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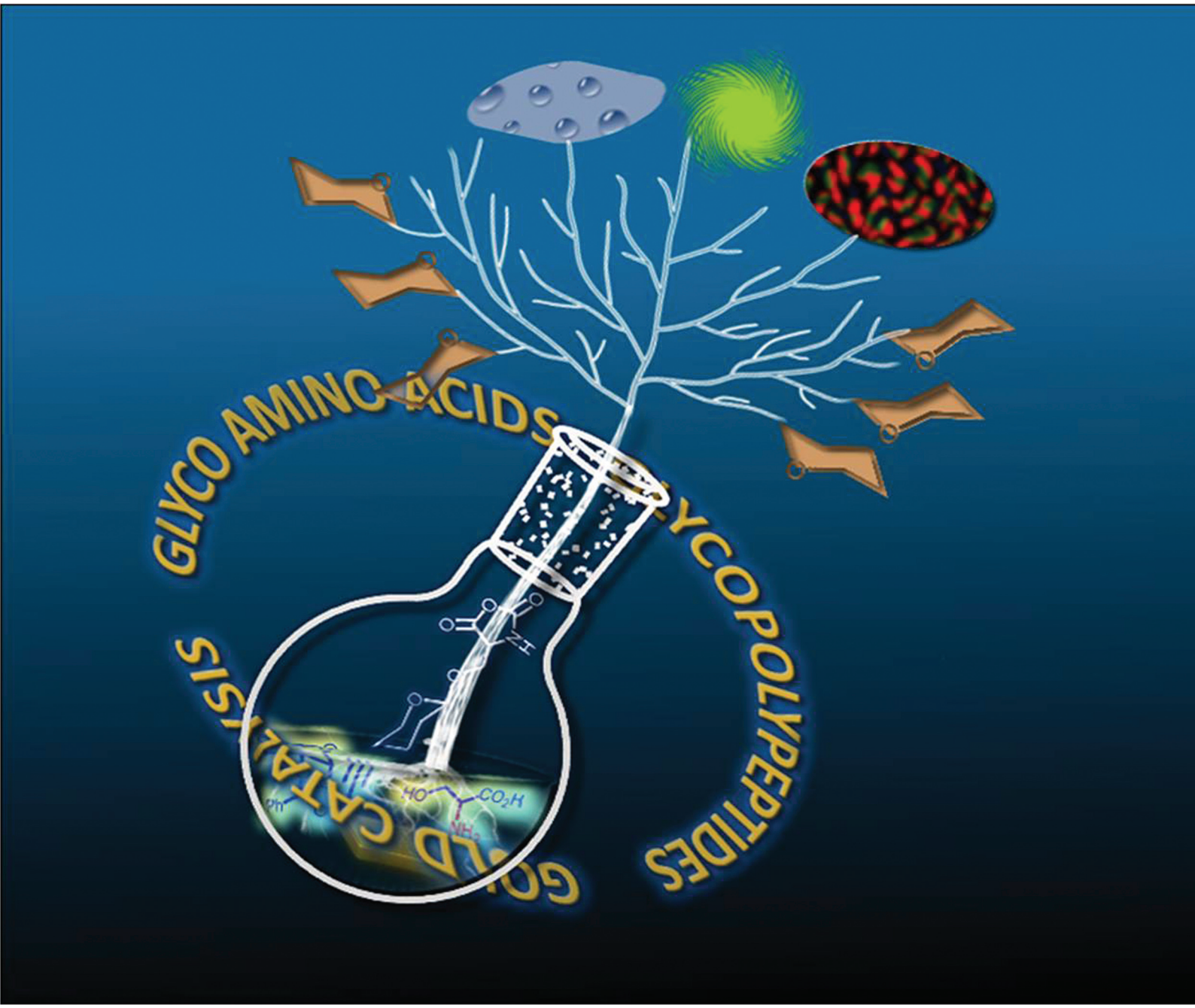

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FULL PAPER
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PAPER

Facile synthesis of unusual glycosyl carbamates and amino acid glycosides from propargyl 1,2-orthoesters as glycosyl donors†

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Propargyl 1,2-*O*-orthoesters are exploited for the synthesis of 1,2-*trans* *O*-glycosides of protected amino acids. *N*-Fmoc- and *N*-Cbz protected serine/threonine - benzyl/methyl esters reacted well with glucosyl-, galactosyl-, mannosyl- and lactosyl- derived propargyl 1,2-orthoesters affording respective 1,2-*trans* glycosides in good yields under $AuBr_3$/4 Å MS Powder/CH_2Cl_2/rt. *t*-Boc serine derivative gave serine 1,2-orthoester and glycosyl carbamate. Optimized conditions enabled preparation of new glycosyl carbamates from *N*-Boc protected amines in a single step using gold catalysts and propargyl 1,2-orthoesters in excellent yields.

Saccharides glycosylated to an aglycone are termed as glycoconjugates and they play an important role in various biological events and are classified in accordance with the type of attached aglycone.[1] For example, if the aglycone is a long chain fatty acid the glycoconjugate is called a glycolipid[2] whereas a protein attached to a saccharide is known as a glycoprotein.[3] Glycoproteins have immense significance in a variety of biological processes including cell signalling, inflammatory responses, neuronal development and immune surveillance.[4] Glycoproteins comprise a saccharide attached to the protein through an *N*-atom or an *O*-atom and are named *N*- or *O*-glycosides (Fig. 1). Furthermore, it has been shown that glycosylated peptides (or antifreeze peptides) are valuable for the survival of aquatic marine life at sub zero temperatures in the Antarctic region.[5] In mammalians, blood group determinants, tumor associated antigens and a host of other significant biological events involve glycoproteins.[6] Thus, synthetic glycopeptides are required for improving our current understanding of those biological events which involve them.

At the heart of any glycopeptide synthesis, the attachment of the sugar residue(s) to the amino acid as a glycoside from a suitable saccharide and a protected amino acid is the key event. However, only a limited number of approaches are available for the attachment of a serine/threonine.[7] For example, one of the earliest and widely used methods couples the CbzSer(OH)Bn and an acetobromosugar by means of environmentally detrimental mercury salts. A notable and significant improvement was reported[7a]

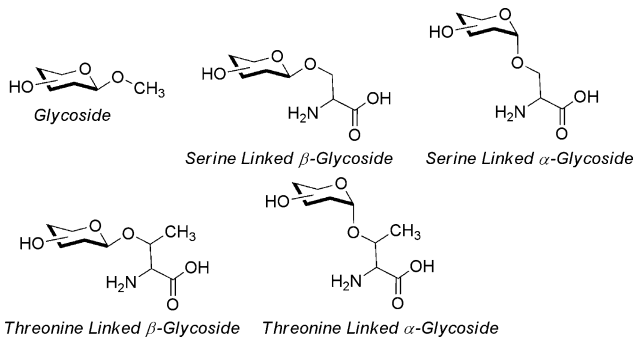

Fig. 1 General glycosides and amino acid glycosides.

by Cameron's group taking advantage of reaction conditions developed by Field *et al.*[7c] In this premise, methods that enable preparation of amino acid glycosides from stable glycosyl donors using catalytic and eco-friendly reagents are essential.[8]

Recent serendipitous observations from our laboratory led to the identification of propargyl glycosides as novel glycosyl donors for transglycosylations exploiting $AuCl_3$ in acetonitrile at 60 °C.[9a] Later on, propargyl 1,2-orthoesters were found to afford[9d] 1,2-*trans* glycosides under $AuBr_3/CH_2Cl_2$/4 Å MS powder/rt and subsequent temperature controlled experiments revealed that propargyl 1,2-orthoesters can be activated[9c] in the presence of propargyl glycosides to obtain propargyl disaccharides.[9]

In continuation of the programme on gold catalyzed glycosylations,[9] we got interested in the exploitation of propargyl 1,2-*O*-orthoesters[9h] for the synthesis of amino acid glycoconjugates. To begin our investigation, initially, propargyl 1,2-orthoesters, Fmoc- and Cbz-protected serine/threonine were considered. Accordingly, per-*O*-benzoylated glucose 1,2-*O*-orthoester **1a** was allowed to react with serine derived aglycone glycosides.

Among various naturally occurring amino acids, hydroxyl containing serine and threonine and their Fmoc-, Cbz- and Boc-protected derivatives are the most widely used. Thus,

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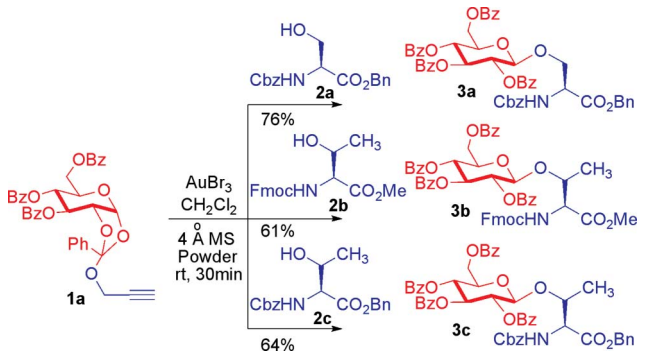
† Electronic supplementary information (ESI) available: General experimental techniques and NMR spectral charts for all compounds. See DOI: 10.1039/c1ob05056g

CbzSer(OH)Bn (**2a**) reacted in the presence of 7 mol% of $AuBr_3/CH_2Cl_2$/4 Å MS powder/rt/30 min to afford serine glucoside **3a** (Scheme 1).[10] The literature indicated that several attempts have been made to synthesize amino acid glycosides that included use of toxic Hg salts, very extensive and laborious purification protocols which led to a poor overall yield of the resulting glycoconjugate.[7a,d] However, $AuBr_3$ catalyzed glycosylation resulted in the isolation of 76% of the amino acid glycoconjugate. Simple gravity flow and conventional silica gel column chromatography would be sufficient to separate propargyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (sole byproduct)[9d,e] from the required serine glucoside **3a**. 1,2-*trans* Glycosidic linkage was confirmed by NMR spectral studies wherein the anomeric proton was noticed at δ 4.78 ppm (d, 1H, J = 7.6 Hz) and the anomeric carbon was observed at the δ101.3 ppm.[10]

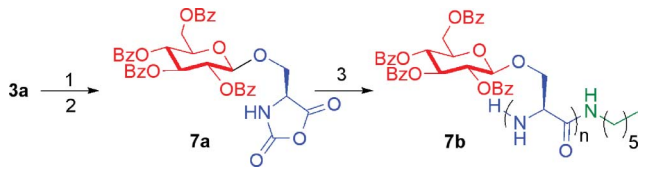


Scheme 1 Synthesis of amino acid glycoconjugates.

We then continued our synthesis endeavour with 1,2-orthoester **1a** that was allowed to react with FmocThr(OH)OMe (**2b**) to give the threoninyl glucoside (**3b**) in good yield. Furthermore, CbzThr(OH)Bn (**2c**) reacted with the glycosyl donor **1a** resulting in the formation of threoninyl glucoside **3c** (Scheme 1). It is interesting to note that the *N*-Cbz- or *N*-Fmoc-groups and benzyl/methyl esters were intact during the gold catalyzed glycosylation.[10] Versatility of the glycosylation methodology with gold reagents was further extended to the other glycosyl donors. For example, galactosyl (**1b**), mannosyl (**1c**) and lactosyl (**1d**) 1,2-orthoesters were allowed to react with serine and threonine derived aglycones (**2a–2d**) to obtain corresponding galactosides (**4a–4c**), mannosides (**5a–5c**) and lactosides (**6a–6c**) respectively in good yields (Table 1). In all the cases, we identified formation of 1,2-*trans* selective glycosides only.[10]

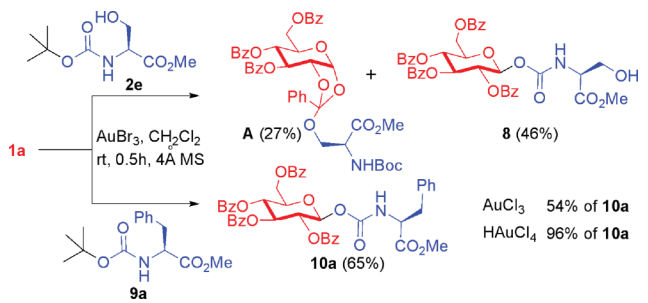
A very important application of these synthesized serine *O*-glycosides is that they can be easily converted to their corresponding *N*-carboxyanhydride (NCA), which in turn can be subjected to ring-opening polymerization to afford glycopolypeptides. The synthesis of glycopolypeptides using the ring-opening polymerization of *O*-linked glycoserine NCA has been known for a long time.[11] However, the synthesis of the NCA monomer was very inefficient and required the usage of toxic Hg salts for the key glycosylation step. An improved synthesis of serine *O*-glycoside NCA was reported by Cameron *et al.*

However no polymerization of these monomers has been reported to date except a recent report wherein Kramer and Deming have reported the synthesis of the non-natural glycosylated-L-lysine-*N*-carboxyanhydride (glyco-K NCA) monomers which efficiently polymerize into glycopolypeptides.[12a] Therefore, we attempted the synthesis of the natural D-glucose-L-serine polypeptide (**7b**) from the serine *O*-glucoside **3a**. The synthesis of the *gluco*-NCA was carried out in two steps: first, we subjected the glycoconjugate **3a** to hydrogenolysis using 10% Pd/C at 400 psi to obtain per-*O*-benzoylated-D-glucose-L-serine which was subsequently converted to its corresponding NCA **7a** using triphosgene and α-pinene[7a] in 80% yield after three crystallizations (Scheme 2). Polymerization of **7a** was attempted using hexylamine as the initiator (M/I = 20) in dry DMF (Scheme 2). The progress of the polymerization was followed by monitoring the complete disappearance (24 h) of the anhydride stretch of the NCA ring at 1787 and 1852 cm^{-1} in FT-IR. The resultant polymer **7b** was purified by reprecipitation. The number average molecular weight (M_n) of the precipitated polymer **7b** was estimated to be 13,600 Da by GPC (expected molecular weight 13,400) and a molecular weight distribution with a PDI of 1.1 was observed. The structure of the resulting polymer **7b** was identified by ^1H and ^{13}C NMR spectral analysis.[10] The overall strategy can be applied to obtain glycosyl NCAs and eventually glycopolypeptides.[12b] Such glycopolypeptides, featuring synthetic macromolecules with pendant carbohydrate moieties, can find widespread applications in various fields such as macromolecular drugs and drug delivery systems, hydrogels, matrices for controlled cell culture, and as models of biological systems.



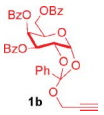
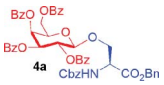
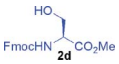
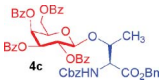
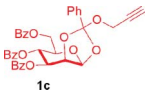
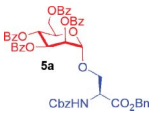
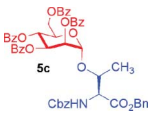
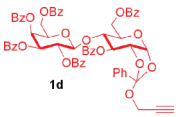
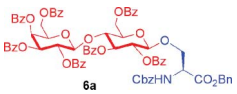
Scheme 2 Synthesis of *N*-carboxyanhydride and glycopeptide. Reagents: (1) Pd/C, H_2, CH_3OH, 400 psi, 4 h; (2) Triphosgene, α-pinene, THF, 50 °C, 2 h; (3) Hexylamine (0.05 eq), 'proton sponge' (0.25 eq), DMF, rt, 24 h.

tert-Butoxy carbamates (*t*-Boc) of serine/threonine are also frequently used in the glycopeptide synthesis.[3] Thus a model gold catalyzed glycosylation was performed between 1,2-orthoester (**1a**) and BocSer(OH)OMe (**2e**). The required amino acid glucoside was not observed and instead, surprisingly an orthoester **A** was obtained in 27% yield; the major compound being a *O*-linked glucosyl carbamate (**8**). The structure of orthoester **A** and carbamate **8** was assigned after thorough characterization (Scheme 3).[10] For example, anomeric proton of compound **A** was noticed at δ 6.01 ppm as a doublet (J = 5.2 Hz) along with anomeric and quaternary carbons at δ 97.6 and 121.1 ppm respectively.



Scheme 3 Glucosyl carbamates from propargyl 1,2-orthoesters.

Table 1 Synthesis of amino acid *O*-glycosides

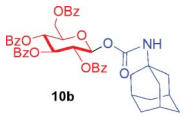
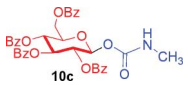
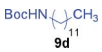
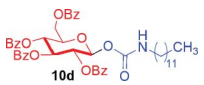
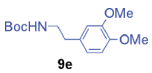
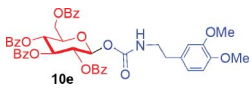
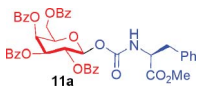
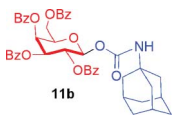
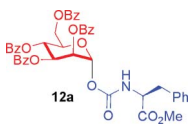
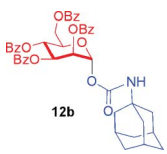
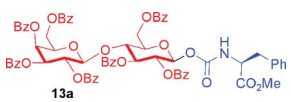
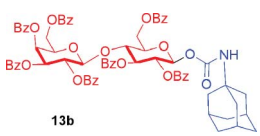
Glycosyl donor	Glycosyl acceptor	Glycoconjugate	Time/ h	Yield (%)
	**2a**		1.0	63
			2.0	67
	2c		1.0	69
	**2a**		2.0	62
	2b		2.0	66
	2c		2.0	62
	**2a**		2.0	61
	2d		2.0	63
	2b		2.0	64

Structural integrity of compound **8** was confirmed as the 1,2-*trans* *O*-carbamate since the anomeric proton was identified in a more deshielded region at δ 6.06 ppm as a doublet (J = 8.4 Hz) and concurrently the anomeric carbon was noticed at δ 93.5 ppm.[10] This unexpected set back was attributed to acidic reaction conditions and hence it has been envisioned that strong Lewis and Brønsted acids would facilitate the glycoside formation.[9] But the presence of the acid labile *t*-Boc group posed a serious hurdle in this direction.

Formation of glucosyl carbamate can be ascribed to reaction conditions that facilitated the cleavage of the tertiary butyl group thereby producing a reactive carbamic acid.[13a] Usually carbamic acids liberate carbon dioxide to afford corresponding amines; however, in this situation, carbamic acid trapped the *in situ* generated oxocarbenium ion from **1a** to give glucosyl carbamate. This peculiar observation was further corroborated, as the *t*-Boc protected phenylalanine also reacted with the glycosyl donor **1a** to give glucosyl carbamate **10a** in 65% yield.[10] Less Brønsted acidic and alkynophilic $AuCl_3$ did not improve the performance of the reaction as the release of HCl will not be facile in an aprotic medium; nevertheless, near quantitative yield of compound **10a** was obtained in 2 h with a catalytic amount of $HAuCl_4$ (Scheme 3).[10] Similar cleavage of the *t*-butyl group and intramolecular cyclization was observed when *N*-Boc protected alkynylamines were treated with gold reagents to give alkylidene 2-oxazolidinones.[13b,c]

The unusual formation of the carbamate linkage needs a special mention. Glycosyl carbamates are important because of their stability to alkaline conditions[13a] and some of them are reported to act as glycosyl donors.[13d,e] In addition, glycosyl carbamates are studied as dopamine prodrugs[13f,g] and surfactants.[13h] Recently, carbamate linkages were explored for studying carbohydrate–protein interactions[13i] and also for ligation.[13j] Glycosyl carbamates can be prepared by a reaction of corresponding lactol and an isocyanate[13l] in the presence of a base[13d] or from glycosyl carbonates.[13k] TMSOTf catalyzed reaction of glycosyl trichloroacetimidates perhaps

Table 2 Synthesis of glycosyl carbamates

Glycosyl donor	Acceptor	Product	Yield (%)
1a	 **9b**	 **10b**	98
	$BocNHCH_3$ **9c**	 **10c**	96
	 **9d**	 **10d**	99
	 **9e**	 **10e**	95
	 **9f**	 **10f**	94
1b	**9a**	 **11a**	97
	9b	 **11b**	98
1c	**9a**	 **12a**	98
	9b	 **12b**	95
1d	**9a**	 **13a**	95
	9b	 **13b**	96

gives easy access but in moderate to good yields depending on the type of substrate.[13a] Thus, methods that enable easy synthesis of glycosyl carbamates without the use of toxic isocyanates from stable glycosyl donors are invaluable. The foregoing discussion clearly highlights the merit of $HAuCl_4$ catalyzed synthesis of glucosyl carbamate from stable propargyl 1,2-orthoester as a glycosyl donor.

The generality of the methodology has been verified by using a panel of *t*-Boc protected amines. Boc-protected amino compounds of alicyclic (**9b**), aliphatic (**9c**, **9d**) and aromatic (**9e,9f**) reacted with glucose 1,2-orthoester **1a** to afford their respective carbamates **10b–10f** (Table 2).[10] Furthermore, galactosyl- (**1b**), mannosyl- (**1c**) and lactosyl- (**1d**) derived propargyl 1,2-orthoesters (**1d**) also participated successfully in the glycosylation reaction to afford the corresponding 1,2-*trans* glycosides **11a–b**, **12a–b** and **13a–b** in near quantitative yields (Table 2).

In conclusion, a new method for the synthesis of amino acid glycoconjugates is described which is more applicable to

Cbz- and Fmoc-protected amino acid Me/benzyl esters. Boc-protected serine derivative was found to give serine 1,2-orthoester in poor yield and the major compound was found to be the glycosyl carbamate. Optimized reaction conditions showed $HAuCl_4$ gave glycosyl carbamates in excellent yields. The generality of the methodology was evaluated using various glycosyl donors, aglycones and building blocks. Several opportunities as a result of the easy access to this novel glycosidic linkage are currently underway.

Experimental

General procedure for the synthesis of amino acid glycosides. To a solution of glycosyl donor (0.1 mmol) and aglycone (0.1 mmol) in anhydrous CH_2Cl_2 (5 mL) was added 4 Å MS powder (50 mg 0.1 $mmol^{-1}$) and 7 mol% of $AuBr_3$ under argon atmosphere at room temperature. The resulting mixture was stirred till the completion of the reaction as judged by TLC analysis. The reaction mixture was concentrated *in vacuo* to obtain a crude residue which was purified by conventional silica gel column chromatography using ethyl acetate–petroleum ether as mobile phase.

General procedure for the synthesis of glycosyl carbamates from propargyl 1,2-orthoesters. To a solution of glycosyl donor (0.1 mmol) and *t*-Boc protected amine (0.1 mmol) in anhydrous CH_2Cl_2 (5 mL) was added 4 Å MS powder (50 mg 0.1 $mmol^{-1}$) and 5 mol% of $HAuCl_4$ under argon atmosphere at room temperature. The resulting mixture was stirred till the completion of the reaction as judged by TLC analysis (2 h). The reaction mixture was concentrated *in vacuo* to obtain a crude residue which was purified by conventional silica gel column chromatography using ethyl acetate–petroleum ether as mobile phase.

General procedure for the glyco *N*-carboxyanhydrides (7a). Hydrogenolysis of compounds **3a** was carried out using 10% Pd/C in MeOH–EtOAc (9 : 1) at 400 psi for 12 h. After completion of the reaction, the reaction mixture was filtered and concentrated under reduced pressure to afford per-*O*-benzoylated-D-glucose-L-serine in almost quantitative yield. The resulting compounds were directly used for NCA synthesis without any further purification.

To a solution of per-*O*-benzoylated-D-glucose-L-serine (0.1 mmol) in freshly distilled anhydrous tetrahydrofuran (30 mL) was added a solution of triphosgene (0.05 mmol) in anhydrous tetrahydrofuran (5 mL) under argon atmosphere. α-Pinene (0.15 mmol) was added and the reaction mixture was heated to 50 °C for 2 h and cooled to room temperature, poured into dry hexane. The white precipitate of the *N*-carboxyanhydride (**7a**) was vacuum filtered quickly and reprecipitated (2×) by dissolving in ethyl acetate followed by addition of light petroleum. The resulting precipitate was filtered and dried under vacuum (Yield 80%).

Procedure for the synthesis of glycopolymer (7b). To a 2 mL solution of glyco-*N*-carboxyanhydride (**7a**) (200 mg, 0.28 mmol) in anhydrous DMF was added 1,8-bis(dimethylamino)naphthalene (0.07 mmol; 1 M) ['proton sponge'] as an additive and hexylamine (14 μL, 1.0 mmol mL^{-1}) as an initiator inside the glove box. The progress of the polymerization was monitored by FT-IR spectroscopy by comparing with the intensity of the initial NCA's anhydride stretching at 1789 cm^{-1} and 1852 cm^{-1}. At the end of the reaction (24 h), an aliquot was removed for GPC analysis. The solvent was removed under reduced pressure and the residue was redissolved in CH_2Cl_2 and the polymer was precipitated out by the addition of methanol. The precipitated polymer was collected by centrifugation and dried to afford white glycopolypeptide **7b** in 90% yield.

Compound characterization data

Benzyl *N*-(benzyloxycarbonyl)-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-L-serinate (3a). $[\alpha]_D^{25}$ = +14.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 3.91(dd, *J* = 3.4, 10.3 Hz, 1 H), 4.01(ddd, *J* = 3.3, 4.9, 8.3 Hz, 1 H), 4.32–4.56(m, 3H), 4.61(dd, *J* = 3.2, 12.2 Hz, 1 H), 4.78(d, *J* = 7.6 Hz, 1 H), 4.99(dd, *J* = 12.3, 19.4 Hz, 2 H), 5.13(dd, *J* = 12.3, 14.3 Hz, 2 H), 5.45(dd, *J* = 7.8, 9.5 Hz, 1 H), 5.61(m, 2H), 5.86(t, *J* = 9.6 Hz, 1 H), 7.20–7.58(m, 22H), 7.78–8.05(m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 54.2, 62.9, 66.9, 67.4, 69.3, 69.4, 71.7, 72.2, 72.5, 101.3, 128.0–129.8, 133.1, 133.2, 133.3, 133.4, 135.2, 136.2, 155.8, 165.1, 165.1, 165.7, 166.1, 169.2; Anal. Calcd for $C_{52}H_{45}NO_{14}$: C, 68.79; H, 5.00; N, 1.54; Found: C, 67.87; H, 5.21; N, 1.66; HRMS (MALDI-TOF): *m*/*z* calcd for $C_{52}H_{45}NO_{14}$+Na: 930.2738, Found: 930.2742.

Methyl *N*-(9-Fluorenylmethoxycarbonyl)-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-L-threoninate (3b). $[\alpha]_D^{25}$ = +12.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 1.14(d, *J* = 6.3 Hz, 3 H), 3.71(s, 3 H), 4.05–4.58(m, 7 H), 4.65(dd, *J* = 3.3, 12.2 Hz, 1 H), 4.87(d, *J* = 7.7 Hz, 1 H), 5.48(dd, *J* = 8.0, 9.7 Hz, 1 H), 5.69(m, 2 H), 5.91(t, *J* = 9.7 Hz, 1 H), 7.20–7.65(m, 20 H), 7.72–8.06(m, 8 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 16.9, 47.0, 52.5, 58.4, 62.8, 67.3, 69.4, 71.8, 72.1, 72.6, 75.1, 99.3, 119.9, 125.2, 127.0–128.8, 133.2, 133.3, 133.3, 133.4, 141.1, 141.2, 143.6, 143.9, 156.7, 165.1, 165.1, 165.7, 166.1, 170.5; Anal. Calcd for $C_{54}H_{47}NO_{14}$: C, 69.44; H, 5.07; N, 1.50; Found: C, 69.18; H, 5.22; N, 1.80; HRMS (MALDI-TOF): *m*/*z* Calcd for $C_{54}H_{47}NO_{14}$+Na, 956.2894; Found, 956.2889.

Benzyl *N*-(benzyloxycarbonyl)-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-L-threoninate (3c). $[\alpha]_D^{25}$ = +4.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 1.11(d, *J* = 6.3 Hz, 3 H), 3.86(td, *J* = 3.5, 9.4 Hz, 1 H), 4.30–4.59(m, 4 H), 4.74(d, 1 H, *J* = 8.0 Hz), 5.04(s, 2 H), 5.18(s, 2 H), 5.38(dd, *J* = 8.0, 9.6 Hz, 1 H), 5.62(m, 2 H), 5.80(t, *J* = 9.5 Hz, 1 H), 7.20–7.58(m, 22 H), 7.79–8.05(m, 8 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 17.0, 58.4, 62.6, 66.9, 67.2, 69.2, 71.9, 72.0, 72.5, 75.0, 99.0, 127.8–129.7, 133.1, 133.2, 133.3, 133.4, 135.4, 136.2, 156.7, 165.0, 165.0, 165.7, 166.0, 169.8; Anal. Calcd for $C_{53}H_{47}NO_{14}$: C, 69.05; H, 5.14; N, 1.52; Found: C, 68.64; H, 5.76; N, 1.77; HRMS (MALDI-TOF): *m*/*z* Calcd. for $C_{53}H_{47}NO_{14}$+Na, 944.2894; Found, 944.2899.

Benzyl *N*-(benzyloxycarbonyl)-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-L-serinate (4a). $[\alpha]_D^{25}$ = +58.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 3.98(dd, *J* = 3.2, 10.4 Hz, 1 H), 4.19(m, 2 H), 4.32–4.80(m, 4 H), 5.00(q, *J* = 12.3, 17.7 Hz, 2 H), 5.17(q, *J* = 12.4, 17.3 Hz, 2 H), 5.56(m, 1 H), 5.73(m, 2 H), 5.96(m, 1 H), 7.20–7.68(m, 22 H), 7.74–8.11(m, 8 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 54.3, 61.8, 66.9, 67.4, 67.9, 69.4, 69.5, 71.4, 71.4, 101.8, 127.9–130.0, 133.2, 133.3, 133.3, 133.6, 135.2, 136.1, 155.8, 165.2, 165.4, 165.5, 166.0, 169.3; Anal. Calcd for $C_{52}H_{45}NO_{14}$: C, 68.79; H, 5.00; N, 1.54; Found: C, 67.86; H, 5.18;

N, 1.62; HRMS (MALDI-TOF): *m/z* Calcd for $C_{52}H_{45}NO_{14}$+Na, 930.2738; Found, 930.2735.

Methyl *N*-(9-Fluorenylmethoxycarbonyl)-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-L-serinate (4b). $[\alpha]_D^{25}$ = +66.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 3.68(s, 3 H), 3.94(dd, *J* = 3.4, 10.4 Hz, 1 H), 4.14(t, *J* = 6.9 Hz, 1 H), 4.25–4.52(m, 6 H), 4.63(dd, *J* = 6.5, 11.1 Hz, 1 H), 4.73(d, *J* = 7.6 Hz, 1 H), 5.52(d, *J* = 8.1 Hz, 1 H), 5.60(dd, *J* = 3.3, 10.2 Hz, 1 H), 5.75(dd, *J* = 7.8, 10.2 Hz, 1 H), 6.00(d, *J* = 3.3 Hz, 1 H), 7.20–7.66(m, 20 H), 7.75–8.11(m, 8 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 47.1, 52.7, 54.3, 61.9, 66.7, 67.9, 69.4, 69.4, 71.4, 71.4, 101.8, 119.9–130.0, 133.2, 133.3, 133.3, 133.6, 141.3, 141.3, 143.7, 143.8, 155.7, 165.2, 165.5, 165.5, 166.0, 169.8; Anal. Calcd for $C_{53}H_{45}NO_{14}$: C, 69.20; H, 4.93; N, 1.52; Found: C, 67.94; H, 4.02; N, 1.66; HRMS (MALDI-TOF): *m/z* Calcd for $C_{53}H_{45}NO_{14}$+Na, 942.2738; Found, 942.2736.

Benzyl *N*-(benzyloxycarbonyl)-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-L-threoninate (4c). $[\alpha]_D^{25}$ = +36.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 1.14(d, *J* = 6.4 Hz, 3 H), 4.06(t, *J* = 6.4 Hz, 1 H), 4.31(dd, *J* = 7.1, 11.3 Hz, 1 H), 4.43(dd, *J* = 2.2, 9.3 Hz, 1 H), 4.48–4.61(m, 2 H), 4.71(d, *J* = 7.8 Hz, 1 H), 5.07(s, 2 H), 5.24(s, 2 H), 5.51(dd, *J* = 3.3, 10.4 Hz, 1 H), 5.61–5.75(m, 2 H), 5.92(d, *J* = 3.8 Hz, 1 H), 7.19–7.66(m, 22 H), 7.75–8.08(m, 8 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 17.4, 58.5, 61.6, 67.0, 67.3, 67.8, 69.8, 71.1, 71.3, 75.6, 99.9, 127.8–130.0, 133.2, 133.3, 133.3, 133.5, 135.4, 136.2, 156.7, 165.2, 165.5, 165.5, 165.9, 169.9; Anal. calcd for $C_{53}H_{47}NO_{14}$: C, 69.05; H, 5.14; N, 1.52; Found: C, 66.49; H, 4.95; N, 1.35; HRMS (MALDI-TOF): *m/z* Calcd for $C_{53}H_{47}NO_{14}$+Na, 944.2894; Found, 944.2890.

Benzyl *N*-(benzyloxycarbonyl)-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-L-serinate (5a). $[\alpha]_D^{25}$ = −42.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 4.14(d, *J* = 2.7 Hz, 2 H), 4.32–4.68(m, 4 H), 4.99(d, *J* = 1.6 Hz, 1 H), 5.14(d, *J* = 1.5 Hz, 2 H), 5.32(dd, *J* = 12.1, 20.5 Hz, 2 H), 5.59(dd, *J* = 1.8, 3.2 Hz, 1 H), 5.79(dd, *J* = 3.2, 10.1 Hz, 1 H), 5.96(d, *J* = 7.9 Hz, 1 H), 6.09(t, *J* = 10.1 Hz, 1 H), 7.20–7.65(m, 22 H), 7.81–8.14(m, 8 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 54.5, 62.6, 66.5, 67.2, 67.8, 67.9, 69.4, 69.7, 70.1, 98.4, 128.1–129.9, 133.0, 133.1, 133.4, 133.5, 135.0, 136.0, 155.9, 165.2, 165.3, 165.4, 166.1, 169.5; Anal. calcd for $C_{52}H_{45}NO_{14}$: C, 68.79; H, 5.00; N, 1.54; Found: C, 68.21; H, 5.58; N, 1.49; HRMS (MALDI-TOF): *m/z* Calcd for $C_{52}H_{45}NO_{14}$+Na, 930.2738; Found, 930.2740.

Methyl *N*-(9-Fluorenylmethoxycarbonyl)-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-L-threoninate (5b). $[\alpha]_D^{25}$ = −30.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 1.43(d, *J* = 6.2 Hz, 3 H), 3.90(s, 3 H), 4.33(dd, *J* = 7.1, 14.4 Hz, 2 H), 4.28–4.75(m, 6 H), 5.17(d, *J* = 1.5 Hz, 1 H), 5.50(dd, *J* = 1.8, 3.1 Hz, 1 H), 5.75–5.95(m, 2 H), 6.10(t, *J* = 9.6 Hz, 1 H), 7.20–8.10(m, 28 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 18.2, 47.1, 53.0, 58.6, 62.9, 66.9, 67.5, 69.4, 69.6, 70.5, 77.8, 99.0, 119.9, 125.2, 127.1–129.8, 133.1, 133.2, 133.5, 133.5, 141.3, 141.3, 143.7, 143.8, 156.7, 165.3, 165.5, 165.5, 166.1, 170.5; Anal. calcd for $C_{54}H_{47}NO_{14}$: C, 69.44; H, 5.07; N, 1.50; Found: C, 66.42; H, 4.20; N, 1.34; HRMS (MALDI-TOF): *m/z* Calcd for $C_{54}H_{47}NO_{14}$+Na, 956.2894; Found, 956.2893.

Benzyl *N*-(benzyloxycarbonyl)-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-L-threoninate (5c). $[\alpha]_D^{25}$ = −40.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 1.42(d, *J* = 6.2 Hz, 3 H), 4.42–4.55(m, 3 H), 4.57–4.71(m, 2 H), 5.07(d, *J* = 1.8 Hz, 1 H), 5.19(s, 2 H), 5.31(s, 2 H), 5.45(dd, *J* = 1.8, 3.1 Hz, 1 H), 5.72–5.85(m, 2 H), 6.06(t, *J* = 9.9 Hz, 1 H), 7.21–7.68(m, 22 H), 7.82–8.10(m, 8 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 18.3, 58.8, 62.9, 66.8, 67.3, 67.9, 69.6, 69.7, 70.5, 77.9, 99.0, 128.1–129.9, 133.1, 133.1, 133.5, 133.5, 135.0, 136.1, 156.7, 165.2, 165.2, 165.4, 166.1, 169.9; Anal. calcd for $C_{53}H_{47}NO_{14}$: C, 69.05; H, 5.14; N, 1.52; Found: C, 69.51; H, 4.67; N, 1.02; HRMS (MALDI-TOF): *m/z* Calcd for $C_{53}H_{47}NO_{14}$+Na, 944.2894; Found, 944.2897.

Benzyl *N*-(benzyloxycarbonyl)-*O*-[2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-β-D-glucopyransyl]-L-serinate (6a). $[\alpha]_D^{25}$ = +46.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 3.59(d, *J* = 9.7 Hz, 1 H), 3.70(d, *J* = 6.5 Hz, 2 H), 3.78–3.92(m, 2 H), 4.18(t, *J* = 9.7 Hz, 1 H), 4.26(dd, *J* = 2.6, 10.4 Hz, 1 H), 4.36–4.59(m, 4 H), 4.81–4.98(m, 3 H), 5.06(s, 2 H), 5.32–5.45(m, 2 H), 5.52(d, *J* = 8.0 Hz, 1 H), 5.69(d, *J* = 9.2 Hz, 2 H), 5.75(d, *J* = 6.2 Hz, 1 H), 7.11–7.64(m, 31 H), 7.69–8.02(m, 14 H); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 54.2, 61.0, 62.1, 66.9, 67.3, 67.5, 69.4, 69.8, 71.3, 71.5, 71.7, 72.5, 73.0, 75.6, 100.9, 101.3, 128.0–130.0, 133.1, 133.2, 133.3, 133.4, 133.4, 133.5, 133.5, 135.1, 136.2, 155.8, 164.8, 165.1, 165.2, 165.3, 165.4, 165.6, 165.8, 169.2; Anal. calcd for $C_{79}H_{67}NO_{22}$: C, 68.64; H, 4.89; N, 1.01; Found: C, 68.36; H, 4.38; N, 1.12; HRMS (MALDI-TOF): *m/z* Calcd for $C_{79}H_{67}NO_{22}$+Na, 1404.4052; Found, 1404.4048.

Methyl *N*-(9-Fluorenylmethoxycarbonyl)-*O*-[2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-β-D-glucopyranosyl]-L-serinate (6b). $[\alpha]_D^{25}$ = +48.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 3.58(s, 3 H), 3.71(d, *J* = 6.4 Hz, 2 H), 3.80(m, 2 H), 3.91(t, *J* = 6.7 Hz, 1 H), 4.11(t, *J* = 6.7 Hz, 1 H), 4.20–4.35(m, 3 H), 4.41(m, 1 H), 4.48(dd, *J* = 4.3, 12.3 Hz, 2 H), 4.59(m, 2 H), 4.88(d, *J* = 7.9 Hz, 1 H), 5.38–5.45(m, 2 H), 5.48(d, *J* = 7.9 Hz, 1 H), 5.73–5.85(m, 3 H), 7.11–8.02(m, 43 H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 47.1, 52.6, 54.2, 61.0, 62.1, 66.8, 67.4, 69.4, 69.8, 71.3, 71.4, 71.6, 72.5, 73.0, 75.7, 101.0, 101.3, 120.0, 125.0, 125.1, 126.9–130.0, 133.2, 133.3., 133.4, 133.4, 133.5, 141.2, 141.3, 143.6, 143.7, 155.7, 164.8, 165.1, 165.2, 165.2, 165.4, 165.5, 165.8, 169.7; Anal. calcd for $C_{80}H_{67}NO_{22}$: C, 68.79; H, 5.00; N, 1.54; Found: C, 68.21; H, 5.58; N, 1.49; HRMS (MALDI-TOF): *m/z* Calcd for $C_{80}H_{67}NO_{22}$+Na, 1416.4052; Found, 1416.4056.

Methyl *N*-(9-Fluorenylmethoxycarbonyl)-*O*-[2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-β-D-glucopyranosyl]-L-threoninate (6c). $[\alpha]_D^{25}$ = +42.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.11(d, *J* = 6.4 Hz, 3 H), 3.57(s, 3 H), 3.70–3.86(m, 3 H), 3.94(t, *J* = 6.6 Hz, 1 H), 4.13–4.45(m, 6 H), 4.52(dt, *J* = 3.9, 12.9 Hz, 1 H), 4.61(ABq, *J* = 14.9 Hz, 1 H), 4.85(ABq, *J* = 8.0 Hz, 2 H), 5.44(m, 2 H), 5.69(d, *J* = 9.3 Hz, 1 H), 5.73–5.87(m, 3 H), 7.12–8.13(m, 43 H); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 16.8, 47.0, 52.3, 58.4, 61.0, 62.1, 67.3, 67.5, 69.9, 71.4, 71.7, 72.6, 73.0, 74.9, 75.7, 77.2, 99.0, 101.0, 119.9, 125.2, 127.0–129.9, 133.2, 133.3, 133.4, 133.5, 133.5, 141.1, 141.2, 143.6, 143.9, 156.7, 164.8, 165.2, 165.2, 165.3, 165.4, 165.5, 165.8, 170.4; Anal. calcd for $C_{81}H_{69}NO_{22}$: C, 69.08; H, 4.94; N, 0.99; Found: C, 67.51; H, 5.02; N, 0.69; HRMS (MALDI-TOF): *m/z* Calcd for $C_{81}H_{69}NO_{22}$+Na, 1430.4209; Found, 1430.4212.

***O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-*N*-carboxy-L-serine anhydride (7a).** IR(cm^{-1}): 1854, 1789; ^1H NMR (500.13 MHz, $CDCl_3$): δ = 3.92(dd, J = 5.8, 11.0 Hz, 1H), 4.11(t, J = 9.0 Hz, 2H), 4.26–4.35(m, 2H), 4.85(d, J = 7.6 Hz, 1H), 4.90(d, J = 12.2 Hz, 1H), 5.40(t, J = 9.5 Hz, 1H), 5.66(t, J = 9.5 Hz, 1H), 5.84(t, J = 9.8 Hz, 1H), 6.69(s, 1H), 7.15–7.54(m, 12H), 7.70(d, J = 7.4 Hz, 2H), 7.86(d, J = 7.2 Hz, 2H), 7.87(d, J = 7.2 Hz, 2H), 8.03(d, J = 7.6 Hz, 2H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 58.5, 62.1, 68.6, 68.7, 71.2, 72.4, 73.2, 101.2, 128.3–130.0, 133.3, 133.5, 133.6, 133.6, 151.5, 165.1, 165.2, 165.7, 166.7, 167.1; MS (ESI): m/z: calcd for $[C_{38}H_{31}NO_{13}+Na]^+$: 732.641; found: 732.145.

3,4,6-tri-*O*-Benzoyl-1,2-*O*-[(2*S*-(2-*tert*-butoxycarbonylamino)-3-methoxy-3-oxopropoxy)phenylmethylene]-α-D-glucopyranoside (A). $[\alpha]_D^{25}$ = +3.8 (c = 1.0, $CHCl_3$); ^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.41(s, 9 H), 3.60(dd, J = 3.2, 9.9 Hz, 1 H), 3.69((m, 1 H), 3.71(s, 3 H), 4.09(ddd, J = 3.1, 4.9, 7.9 Hz, 1 H), 4.37(dd, J = 5.0, 11.7 Hz, 2 H), 4.52(dd, J = 2.8, 11.7 Hz, 1 H), 4.74(t, J = 4.2 Hz, 1 H), 5.31(d, J = 8.8 Hz, 1 H), 5.47(d, J = 8.8 Hz, 1 H), 5.73(bs, 1 H), 6.01(d, J = 5.2 Hz, 1 H), 7.21–7.66(m, 12 H), 7.70(d, J = 7.3 Hz, 2 H), 7.91(d, J = 7.8 Hz, 2 H), 7.94(d, J = 8.2 Hz, 2 H), 8.08(d, J = 7.3 Hz, 2 H); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 28.2(3C). 52.5, 53.4, 63.9, 64.2, 67.6, 68.3, 69.0, 72.2, 80.1, 97.6, 121.1, 126.2, 128.2–130.1, 133.0, 133.5, 133.7, 134.5, 155.3, 164.5, 165.1, 166.0, 170.7; HRMS (MALDI-TOF): m/z Calcd for $C_{43}H_{43}NO_{14}$+Na, 820.2581; Found, 820.2577.

Methyl *N*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyloxycarbonyl)-L-serinate (8). $[\alpha]_D^{25}$ = +32.9 (c = 1.0, $CHCl_3$); ^1H NMR (400.13 MHz, $CDCl_3$): δ 2.44(bs, 1 H), 3.61(s, 3 H), 3.94(ddd, J = 3.2, 11.4, 14.8 Hz, 2 H), 4.29–4.38(m, 2 H), 4.51(dd, J = 4.8, 12.3 Hz, 1 H), 4.65(dd, J = 2.9, 12.3 Hz, 1 H), 5.68(dd, J = 8.3, 9.5 Hz, 1 H), 5.77(t, J = 9.5 Hz, 1 H), 5.97(m, 2 H), 6.06(d, J = 8.4 Hz, 1 H), 7.25–7.61(m, 12 H), 7.85(d, J = 7.4 Hz, 2 H), 7.91(d, J = 7.4 Hz, 2 H), 7.96(d, J = 7.4 Hz, 2 H), 8.05(d, J = 7.4 Hz, 2 H); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 52.6, 56.0, 62.6, 62.6, 68.9, 70.7, 72.8, 73.0, 93.5, 128.3–130.0, 133.2, 133.3, 133.5, 133.5, 153.5, 165.1, 165.2, 165.6, 166.2, 170.2; HRMS (MALDI-TOF): m/z Calcd for $C_{39}H_{35}NO_{14}$+Na, 764.1955; Found, 764.1960.

Methyl *N*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyloxycarbonyl)-L-phenylalaninate (10a). $[\alpha]_D^{25}$ = +46.5 (c = 1.0, $CHCl_3$); ^1H NMR (200.13 MHz, $CDCl_3$): δ = 3.07(ddd, J = 5.6, 13.8, 19.4 Hz, 2 H), 3.54(s, 3 H), 4.29(ddd, J = 3.2, 4.5, 7.6 Hz, 1 H), 4.44–4.71(m, 3 H), 5.44(d, J = 8.3 Hz, 1 H), 5.63(dd, J = 8.3, 9.5 Hz, 1 H), 5.74(t, J = 9.5 Hz, 1 H), 5.92(t, J = 9.6 Hz, 1 H), 6.02(d, J = 8.2 Hz, 1 H), 6.98–7.61(m, 17 H), 7.76–8.10(m, 8 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 37.8, 52.2, 55.0, 62.7, 69.1, 70.6, 72.9, 72.9, 93.3, 127.2, 128.3–130.0, 133.1, 133.3, 133.4, 133.5, 135.2, 153.1, 165.1, 165.1, 165.6, 166.1, 171.0; HRMS (MALDI-TOF): m/z Calcd for $C_{45}H_{39}NO_{13}$+Na, 824.2319; Found, 824.2320.

***N*-(2,3,4,6-tetra-*O*-Benzoyl-β-D-glucopyranosyloxycarbonyl)-adamantylamine (10b).** $[\alpha]_D^{25}$ = +34.6 (c = 1.0, $CHCl_3$); ^1H NMR (200.13 MHz, $CDCl_3$): δ = 1.61(m, 6 H), 1.82(m, 6 H), 2.01(m, 3 H), 4.26(qd, J = 3.1, 4.7, 8.0 Hz, 1 H), 4.48(dd, J = 4.9, 12.3 Hz, 1 H), 4.62(dd, J = 3.0, 12.3 Hz, 1 H), 4.75(s, 1 H), 5.61(dd, J = 8.6, 9.4 Hz, 1 H), 5.72(t, J = 9.5 Hz, 1 H), 5.88–6.03(m, 2 H), 7.23–7.61(m, 12 H), 7.78–8.08(m, 8 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 29.3(3C), 36.1(3C), 41.3(3C), 51.2, 62.7, 69.2, 70.9, 72.8, 73.0, 92.6, 128.2–130.0, 133.0, 133.2, 133.4, 133.5, 151.2, 165.1, 165.3, 165.6, 166.1; HRMS (MALDI-TOF): m/z Calcd for $C_{45}H_{43}NO_{11}$+Na, 796.2734; Found, 796.2730.

***N*-(2,3,4,6-tetra-*O*-Benzoyl-β-D-glucopyranosyloxycarbonyl)-methylamine (10c).** $[\alpha]_D^{25}$ = +47.6 (c = 1.0, $CHCl_3$); ^1H NMR (200.13 MHz, $CDCl_3$): δ = 2.74(d, J = 4.9 Hz, 3 H), 4.31(qd, J = 3.0, 4.3, 7.3 Hz, 1 H), 4.48(dd, J = 4.4, 12.3 Hz, 1 H), 4.64(dd, J = 2.8, 12.3 Hz, 1 H), 4.92(q, J = 4.7, 9.6 Hz, 1 H), 5.66(dd, J = 8.3, 9.6 Hz, 1 H), 5.76(t, J = 9.6 Hz, 1 H), 5.97(t, J = 9.6 Hz, 1 H), 6.05(d, J = 8.1 Hz, 1 H), 7.24–7.61(m, 12 H), 7.79–8.01(m, 8 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 27.4, 62.6, 69.0, 70.8, 72.7, 72.9, 93.1, 128.2–130.0, 133.1, 133.2, 133.4, 133.5, 154.3, 165.1, 165.2, 165.6, 166.1; HRMS (MALDI-TOF): m/z = $C_{36}H_{31}NO_{11}$Na, 676.1795; Found, 676.1790.

***N*-(2,3,4,6-tetra-*O*-Benzoyl-β-D-glucopyranosyloxycarbonyl)-dodecylamine (10d).** $[\alpha]_D^{25}$ = +34.4 (c = 1.0, $CHCl_3$); ^1H NMR (200.13 MHz, $CDCl_3$): δ = 0.88(t, J = 6.1 Hz, 3 H), 1.15–1.45(m, 20 H), 3.10(ddd, J = 1.4, 6.8, 8.7 Hz, 2 H), 4.30(qd, J = 3.0, 4.1, 7.2 Hz, 1 H), 4.48(dd, J = 4.5, 12.3 Hz, 1 H), 4.65(dd, J = 2.9, 12.4 Hz, 1 H), 4.92(t, J = 5.9 Hz, 1 H), 5.64(dd, J = 8.3, 9.6 Hz, 1 H), 5.75(t, J = 9.6 Hz, 1 H), 5.96(t, J = 9.6 Hz, 1 H), 6.05(d, J = 8.3 Hz, 1 H), 7.23–7.68(m, 12 H), 7.79–8.08(m, 8 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 14.1, 22.6, 26.6, 29.1, 29.3, 29.4, 29.4, 29.5, 29.6, 29.6, 31.9, 41.1, 62.7, 69.1, 70.9, 72.8, 72.9, 93.1, 128.2–130.0, 133.1, 133.2, 133.4, 133.4, 153.6, 165.1, 165.2, 165.6, 166.1; HRMS (MALDI-TOF): m/z Calcd for $C_{47}H_{53}NO_{11}$+Na, 830.3516; Found, 830.3520.

***N*-(2,3,4,6-tetra-*O*-Benzoyl-β-D-glucopyranosyloxycarbonyl)-2-(3,4-dimethoxyphenyl)-ethylamine (10e).** $[\alpha]_D^{25}$ = +30.2 (c = 1.0, $CHCl_3$); ^1H NMR (200.13 MHz, $CDCl_3$): δ = 2.66(t, J = 7.1 Hz, 2 H), 3.35(ddd, J = 1.5, 6.1, 8.6 Hz, 2 H), 3.79,3.82(2 s, 6 H), 4.31(qd, J = 2.9, 4.2, 7.9 Hz, 1 H), 4.48(dd, J = 4.6, 12.4 Hz, 1 H), 4.65(dd, J = 2.9, 12.4 Hz, 1 H), 4.97(t, J = 6.0 Hz, 1 H), 5.62(dd, J = 8.4, 9.6 Hz, 1 H), 5.75(t, J = 9.6 Hz, 1 H), 5.96(t, J = 9.6 Hz, 1 H), 6.05(d, J = 8.4 Hz, 1 H), 6.55–6.74(m, 3 H), 7.23–7.61(m, 12 H), 7.75–8.08(m, 8 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 35.1, 42.3, 55.6, 55.7, 62.6, 69.0, 70.8, 72.7, 72.9, 93.1, 111.2, 111.6, 120.5, 128.2–129.8, 130.7, 133.0, 133.2, 133.4, 133.4, 147.5, 148.8, 153.6, 165.0, 165.1, 165.5, 166.0; HRMS (MALDI-TOF): m/z Calcd for $C_{45}H_{41}NO_{13}$+Na, 826.2476; Found, 826.2480.

***N*-(2,3,4,6-tetra-*O*-Benzoyl-β-D-glucopyranosyloxycarbonyl)-aniline (10f).** $[\alpha]_D^{25}$ = +29.2 (c = 1.0, $CHCl_3$); ^1H NMR (200.13 MHz, $CDCl_3$): δ = 4.35(qd, J = 3.1, 4.7, 7.7 Hz, 1 H), 4.50(dd, J = 4.7, 12.3 Hz, 1 H), 4.65(dd, J = 3.1, 12.3 Hz, 1 H), 5.72(dd, J = 8.2, 9.6 Hz, 1 H), 5.77(t, J = 9.7 Hz, 1 H), 6.00(t, J = 9.7 Hz, 1 H), 6.12(d, J = 8.2 Hz, 1 H), 6.92–7.20(m, 2 H), 7.23–7.61(m, 16 H), 7.80–8.08(m, 8 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 62.6, 69.0, 70.8, 72.9, 73.0, 93.2, 118.9, 124.1, 128.2–130.0, 133.1, 133.3, 133.5, 133.6, 136.8, 150.7, 165.1, 165.3, 165.6, 166.1; HRMS (MALDI-TOF): m/z Calcd for $C_{41}H_{33}NO_{11}$+Na, 738.1951; Found, 738.1950.

Methyl *N*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyloxycarbonyl)-L-phenylalaninate (11a). $[\alpha]_D^{25}$ = +96.6 (c = 1.0, $CHCl_3$); ^1H NMR (200.13 MHz, $CDCl_3$): δ = 3.10(ddd, J = 5.7, 13.9, 19.6 Hz, 2 H), 3.53(s, 3 H), 4.35–4.78(m, 4 H), 5.46(d, J = 8.2 Hz, 1 H), 5.65(dd, J = 3.3, 10.2 Hz, 1 H), 5.90(dd, J = 8.3, 10.2 Hz, 1 H), 6.01–6.08(m, 2 H), 7.09(m, 2 H), 7.18–7.70(m, 15

H), 7.73–8.15(m, 8 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 37.7, 52.1, 54.9, 61.7, 67.8, 68.6, 71.7, 72.0, 93.6, 127.2, 128.2–130.0, 133.2, 133.3, 133.3, 133.6, 135.2, 153.1, 165.2, 165.4, 165.4, 165.9, 171.0; HRMS (MALDI-TOF): *m/z* Calcd for $C_{45}H_{39}NO_{13}$+Na, 824.2319; Found, 824.2320.

***N*-(2,3,4,6-tetra-*O*-Benzoyl-β-D-galactopyranosyloxycarbonyl)-adamantylamine (11b).** $[\alpha]_D^{25}$ = +97.3 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 1.61(m, 6 H), 1.83(m, 6 H), 2.01(m, 3 H), 4.34–4.52(m, 2 H), 4.67(dd, *J* = 4.2, 8.6 Hz, 1 H), 4.79(s, 1 H), 5.66(dd, *J* = 3.4, 10.1 Hz, 1 H), 5.87(t, *J* = 8.3 Hz, 1 H), 5.95–6.07(m, 2 H), 7.20–7.68(m, 12 H), 7.75–8.16(m, 8 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 29.2(3C), 36.0(3C), 41.3(3C), 51.2, 61.7, 67.9, 68.9, 71.7, 71.9, 92.9, 128.2–130.0, 133.1, 133.3, 133.4, 133.5, 151.2, 165.3, 165.4, 165.5, 165.9; HRMS (MALDI-TOF): *m/z* Calcd for $C_{45}H_{43}NO_{11}$+Na, 796.2734; Found, 796.2730.

Methyl *N*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyloxycarbonyl)-L-phenylalaninate (12a). $[\alpha]_D^{25}$ = −17.8 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.19 (d, *J* = 5.9 Hz,2 H), 3.75(s, 3 H), 4.45(dd, *J* = 3.6, 9.7 Hz, 1 H), 4.50(m, 1 H), 4.61–4.82(m, 2 H), 5.60(d, *J* = 8.3 Hz,1 H), 5.77(dd, *J* = 2.0, 3.3 Hz, 1 H), 5.89(dd, *J* = 3.3, 10.2 Hz, 1 H), 6.10 (t, *J* = 10.2 Hz, 1 H), 6.29(d, *J* = 2.0 Hz, 1 H), 7.15–7.63(m, 17 H), 7.80–8.14(m, 8 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 38.1, 52.4, 54.9, 62.3, 66.1, 69.2, 69.8, 70.5, 91.7, 127.3, 128.2–130.0, 133.0, 133.3, 133.4, 133.6, 135.3, 152.5, 165.1, 165.2, 165.6, 166.0, 171.6; HRMS (MALDI-TOF): *m/z* Calcd for $C_{45}H_{39}NO_{13}$+Na, 824.2319; Found, 824.2320.

***N*-(2,3,4,6-tetra-*O*-Benzoyl-α-D-mannopyranosyloxycarbonyl)-adamantylamine (12b).** $[\alpha]_D^{25}$ = −41.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 1.61(m, 6 H), 1.83(m, 6 H), 2.01(m, 3 H), 4.34–4.52(m, 2 H), 4.67(dd, *J* = 4.2, 8.6 Hz,1 H), 4.79(s, 1 H), 5.66(dd, *J* = 3.4, 10.1 Hz, 1 H), 5.87(t, *J* = 8.3 Hz, 1 H), 5.95–6.07(m, 2 H), 7.20–7.68(m, 12 H), 7.75–8.16(m, 8 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 29.4(3C), 36.2(3C), 41.5(3C), 51.4, 62.7, 66.4, 69.6, 70.0, 70.3, 90.7, 128.3–130.0, 133.0, 133.3, 133.5, 133.5, 150.5, 165.2, 165.3, 165.7, 166.1; HRMS (MALDI-TOF): *m/z* Calcd for $C_{45}H_{43}NO_{11}$+Na, 796.2734; Found, 796.2730.

Methyl *N*-(2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl- β-D-galactopyranosyl)-β-D-glucopyranosyloxycarbonyl)-L-phenylalaninate (13a). $[\alpha]_D^{25}$ = +54.5 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 3.04(ddd, *J* = 5.8, 13.9, 19.4 Hz, 2 H), 3.52(s, 3 H), 3.58–4.05(m, 4 H), 4.29(t, *J* = 9.6 Hz, 1 H), 4.43–4.65(m, 3 H), 4.85(d, *J* = 7.9 Hz, 1 H), 5.35(dd, *J* = 3.4, 6.5 Hz, 1 H), 5.39(s, 1 H), 5.56(dd, *J* = 8.4, 9.7 Hz, 1 H), 5.72(dd, *J* = 7.9, 10.3 Hz, 2 H), 5.83(t, *J* = 9.4 Hz, 1 H), 5.87(d, *J* = 8.4 Hz, 1 H), 6.95–7.78(m, 26 H), 7.86–8.07(m, 14 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 37.8, 52.2, 54.9, 60.9, 62.0, 67.4, 69.7, 70.4, 71.3, 71.7, 72.9, 73.5, 75.6, 93.2, 101.0, 127.1, 128.2–130.0, 133.1, 133.2, 133.3, 133.3, 133.4, 133.4, 133.5, 135.2, 153.0, 164.7, 165.2, 165.2, 165.3, 165.4, 165.5, 165.8, 171.0; HRMS (MALDI-TOF): *m/z* Calcd for $C_{72}H_{61}NO_{21}$+Na, 1298.3634; Found, 1298.3630.

***N*-(2,3,6-tri-*O*-Benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl- β-D-galactopyranosyl)-β-D-glucopyranosyloxycarbonyl)-L-adamantylamine (13b).** $[\alpha]_D^{25}$ = +48.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 1.58(m, 6 H), 1.78(m, 6 H), 1.99(m, 3 H), 3.60–3.98 (m, 4 H), 4.29(t, *J* = 9.6 Hz, 1 H), 4.48(dd, *J* = 3.7, 12.4 Hz, 1 H), 4.59(dd, *J* = 1.7, 12.4 Hz, 1 H), 4.71(s, 1 H), 4.84(d, *J* = 7.9 Hz, 1 H), 5.35(dd, *J* = 3.3, 10.2 Hz, 1 H), 5.54(t, *J* = 9.0 Hz, 1 H), 5.72(dd, *J* = 7.8, 10.2 Hz, 2 H), 5.79–5.95(m, 2 H), 7.06–7.80(m, 21 H), 7.75–8.06(m, 14 H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 29.2(3C), 36.0(3C), 41.3(3C), 51.1, 60.9, 62.2, 67.4, 69.7, 70.8, 71.3, 71.7, 72.9, 73.5, 75.7, 92.5, 101.0, 128.2–130.0, 133.1, 133.2, 133.3, 133.4, 133.5, 133.6, 133.6, 151.1, 164.8, 165.2, 165.2, 165.4, 165.4, 165.5, 165.8; HRMS (MALDI-TOF): *m/z* Calcd for $C_{72}H_{65}NO_{19}$+Na, 1270.4048; Found, 1270.4050.

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Notes and references

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