 Hz, 1 H; H-1c), 4.50–4.54 (m, 1 H; H-α), 4.51 (d, $^{3}J_{1b,2b}$ = 8.1 Hz, 1 H; H-1b), 4.81 (s, 1 H; H-1d), 4.94 (d, $^{3}J_{1a,2a}$ = 9.5 Hz, 1 H; H-1a), 5.05 (s, 2 H; PhCH_2), 7.29–7.37 ppm (m, 5 H; 5 × Ar-H); MS (ESI): species observed: $[M+Na]^+$ (major); peaks observed: m/z (%): 1033.4 (100), 1034.4 (42), 1035.4 (11), 1036.4 (2); calcd for: 1033.4 (100), 1034.4 (48), 1035.4 (16), 1036.4 (4).

N^4-α-D-Mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→6)]-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-N^2-(benzyloxycarbonyl)-L-asparagine methyl ester (55): *gluco*-Tetrasaccharide oxazoline **9** (350 µg, 664 nmol) and glycosyl amino acid **11** (106 µg, 221 nmol) were dissolved in sodium phosphate buffer (50 µL of a 100 mM solution, pH 6.0). Endo M (10 mU) was added and the temperature maintained at 23 °C. The reaction was analysed by HPLC and UV integration analysis indicated 70 % consumption of **11** to give **55** after 3 h. The product was isolated and characterised by NMR and HRMS. ^{1}H NMR (500 MHz, D_2O): δ = 1.85, 1.97 (2 × s, 6 H; 2 × C(O)CH_3), 2.70 (dd, $^{3}J_{H\text{-}\alpha,H\text{-}\beta'}$ = 7.8, $^{2}J_{H\text{-}\beta,H\text{-}\beta'}$ = 16.0 Hz, 1 H; H-β′), 2.76 (dd, $^{3}J_{H\text{-}\alpha,H\text{-}\beta}$ = 4.5 Hz, 1 H; H-β), 3.28 (at, ^{3}J = 8.4 Hz, 1 H; H-2c), 3.45–3.83 (m, 28 H; CO_2CH_3, H-2a, H-2b, H-3a, H-3b, H-3c, H-3d, H-3e, H-4a, H-4b, H-4c, H-4d, H-4e, H-5a, H-5b, H-5c, H-5e, H-6a, H-6b, H-6c, H-6d, H-6e, H-6′a, H-6′c, H-6′d, H-6′e), 3.85–3.89 (m, 2 H; H-5d, H-6′b), 3.86 (br d, J = 1.5 Hz, 1 H; H-2e), 3.95 (dd, $^{3}J_{1d,2d}$ = 1.8, $^{3}J_{2d,3d}$ = 2.9 Hz, 1 H; H-2d), 4.45 (d, $^{3}J_{1c,2c}$ = 7.9 Hz, 1 H; H-1c), 4.51–4.52 (m, 1 H; H-α), 4.51 (d, $^{3}J_{1b,2b}$ = 8.4 Hz, 1 H; H-1b), 4.80 (s, 1 H; H-1e), 4.94 (d, $^{3}J_{1a,2a}$ = 9.8 Hz, 1 H; H-1a), 5.05 (s, 2 H; PhCH_2), 5.11 (s, 1 H; H-1d), 7.29–7.37 ppm (m, 5 H; 5 × Ar-H); MS (ESI): species observed: $[M+Na]^+$ (major); peaks observed: m/z (%): 1195.4 (100), 1196.4 (50), 1197.4 (16), 1198.4 (4), 1199.4 (1); calcd for: 1195.4 (100), 1196.4 (54), 1197.4 (21), 1198.4 (6), 1199.4 (1).

N^4-α-D-Mannopyranosyl-(1→3)-[α-D-mannopyranosyl-(1→6)]-α-D-mannopyranosyl-(1→6)-[α-D-mannopyranosyl-(1→3)]-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl-N^2-(benzyloxycarbonyl)-L-asparagine methyl ester (56): *gluco*-Hexasaccharide oxazoline **10** (500 µg, 493 nmol) and glycosyl amino acid **11** (48 µg, 99 nmol) were dissolved in sodium phosphate buffer (50 µL of a 100 mM solution, pH 6.0). Endo M (10 mU) was added and the temperature maintained at 23 °C. The reaction was analysed by HPLC and UV integration analysis indicated 60 % consumption of **11** to give **56** after 3 h. The product was isolated and characterised by NMR and HRMS. ^{1}H NMR (500 MHz, D_2O): δ = 1.85, 1.96 (2 × s, 6 H; 2 × C(O)CH_3), 2.70 (dd, $^{3}J_{H\text{-}\alpha,H\text{-}\beta'}$ = 7.2, $^{2}J_{H\text{-}\beta,H\text{-}\beta'}$ = 15.6 Hz, 1 H; H-β′), 2.76 (dd, $^{3}J_{H\text{-}\alpha,H\text{-}\beta}$ = 5.0 Hz, 1 H; H-β), 3.27 (at, ^{3}J = 8.5 Hz, 1 H; H-2c), 3.44–3.48 (m, 1 H; H-5a), 3.51–3.89 (m, 41 H; CO_2CH_3, H-2a, H-2b, H-2e, H-2 g, H-3a, H-3b, H-3c, H-3d, H-3e, H-3f, H-3 g, H-4a, H-4b, H-4c, H-4d, H-4e, H-4f, H-4 g, H-5b, H-5c, H-5d, H-5e, H-5f, H-5 g, H-6a, H-6b, H-6c, H-6d, H-6e, H-6f, H-6 g, H-6′a, H-6′b, H-6′c, H-6′d, H-6′e, H-6′f, H-6′g), 3.96–3.98 (s, 1 H; H-2d), 4.03 (at, ^{3}J = 2.0 Hz, 1 H; H-2f), 4.45 (d, $^{3}J_{1c,2c}$ = 8.0 Hz, 1 H; H-1c), 4.48–4.52 (m, 1 H; H-α), 4.50 (d, $^{3}J_{1b,2b}$ = 8.0 Hz, 1 H; H-1b), 4.75 (s, 1 H; H-1f), 4.80 (d, $^{3}J_{1e,2e}$ = 1.1 Hz, 1 H; H-1e), 4.94 (d, $^{3}J_{1a,2a}$ = 9.4 Hz, 1 H; H-1a), 5.00 (s, 1 H; H-1 g), 5.04 (s, 2 H; PhCH_2), 5.10 (s, 1 H; H-1d), 7.30–7.37 ppm (m, 5 H; 5 × Ar-H); MS (ESI): species observed: $[M+Na]^+$ (major); peaks observed: m/z (%): 1519.5 (100), 1520.5 (61), 1521.5 (25), 1522.5 (8), 1523.5 (2); calcd for: 1519.5 (100), 1520.5 (68), 1521.5 (31), 1522.5 (11), 1523.5 (3).

Acknowledgements

We thank Professor K. Yamamoto and Professor K. Takegawa for kindly providing the Endo M enzyme, and the Endo A plasmid, respectively. We gratefully acknowledge financial support from the BBSRC (BMS committee Studentship to TWDFR and Project Grant BB/D009251/1).

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Received: February 28, 2008
Published online: June 9, 2008

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