Organic & Biomolecular Chemistry

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Cite this: *Org. Biomol. Chem.*, 2021, **19**, 1315

Synthesis of the hyper-branched core tetrasaccharide motif of chloroviruses†

Bijoyananda Mishra, Sujit Manmode, Gulab Walke, Saptashwa Chakraborty, Mahesh Neralkar and Srinivas Hotha *

Received 1st November 2020,
Accepted 4th January 2021

DOI: 10.1039/d0ob02176h

rsc.li/obc

Chemical synthesis of complex oligosaccharides, especially those possessing hyper-branched structures with one or multiple 1,2-*cis* glycosidic bonds, is a challenging task. Complementary reactivity of glycosyl donors and acceptors and proper tuning of the solvent/temperature/activator coupled with compromised glycosylation yields for sterically congested glycosyl acceptors are among several factors that make such syntheses daunting. Herein, we report the synthesis of a semi-conserved hyper-branched core tetrasaccharide motif from chloroviruses which are associated with reduced cognitive function in humans as well as in mouse models. The target tetrasaccharide contains four different sugar residues in which L-fucose is connected to D-xylose and L-rhamnose *via* a 1,2-*trans* glycosidic bond, whereas with the D-galactose residue is connected through a 1,2-*cis* glycosidic bond. A thorough and comprehensive study of various accountable factors enabled us to install a 1,2-*cis* galactopyranosidic linkage in a stereoselective fashion under [Au]/[Ag]-catalyzed glycosidation conditions *en route* to the target tetrasaccharide motif in 14 steps.

1. Introduction

Chlorella viruses or Chloroviruses (CV) are plaque forming viruses which are present in freshwater throughout the world and infect certain unicellular, eukaryotic, chlorella-like green algae, also called Zoochlorellae.[1a–e] These are large, icosahedral (190 nm in diameter), *ds*DNA-containing viruses with an internal lipid membrane.[1f–g] One of the most important features these chloroviruses possess is the ability to use their own glycosylation machinery to encode most, if not all, of the components involved in manipulating carbohydrates.[1d–g,2a] The presence of Chlorovirus ATCV-1 in human oropharyngeal virome, and its association with statistically significant decline of cognitive assessments, visual processing and motor speed in humans and mouse models[2b,c] put these in the limelight. Green microalgae are a promising resource for the large-scale production of high value-added proteins,[3a–c] biofuels and biomaterials.[3d] In addition, there is growing interest to use microalgae as potentially attractive cell factories for biopharmaceutical production.[3e] Therefore, viral infection of these green microalgae could severely impact the biopharmaceutical and food industries. Hence, a detailed study of their glycosylation machinery and the role of their capsid glycoproteins in host infections, particularly for cross kingdom infection, though very rare, is in high demand and for that accessibility of various natural and synthetic analogues is essential.

Slight structural variation in glycan structures is exhibited by different types of Chloroviruses;[4] yet, structural analysis of N-linked glycans showed a common core region.[4c] The core motif contains a hyper-branched fucose unit at the center, two xylose units (one proximal and one distal xylose), one terminal galactose unit, and one glucose unit at the reducing end which is further attached to the asparagine (Asn) moiety of major capsid proteins and a semi-conserved rhamnose (D- or L-) unit **1**.[4c] Although the configuration of the rhamnose residue is highly species dependent, yet, the majority of species contain the L-isomer along with methylation at the *O*-3 position (Fig. 1).[4d]

2. Results and discussion

The first synthesis of the core hexasaccharide with three –OMe groups from the ATCV-1 species was accomplished by Lin *et al.*[5a] and subsequently Wang *et al.*[5b] reported the synthesis of a hexasaccharide and quite recently, a nonasaccharide was reported by Lin *et al.*[5c] Structural complexity coupled with strong biological significance and our continued interest in utilizing silver-assisted gold-catalyzed glycosylations[6a] for bioconjugates encouraged us to investigate the synthesis of hyper-

Department of Chemistry, Indian Institute of Science Education and Research, Pune – 411 008, MH, India. E-mail: s.hotha@iiserpune.ac.in; http://www.iiserpune.ac.in/~s.hotha; Tel: +91 20 25908015

† Electronic supplementary information (ESI) available: Spectral charts for all new compounds. See DOI: 10.1039/d0ob02176h

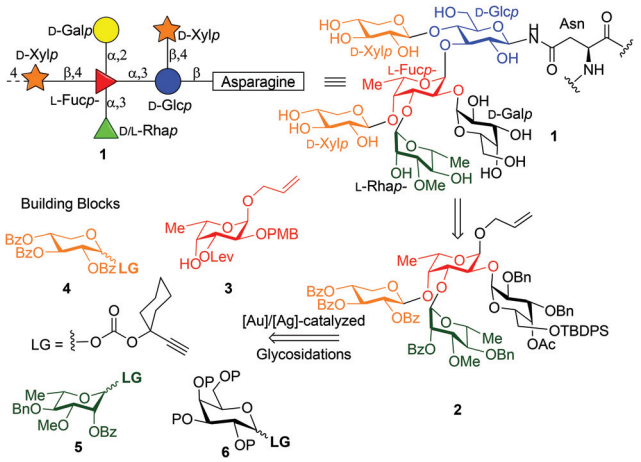


Fig. 1 Structure of N-linked hexasaccharide **1** of ATCV-1, targeted tetrasaccharide **2** and the list of the required monosaccharide building blocks (**3–6**).

branched tetrasaccharide motif **2** having only one –OMe group on L-rhap (Fig. 1).[4c]

The retrosynthetic analysis of the target hyper-branched tetrasaccharide **2** was hypothesized considering all the salient features of [Au]/[Ag]-catalyzed alkynyl carbonate donor chemistry[6a] envisioning that it can be synthesized from four building blocks **3**, **4**, **5** and **6** (Fig. 1). Tetrasaccharide **2** contains two 1,2-*trans* and one 1,2-*cis* glycosidic linkages. The formation of the 1,2-*trans* glycosidic bond (for installation of xylp- and rhap-) using the [Au]/[Ag]-catalyzed glycosylation protocol can be accomplished by invoking neighboring group participation from the C2-esters. With a limited number of possibilities for the central fucose residue, orthogonally cleavable C-3 levulinoate was considered.

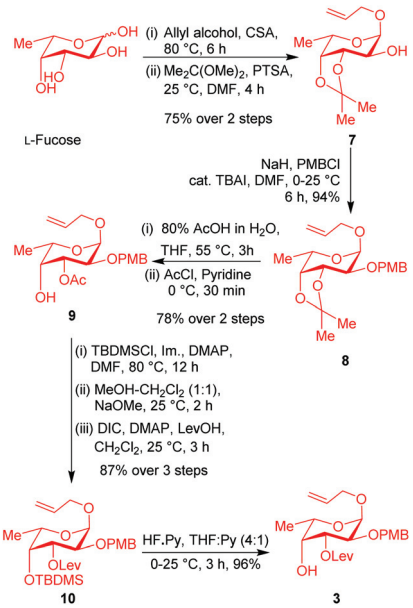
Installation of 1,2-*cis* galactopyranose under mild conditions is challenging. Previous reports suggest that 4,6-di-^{t}butyl silyl protection[7a] or an ester[7b–e] at the C-4 position offers α-predominant galactopyranosides. However, the use of the ^{t}butyl silyl moiety was not considered as it might be susceptible to cleavage under the glycosidation conditions. Hence, a detailed study about the influence of protecting groups was performed to obtain α-galactopyranosides.

Our synthetic endeavor commenced with the synthesis of the central L-fucose acceptor **3**. L-Fucose was treated with allyl alcohol and a catalytic amount of CSA at 80 °C for 6 h, followed by isopropylidenation using 2,2-dimethoxy propane and a catalytic amount of PTSA in DMF at 25 °C for 4 h, which afforded the protected allyl fucoside as an α/β mixture from which α-allyl fucoside **7** was isolated as a major product in 75% yield over two steps.

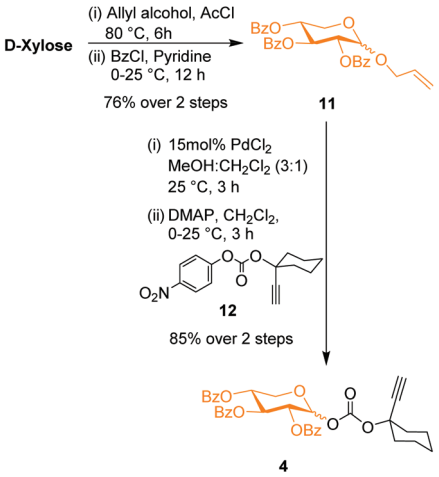
The lone C2-OH of acetonide **7** was protected as a *p*-methoxybenzyl ether using PMBCl/NaH/DMF in 94% yield. Subsequent hydrolysis of acetonide **8** using 80% AcOH in H_2O–THF at 55 °C followed by the regioselective acetylation at the C3 position using AcCl/py at 0 °C afforded the desired allyl fucoside **9** in 78% yield over two steps. Furthermore, silylation of fucoside **9** at the C4 position with TBDMSCl/imidazole in DMF, followed by deprotection of the acetyl group from the C3 position under Zemplén conditions, and subsequent conversion to levulinoate using levulinic acid/DIC/DMAP gave fucoside **10**. Finally, fluoride-mediated cleavage of the silyl ether afforded the required aglycon **3** in 96% yield (Scheme 1).

The synthesis of building block **4** was initiated by the acid-catalyzed reaction of D-xylose with allyl alcohol at 80 °C for 6 h followed by benzoylation using BzCl/py/DMAP to produce the allyl 2,3,4-tri-*O*-benzoyl xylopyranoside **11** as an α/β mixture in 76% yield. Subsequent Pd-mediated hydrolysis of xyloside **11** released the anomeric position, and the reaction with the easily available ethynylcyclohexyl (4-nitrophenyl) carbonate **12**[6a] in the presence of DMAP afforded the xylopyranosyl alkynyl carbonate donor **4** in 85% yield (Scheme 2).

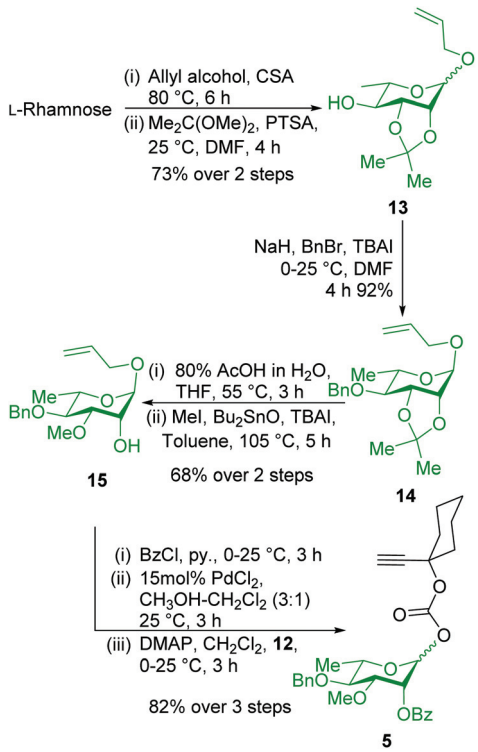
The preparation of building block **5** was initiated by reacting L-rhamnose with allyl alcohol in the presence of a catalytic amount of CSA at 80 °C for 6 h followed by acetonide protection using 2,2-dimethoxy propane and a catalytic amount of PTSA in DMF produced the acetonide protected α-allyl rhamnopyranoside **13** as a major product. C4-*O*-Benzylation of the rhamnoside **13** using BnBr/NaH/TBAI in DMF afforded the benzyl ether **14** that upon hydrolysis of the acetonide under acidic conditions at 55 °C resulted in a diol. The diol was subjected to stannylene-mediated regioselective methylation using MeI/TBAI/Bu_2SnO in toluene at 105 °C giving the allyl rhamnoside **15** in 68% yield over two steps. Furthermore, compound **15** was benzoylated and hydrolysis of the allyl moiety afforded a hemiacetal that was directly taken for the next reaction with easily available ethynylcyclohexyl (4-nitrophenyl) carbonate **12** in the presence of DMAP to afford the desired rhamnosyl alkynyl carbonate donor **5** in 82% yield (Scheme 3).



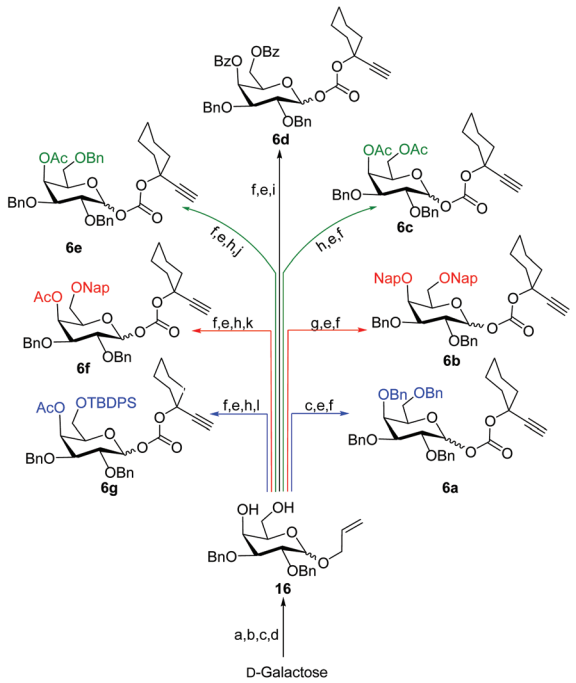
Scheme 1 Synthesis of central L-fucose acceptor **3**.



Scheme 2 Synthesis of D-xylose carbonate donor **4**.



Scheme 3 Synthesis of L-rhamnose carbonate donor **5**.



Scheme 4 Synthesis of various galactopyranosyl carbonate donors. Reagents: (a) Allyl alcohol, AcCl, 80 °C, 6 h, 85%; (b) $PhCH(OMe)_2$, PTSA, DMF, 60 °C, 4 h, 90%; (c) 2.5 equiv. BnBr, NaH, TBAI, DMF, 0–25 °C, 5 h, 94% for **16** and 96% for **6a**; (d) PTSA, CH_2Cl_2–MeOH (1 : 1), 25 °C, 2 h, 96%; (e) $PdCl_2$, CH_2Cl_2–MeOH (1 : 3), 25 °C, 3 h, 96% for **6a**, 94% for **6b**, 92% for **6c**, 95% for **6d**, 93% for **6e**, 92% for **6f** and 94% for **6g** respectively; (f) 1-ethynylcyclohexyl (4-nitrophenyl) carbonate (**12**), DMAP, CH_2Cl_2, 25 °C, 3 h, 95% for **6a**, 93% for **6b**, 94% for **6c**, 92% for **6d**, 95% for **6e**, 96% for **6f** and 93% for **6g** respectively; (g) 3 equiv. NapBr, NaH, TBAI, DMF, 0–25 °C, 12 h, 86%; (h) AcCl, pyridine, DMAP, 0–25 °C, 4 h, 94% for **6c**, 96% for **6e**, 95% for **6f**, 92% for **6g**; (i) BzCl, pyridine, DMAP, 0–25 °C, 6 h, 96%; (j) 1.2 equiv. BnBr, NaH, TBAI, DMF, 0–10 °C, 5 h, 78%; (k) 1.5 equiv. NapBr, NaH, TBAI, DMF, 0–25 °C, 12 h, 80%; (l) TBDPS-Cl, imidazole, DMF, 0–25 °C, 4 h, 90%.

One of the most challenging aspects in the synthesis of tetrasaccharide **2** is the installation of the 1,2-*cis* galactopyranosidic linkage for which a thorough investigation was required. In this direction, several substituted galactosides **6a–6g** which are easily synthesized from a common precursor **16** [6b] were envisioned (Scheme 4).

Two sets of compounds were envisaged, *viz*. one set contained all protecting groups are same whereas the second set had two orthogonally cleavable protecting groups at the C-4,6 positions. Accordingly, diol **16** was first treated with NaH/DMF and BnBr or NapBr respectively to obtain dibenzyl or dinapthyl ethers whereas diacylate and dibenzoate were obtained by the treatment of the corresponding acyl halides in pyridine. Subsequently, all four compounds were subjected to the deprotection of the allyl moiety and converted to the alkynyl carbonates **6a–6d** under the aforementioned reaction conditions (Scheme 4). In parallel, regioselective protection of the primary C-6 hydroxyl group was effected using NaH/BnBr or NapBr at 0 °C; acetylation using AcCl in pyridine followed by the hydrolysis of the allyl ether under Pd-catalysed conditions and subsequent conversion to the corresponding carbonates using carbonate reagent **12** afforded the desired donors **6e** and **6f**. Silyl ether formation, acetylation and subsequent conversion of allyl glycoside to the glycosyl carbonate resulted in the donor **6g**.

For the synthesis of all envisaged galactopyranosyl donors **6a–6g**, the investigation on the α-stereoselective galactopyranosylation commenced with the standard [Au]/[Ag]-catalysed glycosidation reaction between the glycosyl donor **6a** and the model aglycon glucose derivative **17** [6a] as substrates. Earlier

research efforts have shown the formation of 1,2-*cis* galactopyranosides when 1,2-*trans* galactosyl donors were utilized.[7–13]

Accordingly, the anomeric α- and β-isomers of the donor **6a** were separated as **6aα** and **6aβ** and individually subjected to the standard [Au]/[Ag]-catalytic conditions to obtain an anomeric mixture (3.5 : 1.0 α : β) irrespective of the stereochemical identity of the starting **6aα** or **6aβ**; in addition, the anomeric mixture of donor **6a** also yielded the same 3.5 : 1.0 (α : β) mixture of galactopyranosides **19** and thus further screening experiments were conducted with anomeric mixtures only (Table 1). Conducting the galactosylation between **6a** and **17** with standard gold-phosphite catalyst **18a** in CH_3CN diminished the yield as well as reversed the stereoselectivity (entry 2, Table 1) whereas no reaction was noticed when the reaction was conducted in THF or 1,4-dioxane (entries 3 and 4, Table 1). The anomeric α : β ratio reduced from 3.5 : 1.0 in CH_2Cl_2 to 2.0 : 1.0 in toluene (entry 5) and luckily, chlorobenzene afforded an α : β ratio of 8.0 : 1.0 (entry 6) and that of a reaction in bromobenzene showed 10.0 : 1.0 selectivity (entry 7, Table 1). However, the higher boiling point of bromobenzene discouraged us from using it in further reactions. Temperature is yet another factor that influences the stereochemical outcome in the majority of glycosidations.

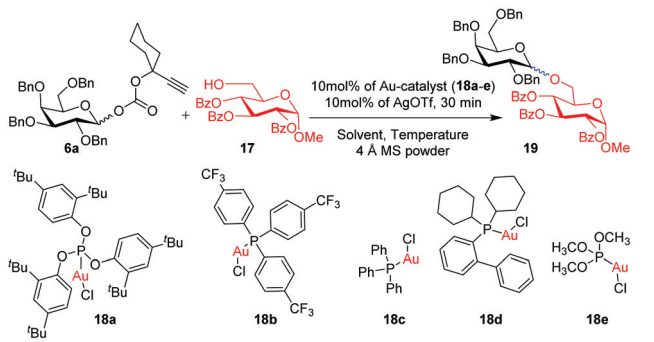
Entries 8–11 clearly demonstrate that the best α-stereoselectivity can be conveniently obtained when the reactions are conducted at 25 °C. In continuation, we also varied the gold catalysts **18b–e** and noticed that the stereochemical outcome does not alter much (entries 12–15) and hence, gold-phosphite **18a** was considered for further experiments. The best optimized conditions were found to be 10 mol% each of Au-phosphite **18a** and AgOTf as catalysts, chlorobenzene as the solvent system at 25 °C in the presence of 4 Å MS powder.

In continuation, other galactosyl carbonates (**6b–6g**) were investigated under the aforementioned conditions using carbonates **6b–6g** as donors and alcohol **17** as the aglycon in the presence of 10 mol% each of Au-phosphite **18a** and AgOTf in chlorobenzene at 25 °C (Table 2). Switching the benzyl ethers at C-4,6 to Nap-ethers as in donor **6b** or acetates as in donor **6c** resulted in the enhancement of the α : β ratio to 12.0 : 1.0 and 16.0 : 1.0 respectively (entries 1 and 2, Table 2) whereas the dibenzoate donor **6d** produced pure 1,2-*cis* or α-galactoside in 95% yield which may be due to the long range participation of the acylate from the C-4 position as evidenced by earlier investigators.[7–13] However, we need orthogonally cleavable protecting groups at the C-4 and C-6 positions and hence, donors **6e–6g** were studied. Donors **6e** and **6f** produced anomeric mixtures whereas donor **6g** afforded pure α-selectivity in an excellent yield.

The successful synthesis of all building blocks and identification of conditions for the stereoselective installation of galactopyranoside residues encouraged us to advance the synthesis of hyper-branched tetrasaccharide motif **2**. Accordingly, the synthesis of hyper-branched tetrasaccharide motif **2** commenced with the preparation of disaccharide **20** from the xylose carbonate donor **4** and fucose acceptor **3** prepared *vide supra* in the presence of 10 mol% each of Au-phosphite **18a** and AgOTf in CH_2Cl_2 at 25 °C with 98% yield. In the ^{13}C NMR spectrum of compound **20**, the appearance of two anomeric carbons at δ 96.2 ppm revealed the presence of two inter-glycosidic linkages and was further confirmed by HRMS analysis, *m*/*z* calculated for $C_{48}H_{50}O_{15}Na^+$, $[M + Na]^+$: 889.3047; found: 889.3042.

Disaccharide **20** is interesting due to the presence of PMB-ether and levulinoates as they are orthogonal to each other which in turn can be orthogonally cleaved off without affecting the benzoates present on the xylopyranoside moiety. Accordingly, the treatment of disaccharide with DDQ in moist dichloromethane at 25 °C afforded the aglycon **21** which was coupled with the galactopyranosyl donor **6g** using 10 mol% each of Au-catalyst **18a** and AgOTf in chlorobenzene at 25 °C to

Table 1 Optimization for stereoselective 1,2-*cis* galactopyranosidic linkage formation



Entry	Au-catalyst	Solvent	*T* (°C)	Yield (%)	α : β ratio
1	**18a**	CH_2Cl_2	25	98	3.5 : 1.0
2	**18a**	CH_3CN	25	20	1.0 : 2.0
3	**18a**	THF	25	0	—
4	**18a**	1,4-Dioxane	25	0	—
5	**18a**	Toluene	25	85	2.0 : 1.0
6	**18a**	C_6H_5Cl	25	95	8.0 : 1.0
7	**18a**	C_6H_5Br	25	89	10.0 : 1.0
8	**18a**	CH_2Cl_2	45	98	3.0 : 1.0
9	**18a**	CH_2Cl_2	−40	80	2.0 : 1.0
10	**18a**	C_6H_5Cl	45	80	8.0 : 1.0
11	**18a**	C_6H_5Cl	−40	80	2.0 : 1.0
12	**18b**	C_6H_5Cl	25	90	8.5 : 1.0
13	**18c**	C_6H_5Cl	25	87	8.5 : 1.0
14	**18d**	C_6H_5Cl	25	75	8.0 : 1.0
15	**18e**	C_6H_5Cl	25	98	8.0 : 1.0

Table 2 Effect of protecting groups on 1,2-*cis* galactopyranosidic bond formation

Entry	Glycosyl donor	Aglycon	α : β ratio	Yield (%)
1	**6b**	**17**	12.0 : 1.0	93
2	**6c**	**17**	16.0 : 1.0	96
3	**6d**	**17**	Pure α	95
4	**6e**	**17**	15.0 : 1.0	93
5	**6f**	**17**	20.0 : 1.0	94
6	**6g**	**17**	Pure α	98

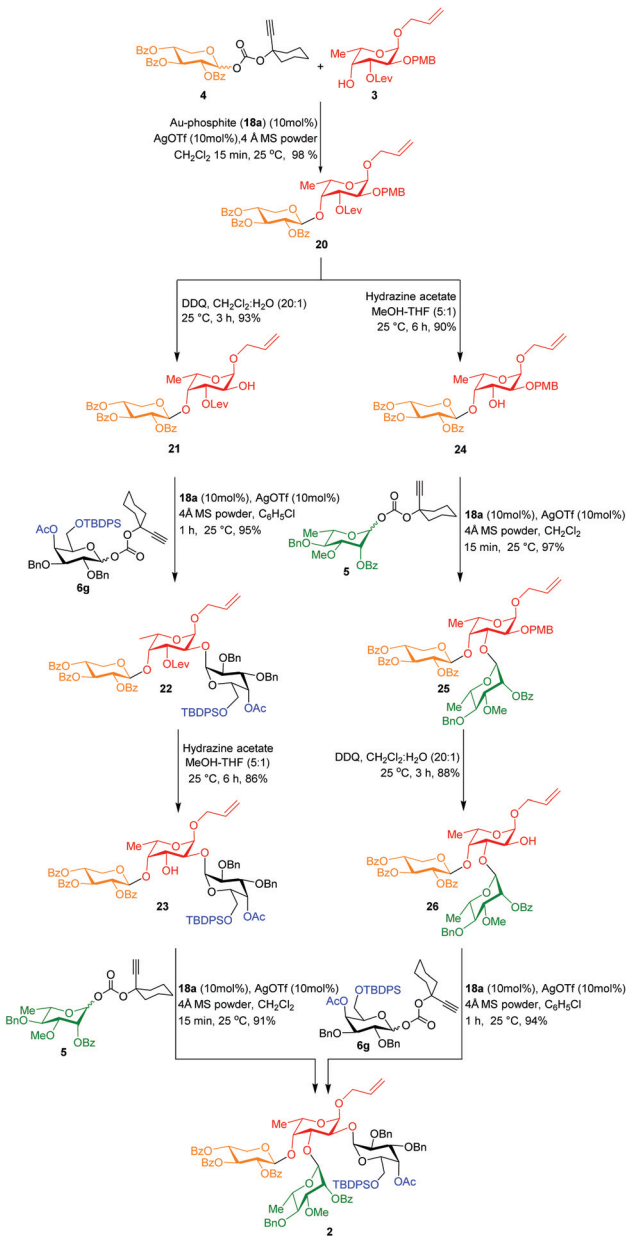
Reaction conditions: Gold-phosphite (**18a**) (10 mol%), AgOTf (10 mol%), C_6H_5Cl, 25 °C, 4 Å MS powder, 1 h.

afford trisaccharide **22** in 95% yield. Gratifyingly, the galactosylation occurred to produce 1,2-*cis* or α-galactoside only (Scheme 5). The ^{13}C NMR spectrum of trisaccharide **22** was confirmed due to the presence of two 1,2-*trans* anomeric carbons at δ 96.5 and 100.5 ppm corresponding to the fucp- and xylp- residues respectively, whilst the characteristic 1,2-*cis* anomeric carbon for the galp- residue was noticed at δ 98.1 ppm.[14] Furthermore, trisaccharide **22** was confirmed by HRMS analysis, *m*/*z* calculated for $C_{78}H_{84}O_{20}SiNa^+$, $[M + Na]^+$: 1391.5223; found: 1391.5220.

Subsequent deprotection of the levulinyl ester of trisaccharide **22** using hydrazine hydrate afforded the corresponding trisaccharide alcohol **23** in 86% yield, which was further subjected to [Au]/[Ag]-assisted glycosylation with rhamnose carbonate donor **5** in the presence of 10 mol% each of Au-catalyst **18a** and AgOTf in CH_2Cl_2 producing the desired tetrasaccharide **2** in 91% yield (Scheme 5). In the ^1H NMR spectrum of tetrasaccharide **2**, resonances from most of the anomeric protons overlapped with that of sugar ring protons and hence, the structural homogeneity was obtained from the ^{13}C NMR and mass spectral studies. In the ^{13}C NMR spectrum of tetrasaccharide **2**, the appearance of an additional anomeric carbon at δ 99.9 ppm for rhap- along with other three anomeric carbons at δ 98.1, 98.8 and 101.2 ppm showed the presence of four inter-glycosidic linkages in tetrasaccharide **2**.[14] In addition, tetrasaccharide **2** was confirmed by HRMS analysis, *m*/*z* calculated for $C_{94}H_{100}O_{23}SiNa^+$, $[M + Na]^+$: 1648.6356; found: 1648.6351.

On the other hand, tetrasaccharide **2** can be obtained by another route from disaccharide **20**. Accordingly, disaccharide **20** was treated with $NH_2NH_2{\cdot}H_2O$ to deprotect the levulinoate which resulted in the formation of aglycon **24** in 90% yield. Furthermore, aglycon **24** was reacted with rhamnose carbonate donor **5** in the presence of 10 mol% each of Au-catalyst **18a** and AgOTf to afford trisaccharide **25** in 97% yield (Scheme 5). In the ^{13}C NMR spectrum, three anomeric carbons were observed at δ 96.0, 98.4 and 99.7 ppm and the characteristic resonances due to four benzoyl groups appeared at δ 165.0, 165.5, 165.6 and 166.2 ppm. In addition, trisaccharide **25** was further confirmed by HRMS analysis, *m*/*z* calculated for $C_{64}H_{66}O_{18}SiNa^+$, $[M + Na]^+$: 1145.4147; found: 1145.4139.

In continuation, the deprotection of the PMB-ether using DDQ converted trisaccharide **25** to the corresponding aglycon **26** in 88% yield, which upon subsequent glycosidation with rhamnose carbonate donor **5** in the presence of 10 mol% each of Au-catalyst **18a** and AgOTf in chlorobenzene at 25 °C for 1 hour afforded the corresponding tetrasaccharide **2** in 94% yield along with 100% α-selectivity (Scheme 5). The perfect matching of NMR and the molecular weight of the tetrasaccharide synthesized by two alternative routes strongly confirmed the successful synthesis of tetrasaccharide **2**.



Scheme 5 Synthesis of hyper-branched tetrasaccharide **24**.

3. Conclusions

In summary, the challenging 1,2-*cis* glycosylation for D-galactose with 1,2-*cis*-stereoselectivity at ambient temperature has been accomplished using our recently developed [Au]/[Ag]-catalysed alkynyl carbonate donor chemistry. In this endeavour, the effects of various factors on 1,2-*cis* galactopyranosylation such as the solvent, temperature, catalyst, and protecting groups have been investigated. The optimized conditions worked outstandingly with the monosaccharide as well as at the branched di- and trisaccharide acceptor levels. Furthermore, the synthesis of the hyper-branched tetrasaccharide in the protected form was completed in 14 steps, which proved that carbonate donor chemistry can be employed to synthesize complex and branched oligosaccharides.

4. Experimental section

4.1 General methods

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. 1-Ethynylcyclohexanol, *p*-nitrophenyl chloroformate and all metal salts were purchased from Sigma-Aldrich. Unless otherwise reported, all reactions were performed under a nitrogen atmosphere. The removal of the solvent *in vacuo* refers to distillation using a rotary evaporator attached to an efficient vacuum pump. Products obtained as solids or syrups were dried under high vacuum. Analytical thin-layer chromatography was performed on pre-coated silica plates (F_{254}, 0.25 mm thickness); compounds were visualized with UV light or by staining with anisaldehyde spray. IR spectra were recorded on a FT-IR spectrometer. NMR spectra were recorded either on a 400 system or a 500 MHz system with $CDCl_3$ as the solvent and TMS as the internal standard. High resolution mass spectroscopy (HRMS) was performed using an ESI-TOF mass analyser. Low resolution mass spectroscopy (LRMS) was performed on a UPLC-MS system with SWADESI-TLC interface.

4.2 Experimental procedures

4.2.1. General procedure for the synthesis of allyl glycosides. (a) To a rapidly stirring solution of sugar (1.0 mmol) in anhydrous allyl alcohol, camphorsulfonic acid (0.5 mmol) was added at 25 °C under a nitrogen atmosphere. The reaction mixture was further heated to 80 °C and stirred for 6 h. After the completion of the reaction, the reaction mixture was cooled to 0 °C, the reaction was quenched with Et_3N and the reaction mixture was concentrated *in vacuo* to obtain a light brown residue which was purified by column chromatography (CH_2Cl_2/MeOH) to obtain the desired allyl glycoside as a white solid. This procedure was utilized for the synthesis of compounds explained in sections 4.3.1 (**7**) and 4.3.8 (**13**).

(b) AcCl (0.3 mmol) was added dropwise to rapidly stirring allyl alcohol (as a solvent) at 0 °C under a nitrogen atmosphere. After 30 min, sugar (1.0 mmol) was added and stirred at 25 °C for 1 h. The reaction mixture was further heated to 80 °C and refluxed for 6 h. After the completion of the reaction, the reaction mixture was cooled to 0 °C, the reaction was quenched with Et_3N and the reaction mixture was concentrated *in vacuo* to obtain a light brown residue which was purified by column chromatography (CH_2Cl_2/MeOH) to obtain the desired allyl glycoside. This procedure was utilized for the synthesis of compounds explained in sections 4.3.6 (**11**), 4.3.12 (**6aβ**), 4.3.13 (**6aα**), 4.3.14 (**6b**), 4.3.15 (**6c**), 4.3.16 (**6d**), 4.3.17 (**6e**) and 4.3.18 (**6f**).

4.2.2. General procedure for the deprotection of allyl glycosides. To a solution of allyl glycoside (1 mmol) in a 3 : 1 mixture of CH_3OH–CH_2Cl_2 (10 mL) was added dropwise $PdCl_2$ (0.15 mmol) in CH_3OH (1 mL) and stirred at 25 °C for 3 h. After the completion of the reaction, the reaction was quenched by the addition of Et_3N and the reaction mixture was concentrated *in vacuo* to obtain a residue that was purified by silica gel column chromatography (*n*-hexane/EtOAc) to obtain the desired hemi-acetal in 90–95% yield. This procedure was utilized for the synthesis of compounds explained in sections 4.3.7 (**4**), 4.3.11 (**5**), 4.3.12 (**6aβ**), 4.3.13 (**6aα**), 4.3.14 (**6b**), 4.3.15 (**6c**), 4.3.16 (**6d**), 4.3.17 (**6e**), 4.3.18 (**6f**) and 4.3.19 (**6g**).

4.2.3. General procedure for the synthesis of ethynylcyclohexyl glycosyl carbonate donors. At first, DMAP (1 mmol) was added to a stirring solution of hemiacetal (1 mmol) in anhydrous CH_2Cl_2 (10 mL) at 25 °C. After 20 min, reagent **12** (1.2 mmol) was added portion-wise (3×) after every 30 min and stirred at 25 °C for 2–3 h. After the completion of the reaction as indicated by TLC, the reaction mixture was concentrated *in vacuo* and the oily residue was partially purified by silica gel column chromatography (*n*-hexane/EtOAc). Eluents containing alkynyl glycosyl carbonate along with trace quantities of 4-nitrophenol were concentrated under diminished pressure. Furthermore, the crude residue was redissolved in CH_2Cl_2 (30 mL) and washed with sat. aq. $NaHCO_3$ (3 × 10 mL) and brine solution to remove 4-nitrophenol. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to obtain the alkynyl glycosyl carbonate donor in an excellent yield. This procedure was utilized for the synthesis of compounds explained in sections 4.3.7 (**4**), 4.3.11 (**5**), 4.3.12 (**6aβ**), 4.3.13 (**6aα**), 4.3.14 (**6b**), 4.3.15 (**6c**), 4.3.16 (**6d**), 4.3.17 (**6e**) and 4.3.18 (**6f**).

4.2.4. General procedure for Bn/PMB/Nap protection of alcohols. To an ice-cooled solution of alcohol (1 mmol) in anhydrous DMF (10 mL), NaH (60% oil dispersion, 1.2 mmol per alcohol) was added and stirred for 10 minutes at 0 °C under a nitrogen atmosphere. BnBr/PMBCl/NapBr (1.2 mmol per alcohol) was further added dropwise into the reaction mixture followed by TBAI (0.1 mmol per alcohol) addition at 0 °C. The reaction mixture was gradually warmed up to 25 °C and stirred for 4 h. After complete consumption of the alcohol as indicated by TLC, the reaction mixture was poured into ice cold water with vigorous shaking and extracted with ethyl acetate (3 × 20 mL) and the combined EtOAc layer was washed with cold water and brine solution, dried over Na_2SO_4 and evaporated *in vacuo*. The crude residue was further purified by column chromatography (*n*-hexane/EtOAc) to obtain the Bn/PMB/NAP ether as a pale-yellow coloured syrup. This procedure was utilized for the synthesis of compounds explained in sections 4.3.2 (**8**), 4.3.9 (**14**), 4.3.12 (**6aβ**), 4.3.13 (**6aα**), 4.3.14 (**6b**), 4.3.15 (**6c**), 4.3.16 (**6d**), 4.3.17 (**6e**) and 4.3.18 (**6f**).

4.2.5. General procedure for the deprotection of the isopropylidene group. To a solution of the isopropylidene compound (1 mmol) in aqueous THF [THF : H_2O = 7 : 3] (10 mL), 80% AcOH (2 mL) was added at 25 °C and the reaction mixture was allowed to stir at 55 °C for 3 h. The progress of the reaction and complete consumption of the starting material were checked by TLC. At the end of the reaction, the reaction was quenched with sat. aq. $NaHCO_3$ (20 mL) at 0 °C and the reaction mixture was extracted with ethyl acetate (50 mL). The organic layer was washed with water (25 mL) and brine solution (25 mL), dried over Na_2SO_4 and evaporated *in vacuo* to obtain a crude residue which was purified by silica gel column

chromatography (*n*-hexane/EtOAc) to afford the desired product. This procedure was utilized for the synthesis of compounds explained in sections 4.3.3 (**9**) and 4.3.10 (**15**).

4.2.6. General procedure for benzoate/acetate ester protection of alcohols. To a solution of alcohol (1 mmol) in anhydrous pyridine (10 mL), benzoyl chloride/acetic anhydride (1.2 mmol per alcohol) was added dropwise at 0 °C under a nitrogen atmosphere. The reaction mixture was gradually warmed up to 25 °C and stirred for 6–12 h. The progress of the reaction and consumption of the starting alcohol were checked by TLC. After the completion of the reaction, the reaction was quenched by adding ice-cooled water, the reaction mixture was extracted with CH_2Cl_2 (50 mL) and the CH_2Cl_2 layer was washed with 1 N HCl (2 × 50 mL), water, sat. aq. $NaHCO_3$ solution and finally brine solution. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo* and the resulting crude residue was purified by silica gel column chromatography (*n*-hexane/EtOAc) to obtain the desired compound. This procedure was utilized for the synthesis of compounds explained in sections 4.3.3 (**9**), 4.3.6 (**11**), 4.3.11 (**5**), 4.3.15 (**6c**), 4.3.16 (**6d**), 4.3.17 (**6e**), 4.3.18 (**6f**) and 4.3.19 (**6g**).

4.2.7. General procedure for TBDMS/TBDPS-protection of alcohols. To a rapidly stirring solution of alcohol (1.0 mmol) and imidazole (1.3 mmol) in anhydrous DMF (10 mL) was added TBDMSCl/TBDPSCl (1.2 mmol) dropwise and stirred for 4 h at 25 °C. At the end of the reaction, the reaction mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with water (2 × 50 mL) and brine solution (1 × 50 mL), dried over Na_2SO_4 and evaporated *in vacuo* to obtain a crude residue which was purified by silica gel column chromatography (*n*-hexane/EtOAc) to afford the desired product. This procedure was utilized for the synthesis of compounds explained in sections 4.3.4 (**10**) and 4.3.19 (**6g**).

4.2.8. General procedure for the saponification of ester. To a solution of benzoate/acetate (1 mmol) in a 3 : 1 mixture of anhydrous CH_2Cl_2–MeOH (20 mL), freshly prepared 1 M NaOMe in MeOH (0.3 mmol) was added and the reaction mixture was stirred at 25 °C for 2 h. After complete conversion, the reaction mixture was neutralized with Amberlite IR120 resin and concentrated *in vacuo* to obtain a residue that was purified by column chromatography (*n*-hexane/EtOAc) to afford the desired alcohol. This procedure was utilized for the synthesis of compounds explained in section 4.3.4 (**10**).

4.2.9. General procedure for levulinoate ester protection of alcohols. To a stirring solution of alcohol (1.0 mmol) in anhydrous CH_2Cl_2 (4 mL), DMAP (1.0 mmol), levulinic acid (1.5 mmol) and *N*,*N*′-diisopropylcarbodiimide (1.5 mmol) were added sequentially at 0 °C under a nitrogen atmosphere. The reaction mixture was gradually warmed up to 25 °C and stirred for 4 h. After complete consumption of the starting alcohol, the reaction mixture was concentrated *in vacuo* and purified by silica gel column chromatography (*n*-hexane/EtOAc) to afford the corresponding levulinoate ester. This procedure was utilized for the synthesis of compounds explained in section 4.3.4 (**10**).

4.2.10. General procedure for the deprotection of the TBDPS-ethers. To a solution of the silyl ether compound (1 mmol) in a 5 : 1 mixture of THF–Py (10 mL), HF·py (3 mmol) was added dropwise at 0 °C under a nitrogen atmosphere and stirred at 25 °C. After 4 h, the reaction was quenched with 2 N HCl at 0 °C and the reaction mixture was diluted with EtOAc (30 mL) and washed with ice cold water (2 × 20 mL), sat. aq. $NaHCO_3$ (20 mL) and brine solution (20 mL) sequentially. The EtOAc layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified by silica gel column chromatography (*n*-hexane/EtOAc) to furnish the corresponding alcohol. This procedure was utilized for the synthesis of compounds explained in section 4.3.5 (**3**).

4.2.11. General procedure for acetonide protection of diols. To a rapidly stirring solution of diol (1.0 mmol) in anhydrous acetone, 2,2-dimethoxy propane (1.5 mmol) and PTSA (0.2 mmol) were added and the reaction mixture was stirred at 25 °C overnight (12 h). After complete consumption of the diol, the reaction was quenched with Et_3N and the reaction mixture was concentrated *in vacuo* to obtain a light yellow residue which was purified by column chromatography (*n*-hexane/EtOAc) to obtain the desired acetonide product as a white solid. This procedure was utilized for the synthesis of compounds explained in sections 4.3.1 (**7**) and 4.3.8 (**13**).

4.2.12. General procedure for selective methyl ether protection. To a solution of alcohol (1 mmol) in toluene (10 mL), Bu_2SnO (1.2 mmol) was added and refluxed at 105 °C. After 2 h, MeI (3 mmol) and TBAI (0.2 mmol) were added and the reaction mixture was stirred at 25 °C for another 3 h. The reaction was monitored by TLC and upon completion of the reaction, the reaction mixture was concentrated under reduced pressure to obtain the crude residue which was purified by silica gel column chromatography (CH_2Cl_2/MeOH) to afford the desired methyl ether as a colourless syrup. This procedure was utilized for the synthesis of compounds explained in section 4.3.10 (**15**).

4.2.13. General procedure for benzylidine protection of diols. To a rapidly stirring solution of diol (1.0 mmol) in anhydrous DMF, benzaldehyde 1,1-dimethylacetal (1.5 mmol) and PTSA (0.2 mmol) were added and the reaction mixture was stirred at 25 °C overnight (12 h). After complete consumption of the diol, the reaction was quenched with Et_3N and the reaction mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with water (2 × 50 mL) and brine solution (1 × 50 mL), dried over Na_2SO_4 and evaporated *in vacuo* to obtain a crude residue which was purified by silica gel column chromatography (*n*-hexane/EtOAc) to afford the desired product. This procedure was utilized for the synthesis of compounds explained in sections 4.3.12 (**6aβ**), 4.3.13 (**6aα**), 4.3.14 (**6b**), 4.3.15 (**6c**), 4.3.16 (**6d**), 4.3.17 (**6e**) and 4.3.18 (**6f**).

4.2.14. General procedure for the deprotection of the benzylidine group. To a solution of the benzylidine compound (1 mmol) in MeOH was added PTSA (0.2 mmol) and the reaction mixture was stirred at 25 °C for 30 minutes. After the completion of the reaction (as indicated by TLC), the reaction was

quenched with Et_3N and the reaction mixture was concentrated *in vacuo* to obtain a pale yellow residue which was purified by column chromatography (*n*-hexane/EtOAc) to afford the desired product. This procedure was utilized for the synthesis of compounds explained in sections 4.3.12 (**6aβ**), 4.3.13 (**6aα**), 4.3.14 (**6b**), 4.3.15 (**6c**), 4.3.16 (**6d**), 4.3.17 (**6e**), 4.3.18 (**6f**) and 4.3.19 (**6g**).

4.2.15. Procedure for glycosylation. To a stirred solution of the alkynyl carbonate donor (1 mmol) and acceptor (1 mmol) in an anhydrous solvent (4 mL) containing 4 Å MS powder (100 mg), the Au-complex (0.10 mmol) and the Ag-salt (0.10 mmol) were added and stirred at 25 °C. Upon completion of the reaction (in 15 min), the reaction was quenched by the addition of Et_3N and the reaction mixture was concentrated *in vacuo* to obtain a residue that was purified by silica gel column chromatography (*n*-hexane/EtOAc) to afford the desired glycoside. This procedure was utilized for the synthesis of compounds explained in sections 4.3.20 (**19**), 4.3.21 (**20**), 4.3.23 (**22**), 4.3.26 (**25**) and 4.3.28 (**26**).

4.2.16. General procedure for the deprotection of PMB ethers. To a solution of the PMB ether compound (1 mmol) in the 20 : 1 mixture of CH_2Cl_2–H_2O (10 mL) was added DDQ (2 mmol) at 25 °C and stirred for 2 h. After the completion of the reaction (as indicated by TLC), the reaction was quenched with Et_3N and the reaction mixture was concentrated *in vacuo* to obtain a dark yellow residue which was purified by silica gel column chromatography (*n*-hexane/EtOAc) to obtain the desired alcohol as a colourless syrup. This procedure was utilized for the synthesis of compounds explained in sections 4.3.22 (**21**) and 4.3.27 (**26**).

4.2.17. General procedure for the deprotection of levulinoates. To a rapidly stirring solution of the levulinoate compound (1.0 mmol) in MeOH (10 mL), hydrazine acetate (4 mmol) in THF (4 mL) was added at 25 °C. After 4 h, the reaction was quenched with ice cold 1 N HCl solution and the reaction mixture was extracted with EtOAc and washed with water, sat. aq. $NaHCO_3$ and brine solution sequentially. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to obtain the crude residue which was purified by silica gel column chromatography (*n*-hexane/EtOAc) to afford the desired alcohol in a good yield. This procedure was utilized for the synthesis of compounds explained in sections 4.3.24 (**23**) and 4.3.25 (**24**).

4.3. Characterization data

4.3.1. Allyl 3,4-*O*-isopropylidene α-L-fucopyranoside (7). The title compound was prepared according to the general procedures 4.2.1a and 4.2.11; syrup (3.352 g, 75% yield); $[\alpha]_{25}^{D}$ ($CHCl_3$, *c* 1.0): −126.4; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.24 (d, *J* = 6.7 Hz, 3H), 1.28 (s, 3H), 1.43 (s, 3H), 2.68 (s, 1H), 3.57–3.79 (m, 1H), 3.94–4.01 (m, 2H), 4.06 (qd, *J* = 6.6, 2.3 Hz, 1H), 4.12–4.19 (m, 1H), 4.78 (d, *J* = 3.9 Hz, 1H), 5.13 (ddd, *J* = 10.4, 2.8, 1.3 Hz, 1H), 5.23 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.85 (dddd, *J* = 17.1, 10.4, 6.1, 5.3 Hz, 1H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 16.2, 25.9, 27.8, 63.9, 68.4, 69.4, 75.7, 76.2, 96.8, 109.1, 117.6, 133.8; HRMS (ESI): *m*/*z* calcd for $C_{12}H_{20}O_5$, $[M + Na]^+$: 267.1208; found: 267.1204.

4.3.2. Allyl 2-*O*-(*p*-methoxybenzyl)-3,4-*O*-isopropylidene α-L-fucopyranoside (8). The title compound was prepared according to the general procedure 4.2.4; syrup (4.628 g, 94% yield); $[\alpha]_{25}^{D}$ ($CHCl_3$, *c* 1.0): −97.2; IR (cm^{-1}, $CHCl_3$):1605, 1440, 1335, 1245, 1078, 1026, 940, 710; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.23 (d, *J* = 6.7 Hz, 3H), 1.34 (s, 3H), 1.27 (s, 3H), 3.42 (dd, *J* = 7.9, 3.6 Hz, 1H), 3.72 (s, 3H), 3.91 (dd, *J* = 13.0, 6.2 Hz, 1H), 3.96 (dd, *J* = 5.5, 2.5 Hz, 1H), 4.01–4.10 (m, 2H), 4.24 (dd, *J* = 7.8, 5.5 Hz, 1H), 4.56 (d, *J* = 12.2 Hz, 1H), 4.65 (d, *J* = 12.2 Hz, 1H), 4.68 (d, *J* = 3.6 Hz, 1H), 5.13 (dd, *J* = 10.4, 1.3 Hz, 1H), 5.24 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.86 (dddd, *J* = 17.1, 10.4, 6.1, 5.3 Hz, 1H), 6.79 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 16.4, 26.5, 28.3, 55.4, 63.3, 68.4, 72.0, 76.0, 76.0, 76.3, 96.2, 108.8, 113.8, 113.8, 117.8, 129.6, 129.6, 130.6, 134.0, 159.4; HRMS (ESI): *m*/*z* calcd for $C_{19}H_{26}O_7$, $[M + Na]^+$: 387.1784; found: 387.1780.

4.3.3. Allyl 2-*O*-(*p*-methoxybenzyl)-3-*O*-acetyl α-L-fucopyranoside (9). The title compound was prepared according to the general procedures 4.2.5 and 4.2.6; syrup (3.604 g, 78% yield); $[\alpha]_{25}^{D}$ ($CHCl_3$, *c* 1.0): −132.7; IR (cm^{-1}, $CHCl_3$):1730, 1610, 1430, 1328, 1239, 1063, 1020, 706; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.14 (d, *J* = 6.6 Hz, 3H), 2.02 (s, 3H), 3.72 (s, 3H), 3.78 (dd, *J* = 10.5, 3.7 Hz, 1H), 3.82 (s, 1H), 3.93 (ddd, *J* = 13.0, 7.1, 3.8 Hz, 1H), 3.98 (q, *J* = 6.6 Hz, 1H), 4.07 (ddd, *J* = 7.2, 5.2, 3.3 Hz, 1H), 4.48 (dd, *J* = 29.4, 12.0 Hz, 2H), 4.71 (d, *J* = 3.7 Hz, 1H), 5.07–5.20 (m, 2H), 5.24 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.89 (dddd, *J* = 17.1, 10.4, 6.1, 5.3 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 16.0, 21.2, 55.3, 65.4, 68.5, 70.8, 72.5, 72.8, 72.9, 96.2, 113.8, 113.8, 117.8, 129.5, 129.5, 130.4, 133.9, 1559.4, 170.3; HRMS (ESI-MS): *m*/*z* calcd for $C_{19}H_{26}O_7$, $[M + Na]^+$: 389.1576; found: 389.1579.

4.3.4. Allyl 2-*O*-(*p*-methoxybenzyl)-3-*O*-(4-oxopentanoyl)-4-*O*-(*tert*-butyldimethyl silyl) α-L-fucopyranoside (10). The title compound was prepared according to the general procedures 4.2.7, 4.2.8 and 4.2.9; syrup (4.525 g, 87% yield); $[\alpha]_{25}^{D}$ ($CHCl_3$, *c* 1.0): −84.8; IR (cm^{-1}, $CHCl_3$): 1726, 1613, 1448, 1355, 1269, 1107, 1025, 715; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 0.07 (s, 3H), 0.09 (s, 3H), 0.87 (s, 9H), 1.08 (d, *J* = 6.6 Hz, 3H), 2.17 (s, 3H), 2.63–2.78 (m, 4H), 3.58 (dd, *J* = 9.7, 3.7 Hz, 1H), 3.79–3.80 (m, 3H), 3.94–4.05 (m, 2H), 4.08–4.14 (m, 2H), 4.48 (d, *J* = 11.8 Hz, 1H), 4.61–4.76 (m, 2H), 5.10 (d, *J* = 3.4 Hz, 1H), 5.19 (d, *J* = 10.4 Hz, 1H), 5.30 (d, *J* = 17.2 Hz, 1H), 5.91 (ddt, *J* = 16.7, 11.3, 5.8 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ −4.9, −4.6, 16.1, 18.0, 25.8, 25.8, 25.8, 28.1, 29.9, 38.1, 55.3, 64.7, 68.4, 69.2, 72.9, 74.6, 76.1, 96.5, 113.7, 113.7, 117.8, 129.6, 129.6, 130.8, 134.1, 159.3, 172.3, 206.3; HRMS (ESI): *m*/*z* calcd for $C_{28}H_{44}O_8Si$, $[M + Na]^+$: 559.2703; found: 559.2697.

4.3.5. Allyl 2-*O*-(*p*-methoxybenzyl)-3-*O*-(4-oxopentanoyl) α-L-fucopyranoside (3). The title compound was prepared according to the general procedure 4.2.10; syrup (3.410 g, 96% yield); $[\alpha]_{25}^{D}$ ($CHCl_3$, *c* 1.0): −38.5; IR (cm^{-1}, $CHCl_3$): 1720, 1610, 1453, 1365, 1263, 1090, 1034, 715; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.07 (d, *J* = 6.6 Hz, 3H), 2.13 (s, 3H), 2.55–2.80 (m,

5H), 3.60 (dd, J = 10.1, 3.6 Hz, 1H), 3.91 (dd, J = 12.9, 6.4 Hz, 1H), 3.75 (s, 3H), 4.00 (q, J = 6.5 Hz, 1H), 4.05–4.13 (m, 1H), 4.53–4.62 (m, 2H), 4.79 (d, J = 3.5 Hz, 1H), 5.08–5.21 (m, 2H), 5.28 (dd, J = 17.2, 1.4 Hz, 1H), 5.87 (dddd, J = 17.1, 10.4, 6.1, 5.3 Hz, 1H), 6.83 (d, J = 8.6 Hz, 2H), 7.25 (d, J = 8.5 Hz, 1H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 16.1, 28.1, 29.9, 38.2, 55.3, 64.9, 68.1, 68.6, 72.4, 73.6, 76.3, 96.0, 113.9, 113.9, 117.9, 129.8 (3C), 130.3, 133.9, 172.9, 206.9; HRMS (ESI): m/z calcd for $C_{22}H_{30}O_8$, $[M + Na]^+$: 445.1838; found: 445.1834.

4.3.6. Allyl 2,3,4-tri-*O*-benzoyl α/β-D-xylopyranoside [α : β (2.0 : 1.0)] (11). The title compound was prepared according to the general procedures 4.2.1b and 4.2.6; white solid (5.097 g, 76% yield); mp 74.5 °C; $[\alpha]_{25}^{D}$ ($CHCl_3$, c 1.0): +56.3; IR (cm^{-1}, $CHCl_3$): 3277, 2939, 1720, 1634, 1425, 1250, 1095, 910, 717; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 3.75–4.18 (m, 6H), 4.29–4.38 (m, 2H), 4.45–5.24 (m, 4H), 5.32–5.37 (m, 5H), 5.42–5.97 (m, 4H), 6.24 (t, J = 9.4 Hz, 1H), 7.28–7.59 (m, 18H), 7.96–8.06 (m, 12H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 58.8, 61.1, 68.8, 69.1, 69.4, 70.0, 70.2, 70.2, 70.3, 71.9, 95.3, 98.9, 117.7, 117.8, 128.3–128.4 (12C), 129.1, 129.1, 129.2, 129.3, 129.4, 129.4, 129.7–129.9 (12C), 133.1, 133.3, 133.3, 133.4, 133.4, 133.4, 133.5, 133.5, 165.2, 165.4, 165.6, 165.6, 165.8, 165.8; HRMS (ESI-MS): m/z calcd for $C_{29}H_{26}O_8$, $[M + Na]^+$: 525.1525; found: 525.1519.

4.3.7. 1-*O*-(((1-Ethynylcyclohexyl)oxy)carbonyl)-2,3,4-tri-*O*-benzoyl α/β-D-xylopyranoside [α : β (1.0 : 1.5)] (4). The title compound was prepared according to the general procedures 4.2.2 and 4.2.3; white solid (5.175 g, 85% yield); mp 52.8 °C; $[\alpha]_{25}^{D}$ ($CHCl_3$, c 1.0): +37.5; IR (cm^{-1}, $CHCl_3$): 3277, 2939, 2862, 1727, 1600, 1451, 1263, 1096, 908, 709; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.29–1.40 (m, 2H), 1.47–1.76 (m, 10H), 1.77–2.28 (m, 8H), 2.48 (s, 1H), 2.65 (s, 1H), 3.95–4.16 (m, 2H), 4.27–4.59 (m, 2H), 5.21–5.60 (m, 4H), 5.71–6.53 (m, 4H), 7.29–7.61 (m, 18H), 7.89–8.16 (m, 12H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 22.4, 22.5, 22.5, 22.5, 24.9, 24.9, 36.6, 36.7, 36.7, 36.7, 61.2, 61.4, 67.6, 67.9, 68.0, 69.5, 69.7, 70.3, 75.3, 75.4, 78.5, 78.7, 82.4, 82.4, 92.8, 94.8, 128.4–128.5 (12C), 128.8, 128.9 (2C), 129.0, 129.1, 129.2, 129.7–130.1 (12C), 133.3, 133.4, 133.5, 133.5, 133.5, 133.5, 150.8, 150.9, 164.9, 164.9, 165.4, 165.5, 165.5, 165.8; HRMS (ESI): m/z calcd for $C_{35}H_{32}O_{10}$, $[M + Na]^+$: 635.1893; found: 635.1891.

4.3.8. Allyl 2,3-*O*-isopropylidene α/β-L-rhamnopyranoside [α : β = 8 : 1] (13). The title compound was prepared according to the general procedures 4.2.1a and 4.2.11; syrup (3.258 g, 73% yield). For characterization, an analytical sample was subjected to flash purification and the major compound was characterized to be the α-anomer. $[\alpha]_{25}^{D}$ ($CHCl_3$, c 1.0): −34.9; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.29 (d, J = 6.3 Hz, 3H), 1.34 (s, 3H), 1.52 (s, 3H), 2.71 (bs, 1H), 3.39 (dd, J = 8.5, 8.0 Hz, 1H), 3.68 (dq, J = 9.3, 6.1 Hz, 1H), 4.01 (ddt, J = 12.8, 6.2, 1.3 Hz, 1H), 4.09 (dd, J = 8.5, 8.0 Hz, 1H), 4.15 (d, J = 4.0 Hz, 1H), 4.19 (ddt, J = 12.8, 6.2, 1.3 Hz), 5.00 (s, 1H), 5.20 (ddd, J = 10.4, 2.7, 1.2 Hz, 1H), 5.29 (ddd, J = 17.6, 3.1, 1.6 Hz, 1H), 5.89 (dddd, J = 16.7, 10.4, 6.2, 5.3 Hz, 1H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 17.6, 26.3, 28.1, 66.1, 68.1, 74.6, 76.0, 78.5, 96.4, 109.6, 118.0, 133.7; HRMS (ESI): m/z calcd for $C_{12}H_{20}O_5$, $[M + Na]^+$: 267.1208; found: 267.1213.

4.3.9. Allyl 2,3-*O*-isopropylidene-4-*O*-benzyl α-L-rhamnopyranoside (14). The title compound was prepared according to the general procedure 4.2.4; syrup (4.034 g, 92% yield); $[\alpha]_{25}^{D}$ ($CHCl_3$, c 1.0): −59.4; IR (cm^{-1}, $CHCl_3$): 1610, 1429, 1320, 1235, 1067, 1045, 718; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.28 (d, J = 6.3 Hz, 3H), 1.37 (s, 3H), 1.50 (s, 3H), 3.22 (dd, J = 9.8, 7.1 Hz, 1H), 3.71 (dd, J = 9.8, 6.2 Hz, 1H), 3.93–4.03 (m, 1H), 4.12–4.19 (m, 2H), 4.24–4.31 (m, 1H), 4.62 (d, J = 11.6 Hz, 1H), 4.90 (d, J = 11.6 Hz, 1H), 5.00 (s, 1H), 5.20 (ddd, J = 10.4, 2.7, 1.2 Hz, 1H), 5.23–5.34 (m, 1H), 5.89 (dddd, J = 16.7, 10.4, 6.2, 5.3 Hz, 1H), 7.24–7.29 (m, 1H), 7.30–7.37 (m, 4H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 17.9, 26.5, 28.1, 64.7, 68.0, 73.1, 76.2, 78.8, 81.3, 96.2, 109.3, 117.8, 127.7, 128.1, 128.1, 128.4, 128.4, 133.8, 138.5; HRMS (ESI-MS): m/z calcd for $C_{19}H_{26}O_5$, $[M + Na]^+$: 357.1678; found: 357.1674.

4.3.10. Allyl 3-*O*-methyl-4-*O*-benzyl α-L-rhamnopyranoside (15). The title compound was prepared according to the general procedures 4.2.5 and 4.2.12; syrup (2.451 g, 68% yield); $[\alpha]_{25}^{D}$ ($CHCl_3$, c 1.0): −51.6; IR (cm^{-1}, $CHCl_3$): 1622, 1420, 1320, 1228, 1055, 1036, 720; ^{1}H NMR (400.31 MHz, $CDCl_3$): 1.30 (d, J = 6.3 Hz, 3H), 2.81 (s, 1H), 3.39 (t, J = 9.3 Hz, 1H), 3.48 (s, 3H), 3.57 (dd, J = 9.1, 3.3 Hz, 1H), 3.72 (dq, J = 9.7, 6.3 Hz, 1H), 3.96 (ddt, J = 12.9, 6.2, 1.3 Hz, 1H), 4.06 (s, 1H), 4.10–4.18 (m, 1H), 4.61 (d, J = 11.0 Hz, 1H), 4.84 (d, J = 4.1 Hz, 1H), 4.85 (d, J = 5.4 Hz, 1H), 5.17 (ddd, J = 10.4, 2.8, 1.2 Hz, 1H), 5.27 (ddd, J = 17.2, 3.2, 1.6 Hz, 1H), 5.88 (dddd, J = 21.9, 10.4, 6.1, 5.2 Hz, 1H), 7.24–7.29 (m, 1H), 7.30–7.37 (m, 4H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 17.9, 57.4, 67.3, 67.8, 67.9, 75.2, 79.9, 81.8, 98.3, 117.4, 127.6, 127.9, 127.9, 128.3, 128.3, 133.8, 138.5; HRMS (ESI): m/z calcd for $C_{17}H_{24}O_5$, $[M + Na]^+$: 331.1521; found: 331.1522.

4.3.11. 1-*O*-(((1-Ethynylcyclohexyl)oxy)carbonyl)-2-*O*-benzoyl-3-*O*-methyl-4-*O*-benzyl α-L-rhamnopyranoside (5). The title compound was prepared according to the general procedures 4.2.6, 4.2.2 and 4.2.3; white solid (3.340 g, 82% yield); mp 66.3 °C; $[\alpha]_{25}^{D}$ ($CHCl_3$, c 1.0): −40.6; IR (cm^{-1}, $CHCl_3$): 3293, 2940, 1740, 1465, 1372, 1265, 1090, 1032, 708; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.24–1.30 (m, 1H), 1.44 (d, J = 6.0 Hz, 3H), 1.49–1.67 (m, 5H), 1.76–1.88 (m, 2H), 2.11–2.17 (m, 2H), 2.63 (s, 1H), 3.43–3.50 (m, 4H), 3.51–3.62 (m, 2H), 4.63 (d, J = 10.9 Hz, 1H), 4.89 (d, J = 10.9 Hz, 1H), 5.71 (s, 1H), 5.86 (d, J = 2.9 Hz, 1H), 7.21–7.39 (m, 5H), 7.45–7.49 (m, 2H), 7.57–7.60 (m, 1H), 8.10–8.12 (m, 2H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 18.2, 18.2, 22.5, 25.0, 36.6, 36.8, 57.6, 67.6, 72.7, 75.4, 75.5, 78.7, 79.4, 82.6, 82.8, 94.0, 127.9, 128.2 (2C), 128.5 (4C), 129.9, 130.2 (2C), 133.3, 138.3, 151.1, 165.8; HRMS (ESI): m/z calcd for $[C_{30}H_{34}O_8Na]^+$: 545.2151; found: 545.2156.

4.3.12. 1-*O*-(((1-Ethynylcyclohexyl)oxy)carbonyl)-2,3,4,6-tetra-*O*-benzyl β-D-galactopyranoside (6aβ). The title compound was prepared according to the general procedures 4.2.1b, 4.2.13, 4.2.4, 4.2.14, 4.2.2 and 4.2.3; syrup (2.250 g, 45% yield); $[\alpha]_{25}^{D}$ ($CHCl_3$, c 1.0): +25.7; IR (cm^{-1}, $CHCl_3$): 3280, 3025, 2922, 1760, 1492, 1460, 1255, 1230, 1089, 914, 726; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.33–1.41 (m, 1H), 1.52–1.58 (m, 1H), 1.62–1.72 (m, 4H), 1.90–1.97 (m, 2H), 2.15–2.22 (m, 2H), 2.62 (s, 1H), 3.59–3.76 (m, 4H), 3.95–4.06 (m, 2H), 4.47 (q, J = 11.7 Hz, 2H),

4.65 (d, J = 11.5 Hz, 1H), 4.76 (s, 2H), 4.85 (s, 2H), 5.00 (d, J = 11.5 Hz, 1H), 5.53 (d, J = 8.0 Hz, 1H), 7.09–7.54 (m, 20H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 22.6 (2C), 25.0, 36.8, 36.9, 68.1, 73.0, 73.3, 73.6, 74.3, 74.8, 75.1, 75.6, 78.2, 78.4, 82.3, 82.8, 97.9, 127.7 (3C), 127.8 (2C), 128.1 (4C), 128.2 (2C), 128.4 (3C), 128.6 (4C), 137.9, 138.4, 138.4, 138.7, 151.5; HRMS (ESI-MS): m/z calcd for $C_{43}H_{46}O_8$, $[M + Na]^+$: 713.3090; found: 713.3087.

4.3.13. 1-*O*-(((1-Ethynylcyclohexyl)oxy)carbonyl)-2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside (6aα). The title compound was prepared according to the general procedures 4.2.1b, 4.2.13, 4.2.4, 4.2.14, 4.2.2 and 4.2.3; syrup (760 mg, 15% yield); $[\alpha]_{25}^{D}$ ($CHCl_3$, c 1.0): +30.2; IR (cm^{-1}, $CHCl_3$): 3275, 3020, 2935, 1765, 1486, 1468, 1250, 1237, 1076, 910, 715; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.29–1.36 (m, 1H), 1.52–1.59 (m, 1H), 1.60–1.68 (m, 4H), 1.84–1.92 (m, 2H), 2.16–2.23 (m, 2H), 2.58 (s, 1H), 3.58 (dd, J = 6.5, 1.2 Hz, 2H), 3.96 (dd, J = 10.1, 2.7 Hz, 1H), 4.05 (d, J = 1.8 Hz, 1H), 4.13 (t, J = 6.5 Hz, 1H), 4.19 (dd, J = 10.0, 3.7 Hz, 1H), 4.42 (d, J = 11.8 Hz, 1H), 4.50 (d, J = 11.8 Hz, 1H), 4.59 (d, J = 11.3 Hz, 1H), 4.72–4.80 (m, 3H), 4.86 (d, J = 11.8 Hz, 1H), 4.97 (d, J = 11.3 Hz, 1H), 6.28 (d, J = 3.7 Hz, 1H), 7.26–7.42 (m, 20H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 22.6 (2C), 25.1, 36.7, 37.0, 68.5, 72.1, 73.2, 73.5, 73.6, 74.7, 75.1, 75.6, 78.0, 78.6, 82.3, 82.8, 94.6, 127.5 (2C), 127.7 (2C), 127.8, 127.9, 128.0 (2C), 128.1 (2C), 128.3 (2C), 128.4 (4C), 128.5 (4C), 138.0, 138.2, 138.6, 138.8, 151.7; HRMS (ESI): m/z calcd for $C_{43}H_{46}O_8$, $[M + Na]^+$: 713.3090; found: 713.3092.

4.3.14. 1-*O*-(((1-Ethynylcyclohexyl)oxy)carbonyl)-2,3-di-*O*-benzyl-4,6-di-*O*-(naphthalen-1-yl methyl) α/β-D-galactopyranoside [α : β (1.0 : 8.0)] (6b). The title compound was prepared according to the general procedures 4.2.1b, 4.2.13, 4.2.4, 4.2.14, 4.2.2 and 4.2.3; white solid (1.489 g, 52% yield); mp 78.5 °C; $[\alpha]_{25}^{D}$ ($CHCl_3$, c 1.0): +60.5; IR (cm^{-1}, $CHCl_3$): 3245, 2910, 1710, 1628, 1435, 1277, 1102, 924, 718; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.35–1.39 (m, 2H), 1.53–1.79 (m, 10H), 1.90–2.01 (m, 4H), 2.18–2.28 (m, 4H), 2.63–2.68 (m, 2H), 3.70–4.32 (m, 12H), 4.55–4.69 (m, 4H), 4.80–5.19 (m, 12H), 5.60–6.42 (m, 2H), 7.30–7.58 (m, 32H), 7.71–7.84 (m, 16H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 22.6 (4C), 25.1, (2C), 36.8 (2C), 36.9 (2C), 68.2, 68.6, 72.3, 73.1, 73.3, 73.3, 73.6, 73.8, 74.4, 74.6, 74.8, 75.1, 75.3, 75.3, 75.6, 75.8, 78.1, 78.3, 78.5, 78.8, 82.4, 82.4, 82.9, 83.1, 94.7, 98.0, 126.0–126.4 (12C), 126.8–127.0 (6C), 127.6–127.9 (14C), 128.1–128.3 (10C), 128.4–128.6 (10C), 133.1, 133.2, 133.3, 133.3, 135.4, 135.4, 136.0, 136.2, 138.3, 138.4, 138.5, 138.9, 151.6, 151.8; HRMS (ESI): m/z calcd for $C_{51}H_{50}O_8$, $[M + Na]^+$: 813.3403; found: 813.3400.

4.3.15. 1-*O*-(((1-Ethynylcyclohexyl)oxy)carbonyl)-2,3-di-*O*-benzyl-4,6-di-*O*-acetyl α/β-D-galactopyranoside [α : β (1.0 : 2.5)] (6c). The title compound was prepared according to the general procedures 4.2.1b, 4.2.13, 4.2.4, 4.2.14, 4.2.5, 4.2.2 and 4.2.3; syrup (1.216 g, 56% yield); $[\alpha]_{25}^{D}$ ($CHCl_3$, c 1.0): +49.3; IR (cm^{-1}, $CHCl_3$): 3271, 2937, 1730, 1453, 1368, 1267, 1090, 1025, 723; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.26–1.40 (m, 2H), 1.46–1.72 (m, 10H), 1.85–1.89 (m, 4H), 2.04 (s, 3H), 2.05 (s, 3H), 2.09–2.22 (m, 10H), 2.62 (s, 1H), 2.64 (s, 1H), 3.65–3.95 (m, 5H), 4.11–4.29 (m, 5H), 4.50–4.58 (m, 2H), 4.71–4.81 (m, 6H), 5.51–6.25 (m, 4H), 7.25–7.36 (m, 20H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 20.8 (2C), 20.9 (2C), 22.5 (2C), 22.9, 22.6, 25.0 (2C), 36.6, 36.8, 36.9 (2C), 61.7, 62.1, 66.2, 67.2, 69.3, 71.8, 72.2, 72.3, 73.7, 74.6, 75.2, 75.4, 75.6 (2C), 77.5, 78.2, 78.5, 79.3, 82.6, 82.9, 94.2, 97.3, 127.8–128.1 (10C), 128.2–128.4 (8C), 128.5 (2C), 137.6, 138.0 (3C), 151.2, 151.4, 170.3 (2C), 170.5 (2C); HRMS (ESI): m/z calcd for $C_{33}H_{38}O_{10}$, $[M + Na]^+$: 617.2363; found: 617.2358.

4.3.16. 1-*O*-(((1-Ethynylcyclohexyl)oxy)carbonyl)-2,3-di-*O*-benzyl-4,6-di-*O*-benzoyl α/β-D-galactopyranoside [α : β (1.0 : 2.0)] (6d). The title compound was prepared according to the general procedures 4.2.1b, 4.2.13, 4.2.4, 4.2.14, 4.2.6, 4.2.10 and 4.2.11; white solid (1.513 g, 58% yield); mp 62.6 °C; $[\alpha]_{25}^{D}$ ($CHCl_3$, c 1.0): +64.2; IR (cm^{-1}, $CHCl_3$): 3262, 2930, 1736, 1447, 1362, 1256, 1105, 978, 716; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.28–1.38 (m, 2H), 1.52–1.70 (m, 10H), 1.83–1.96 (m, 4H), 2.16–2.27 (m, 4H), 2.59 (s, 1H), 2.65 (s, 1H), 3.78–4.42 (m, 7H), 4.43–4.65 (m, 5H), 4.67–4.77 (m, 4H), 4.77–4.90 (m, 2H), 5.67–6.36 (m, 4H), 7.25–7.36 (m, 20H), 7.41–7.50 (m, 8H), 7.52–7.64 (m, 4H), 8.00–8.18 (m, 8H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 22.6, 22.7 (3C), 25.1 (2C), 36.8 (2C), 37.0 (2C), 62.5, 62.9, 67.1, 68.2, 69.7, 72.1, 72.2, 72.3, 73.8, 74.3, 75.3, 75.5, 75.7, 75.9, 77.7, 78.3, 78.8, 79.6, 82.6, 82.8, 94.4, 97.5, 127.7 (2C), 127.9 (4C), 127.6, 128.2 (6C), 128.4 (4C), 128.5 (8C), 128.6 (2C), 128.7, 129.6 (2C), 129.7 (2C), 130.0 (4C), 130.1, 130.1, 130.2, 130.2, 133.3, 133.3, 133.5, 133.5, 137.6, 137.9, 138.0, 138.2, 151.2, 151.4, 165.7, 165.8, 166.2, 166.2; HRMS (ESI): m/z calcd for $C_{43}H_{42}O_{10}$, $[M + Na]^+$: 741.2676; found: 741.2676.

4.3.17. 1-*O*-(((1-Ethynylcyclohexyl)oxy)carbonyl)-4-*O*-acetyl-2,3,6-tri-*O*-benzyl α/β-D-galactopyranoside [α : β (1.0 : 3.0)] (6e). The title compound was prepared according to the general procedures 4.2.1b, 4.2.13, 4.2.4, 4.2.14, 4.2.6, 4.2.2 and 4.2.3; syrup (1.056 g, 45% yield); $[\alpha]_{25}^{D}$ ($CHCl_3$, c 1.0): +54.1; IR (cm^{-1}, $CHCl_3$): 3028, 2926, 1740, 1509, 1450, 1362, 1225, 1095, 908, 735, 698; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.22–1.43 (m, 2H), 1.48–1.74 (m, 10H), 1.84–2.00 (m, 4H), 2.07 (s, 3H), 2.09 (s, 3H), 2.15–2.25 (m, 4H), 2.61 (s, 1H), 2.64 (s, 1H), 3.45–3.63 (m, 4H), 3.65–3.81 (m, 3H), 3.84–4.33 (m, 3H), 4.45–4.48 (m, 2H), 4.51–4.66 (m, 4H), 4.66–4.94 (m, 6H), 5.55–6.30 (m, 4H), 6.97–7.65 (m, 30H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 21.0 (2C), 22.6 (4C), 25.1 (2C), 36.8 (4C), 66.4–68.1 (4C), 70.5, 72.1, 72.2, 73.0, 73.7 (3C), 74.7, 75.3, 75.4, 75.6, 75.9, 77.7, 78.2, 78.4, 79.6, 82.7, 82.9, 94.3, 97.5, 127.8–128.1 (10C), 128.2–128.4 (11C), 128.5–128.6 (9C), 137.7 (2C), 137.8, 138.2, 138.2, 138.3, 151.3, 151.5, 170.3, 170.3; HRMS (ESI): m/z calcd for $C_{38}H_{42}O_9$, $[M + Na]^+$: 665.2727; found: 665.2734.

4.3.18. 1-*O*-(((1-Ethynylcyclohexyl)oxy)carbonyl)-2,3-di-*O*-benzyl-4-*O*-acetyl-6-*O*-(naphthalen-1-yl methyl) α/β-D-galactopyranoside [α : β (1.0 : 3.5)] (6f). The title compound was prepared according to the general procedures 4.2.1b, 4.2.13, 4.2.4, 4.2.14, 4.2.6, 4.2.2 and 4.2.3; white solid (1.164 g, 46% yield); mp 72.5 °C; $[\alpha]_{25}^{D}$ ($CHCl_3$, c 1.0): +82.3; IR (cm^{-1}, $CHCl_3$): 2925, 2858, 2320, 1735, 1604, 1513, 1455, 1360, 1265, 1110, 968, 711; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.25–1.41 (m, 2H), 1.47–1.77 (m, 10H), 1.91–1.93 (m, 4H), 2.03 (s, 3H), 2.04 (s, 3H), 2.14–2.18 (m, 4H), 2.50–2.66 (m, 2H), 3.48–3.73 (m, 6H),

4.76–3.42 (m, 4H), 4.47–4.66 (m, 4H), 4.70–4.92 (m, 8H), 5.49–6.38 (m, 4H), 7.26–7.40 (m, 20H), 7.45–7.50 (m, 6H), 7.78–7.86 (m, 8H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 21.0 (2C), 22.6 (4C), 25.0 (2C), 36.7, 36.8 (2C), 37.0, 66.5, 67.5, 67.6, 68.1, 70.5, 72.1, 72.2, 73.0, 73.7, 73.8 (2C), 74.7, 75.2, 75.4, 75.6, 75.9, 77.7, 78.2, 78.5, 79.6, 82.6, 82.9, 94.3, 97.5, 126.1–126.3 (6C), 126.9, 127.1, 127.8–128.1 (13C), 128.3–128.5 (13C), 133.2 (2C), 133.3 (2C), 135.1, 135.2, 137.7, 138.1 (2C), 138.3, 151.3, 151.5, 170.3 (2C); HRMS (ESI): *m*/*z* calcd for $C_{42}H_{44}O_9$, $[M + Na]^+$: 715.2883; found: 715.2881.

4.3.19. 1-*O*-(((1-Ethynylcyclohexyl)oxy)carbonyl)-2,3-di-*O*-benzyl-4-*O*-acetyl-6-*O*-*tert*-butyldiphenyl silyl α/β-D-galactopyranoside [α : β (1.0 : 2.0)] (6g). The title compound was prepared according to the general procedures 4.2.1b, 4.2.13, 4.2.4, 4.2.14, 4.2.7, 4.2.6, 4.2.2 and 4.2.3; syrup (1.432 g, 50% yield); $[\alpha]_{25}^{D}$ ($CHCl_3$, *c* 1.0): +10.4; IR (cm^{-1}, $CHCl_3$): 3015, 2935, 2862, 1725, 1615, 1458, 1366, 1260, 1117, 950, 709; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.05 (s, 9H), 1.08 (s, 9H), 1.25–1.41 (m, 2H), 1.49–1.57 (m, 2H), 1.56–1.74 (m, 8H), 1.81–1.96 (m, 4H), 2.01 (s, 3H), 2.04 (s, 3H), 2.07–2.26 (m, 4H), 2.58–2.61 (m, 2H), 3.59–3.90 (m, 8H), 3.88–4.25 (m, 2H), 4.47–4.87 (m, 8H), 5.39–6.30 (m, 4H), 7.26–7.47 (m, 32H), 7.64–7.68 (m, 8H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 19.2 (2C), 20.9 (2C), 22.5 (2C), 22.6 (2C), 25.0, 25.1, 26.8 (2C), 26.9 (4C), 36.7–37.0 (4C), 61.1, 61.5, 65.3, 67.0, 71.7, 72.2, 72.3, 73.7, 74.0, 74.7, 75.2, 75.3, 75.7, 76.1, 77.8, 78.2, 78.3, 79.7, 82.6, 82.9, 94.4, 97.4, 127.7–128.0 (16C), 128.1–128.6 (16C), 129.9 (3C), 130.0, 133.0 (2C), 133.1 (2C), 135.6, 135.7 (2C), 135.8, 137.8, 138.2 (2C), 138.3, 151.3, 151.6, 170.0, 170.1; HRMS (ESI): *m*/*z* calcd for $C_{47}H_{54}O_9Si$, $[M + Na]^+$: 813.3435; found: 813.3439.

4.3.20. Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl α/β D-galactopyranosyl) α-D-glucopyranoside [α : β (8.0 : 1.0)] (19). The title compound was prepared according to the general procedure 4.2.15; white solid (39 mg, 95% yield); mp 67.4 °C; $[\alpha]_{25}^{D}$ ($CHCl_3$, *c* 1.0): +28.6; IR (cm^{-1}, $CHCl_3$): 3015, 2965, 1730, 1510, 1445, 1365, 1215, 1095, 910, 715; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 3.38–3.39 (m, 6H), 3.43–3.57 (m, 5H). 3.61–3.65 (m, 2H), 3.84–4.13 (m, 10H), 4.28–4.53 (m, 6H), 4.53–4.65 (m, 2H), 4.67–4.74 (m, 2H), 4.74–4.80 (m, 2H), 4.82–4.99 (m, 7H), 5.17–5.32 (m, 4H), 5.53–6.24 (m, 4H), 7.12–7.31 (m, 26H), 7.33–7.56 (m, 32H), 7.83–8.05 (m, 12H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 55.5, 55.5, 66.7, 66.7, 68.6, 68.6, 68.8, 68.8, 69.4, 69.4, 69.6, 69.6, 70.8, 70.8, 72.3, 72.3, 73.0, 73.0, 73.3, 73.3, 73.3, 73.3, 74.9, 74.9, 75.1, 75.1, 76.5, 76.5, 78.6, 78.6, 96.8, 96.9, 98.0, 104.3, 127.5–127.7 (9), 127.8–127.9 (8), 127.9–128.0 (8), 128.1–128.2 (14), 128.3–128.5 (14), 128.5–128.6 (6), 129.0, 129.2, 129.2, 129.2, 129.4, 129.4, 129.8–129.8(6), 133.2, 133.2, 133.5, 133.5, 133.5, 133.5, 137.9, 138.2, 138.6, 138.7, 138.8, 138.9, 139.1, 165.5, 165.7, 165.9, 165.9, 166.0, 166.3; HRMS (ESI): *m*/*z* calcd for $C_{62}H_{60}O_{14}$, $[M + Na]^+$: 1051.3881; found: 1051.3884.

4.3.21. Allyl 2-*O*-(*p*-methoxybenzyl)-3-*O*-(4-oxopentanoyl)-4-*O*-(2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl)-α-L-fucopyranoside (20). The title compound was prepared according to the general procedure 4.2.15; white solid (704 mg, 98% yield); mp 87.2 °C; $[\alpha]_{25}^{D}$ ($CHCl_3$, *c* 1.0): −74.6; IR (cm^{-1}, $CHCl_3$): 3014, 2930, 2849, 1760, 1720, 1628, 1465, 1357, 1265, 1105, 930, 720; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.07 (d, *J* = 6.5 Hz, 3H), 2.01 (s, 3H), 2.13 (ddd, *J* = 14.5, 8.3, 5.5 Hz, 1H), 2.31 (ddd, *J* = 14.5, 8.3, 5.5 Hz, 1H), 2.38–2.56 (m, 2H), 3.62–3.70 (m, 3H), 3.77(s, 3H), 3.93–4.05 (m, 2H), 4.11 (dd, *J* = 12.9, 5.2 Hz, 1H), 4.37 (dd, *J* = 10.2, 3.4 Hz, 1H), 4.50–4.81 (m, 4H), 5.05 (d, *J* = 4.1 Hz, 1H), 5.14–5.36 (m, 5H), 5.66 (t, *J* = 6.3 Hz, 1H), 5.90 (dddd, *J* = 17.1, 10.4, 6.5, 5.3 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 1H), 7.16–7.40 (m, 8H), 7.44–7.56 (m, 3H), 7.84–8.12 (m, 6H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 16.1, 27.7, 29.7, 37.7, 55.3, 60.9, 64.5, 68.5, 69.0, 69.8, 70.1, 70.1, 72.6, 73.0, 74.0, 96.2, 96.2, 113.9, 113.9, 118.3, 128.4 (4C), 128.5 (2C), 129.4, 129.4, 129.4, 129.8 (2C), 129.9 (2C), 130.0 (2C), 130.1 (2C), 130.4, 133.3, 133.4, 133.5, 133.9, 159.4, 165.0, 165.3, 165.6, 172.4, 206.4; HRMS (ESI-MS): *m*/*z* calcd for $C_{48}H_{50}O_{15}$, $[M + Na]^+$: 889.3047; found: 889.3042.

4.3.22. Allyl 3-*O*-(4-oxopentanoyl)-4-*O*-(2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl)-α-L-fucopyranoside (21). The title compound was prepared according to the general procedure 4.2.16; white solid (240 mg, 93% yield); mp 97.5 °C; $[\alpha]_{25}^{D}$ ($CHCl_3$, *c* 1.0): −37.4; IR (cm^{-1}, $CHCl_3$): 3025, 2923, 2820, 1735, 1630, 1450, 1365, 1243, 1108, 936, 714; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 1.12 (d, *J* = 6.6 Hz, 3H), 2.06 (s, 3H), 2.15–2.29 (m, 1H), 2.34–2.45 (m, 1H), 2.47–2.62 (m, 2H), 2.72 (s, 1H), 3.78 (dd, *J* = 12.4, 6.0 Hz, 1H), 3.94 (dd, *J* = 10.0, 3.9 Hz, 1H), 4.00–4.15 (m, 3H), 4.22 (ddt, *J* = 12.8, 5.4, 1.3 Hz, 1H), 4.68 (dd, *J* = 12.4, 3.9 Hz, 1H), 5.03 (dd, *J* = 6.3, 4.3 Hz, 2H), 5.22–5.28 (m, 2H), 5.29–5.37 (m, 3H), 5.73 (t, *J* = 6.6 Hz, 1H), 5.96 (dddd, *J* = 16.9, 10.4, 6.3, 5.5 Hz, 1H), 7.32–7.39 (m, 6H), 7.47–7.56 (m, 3H), 7.94–8.04 (m, 6H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 16.0, 27.6, 29.7, 37.7, 61.0, 64.9, 67.6, 68.7, 68.9, 69.5, 69.6, 70.1, 75.7, 97.4, 97.6, 118.2, 128.3 (2C), 128.3 (4C), 129.1, 129.2, 129.3, 129.9 (4C), 130.0 (2C), 133.2, 133.4 (2C), 133.6, 164.9, 165.2, 165.5, 172.2, 206.4; HRMS (ESI): *m*/*z* calcd for $C_{40}H_{42}O_{14}$, $[M + Na]^+$: 769.2472; found: 769.2473.

4.3.23. Allyl 2-*O*-(2,3-di-*O*-benzyl-4-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl α-D-galactopyranosyl)-3-*O*-(4-oxopentanoyl)-4-*O*-(2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl)-α-L-fucopyranoside (22). The title compound was prepared according to the general procedure 4.2.15; syrup (383 mg, 95% yield); $[\alpha]_{25}^{D}$ ($CHCl_3$, *c* 1.0): −78.1; IR (cm^{-1}, $CHCl_3$): 3280, 3025, 2930, 2855, 1752, 1486, 1450, 1265, 1232, 1105, 1030, 915, 710; ^{1}H NMR (400.31 MHz, $CDCl_3$): δ 0.95–1.24 (m, 12H). 1.88–2.03 (m, 7H), 2.09–2.19 (m, 1H), 2.27–2.45 (m, 2H), 3.50–3.77 (m, 3H), 3.89 (dd, *J* = 10.2, 3.5 Hz, 1H), 3.93 (dd, *J* = 10.3, 3.5 Hz, 1H), 3.98–4.16 (m, 4H), 4.26 (t, *J* = 6.7 Hz, 1H), 4.52 (dd, *J* = 10.3, 3.2 Hz, 1H), 4.62–4.77 (m, 3H), 4.85 (d, *J* = 5.8 Hz, 1H), 4.88 (d, *J* = 4.7 Hz, 1H), 4.97–5.10 (m, 3H), 5.16 (d, *J* = 10.3 Hz, 1H), 5.27–5.36 (m, 4H), 5.75–5.79 (m, 2H), 5.93 (dddd, *J* = 16.9, 10.4, 6.3, 5.5 Hz, 1H), 7.22–7.56 (m, 25H), 7.57–7.72 (m, 4H), 7.81–8.07 (m, 6H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 16.1, 19.2, 21.0, 27.0, 27.5, 27.5, 27.5, 29.7, 37.6, 62.0, 62.9, 64.6, 68.0, 68.7, 69.3, 69.7, 70.8, 71.2, 71.3, 71.4, 72.5, 72.8, 75.5, 75.9, 76.0, 96.5, 98.1, 100.5, 117.6, 127.6–127.8 (10C), 128.4–128.5 (12C), 129.4, 129.5, 129.6, 129.9–130.1 (8C), 132.9, 133.1, 133.3, 133.3, 133.3, 134.3, 135.8, 135.9, 138.5, 138.8, 165.0, 165.5, 165.6, 170.2,

172.3, 206.2; HRMS (ESI): *m*/*z* calcd for $C_{78}H_{84}O_{20}Si$, $[M + Na]^+$: 1391.5223; found: 1391.5220.

4.3.24. Allyl 2-*O*-(2,3-di-*O*-benzyl-4-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl α-D-galactopyranosyl)-4-*O*-(2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl)-α-L-fucopyranoside (23). The title compound was prepared according to the general procedure 4.2.17; syrup (279 mg, 86% yield); $[\alpha]_{25}^{D}$ ($CHCl_3$, *c* 1.0): −112.6; IR (cm^{-1}, $CHCl_3$): 3020, 2918, 2837, 1730, 1470, 1463, 1255, 1226, 1118, 1026, 917, 715; ^1H NMR (400.31 MHz, $CDCl_3$): δ 1.08 (s, 9H), 1.24 (d, *J* = 6.6 Hz, 3H), 1.93 (s, 3H), 2.58 (s, 1H), 3.55 (dd, *J* = 12.9, 5.3 Hz, 1H), 3.58–3.68 (m, 2H), 3.80–3.87 (m, 2H), 3.88–3.98 (m, 3H), 4.03 (dd, *J* = 12.9, 5.8 Hz, 1H), 4.09 (dd, *J* = 10.2, 3.3 Hz, 1H), 4.22–4.27 (m, 1H), 4.30 (dd, *J* = 10.1, 3.1 Hz, 1H), 4.63–4.72 (m, 2H), 4.77–4.94 (m, 4H), 4.96–5.04 (m, 2H), 5.09–5.19 (m, 3H), 5.28 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.78 (d, *J* = 2.1 Hz, 1H), 5.83 (dd, *J* = 9.5, 7.9 Hz, 1H), 5.91 (dddd, *J* = 17.0, 10.3, 6.6, 5.3 Hz, 1H), 7.22–7.28 (m, 1H), 7.30–7.44 (m, 17H), 7.45–7.58 (m, 7H), 7.57–7.65 (m, 4H), 7.86–8.02 (m, 6H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 16.1, 19.1, 20.9, 26.9, 26.9, 26.9, 61.6, 63.0, 65.0, 67.7, 68.2, 68.4, 68.6, 69.4, 70.9, 72.3, 72.8, 73.1, 73.9, 76.0, 76.0, 76.1, 97.1, 98.1, 100.6, 117.2, 127.4–127.7 (10C), 128.2–128.5 (12C), 128.8, 129.2, 129.4, 129.7–129.9 (8C), 132.8, 133.0, 133.3, 133.3, 133.6, 134.2, 135.7, 135.9, 138.5, 139.0, 165.4, 165.6, 165.8, 170.0; HRMS (ESI): *m*/*z* calcd for $C_{73}H_{78}O_{18}Si$, $[M + Na]^+$: 1293.4855; found: 1293.4861.

4.3.25. Allyl 2-*O*-(*p*-methoxybenzyl)-4-*O*-(2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl)-α-L-fucopyranoside (24). The title compound was prepared according to the general procedure 4.2.17; white solid (240 mg, 90% yield); mp 93.5 °C; $[\alpha]_{25}^{D}$ ($CHCl_3$, *c* 1.0): −109.0; IR (cm^{-1}, $CHCl_3$): 3015, 2935, 2849, 1715, 1625, 1460, 1355, 1260, 1102, 937, 710; ^1H NMR (400.31 MHz, $CDCl_3$): δ 1.16 (d, *J* = 6.6 Hz, 3H), 2.48 (s, 1H), 3.59 (dd, *J* = 12.2, 7.0 Hz, 1H), 3.71 (d, *J* = 4.3 Hz, 1H), 3.76 (s, 3H), 3.77–3.89 (m, 2H), 3.96 (dd, *J* = 13.0, 6.6 Hz, 1H), 4.09 (dd, *J* = 13.0, 5.2 Hz, 1H), 4.14 (dd, *J* = 9.9, 3.1 Hz, 1H), 4.47–4.60 (m, 2H), 4.67–4.77 (m, 2H), 5.02 (d, *J* = 5.1 Hz, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 5.28 (dd, *J* = 17.2, 1.3 Hz, 1H), 5.22–5.32 (m, 2H), 5.80 (t, *J* = 7.7 Hz, 1H), 5.89 (dddd, *J* = 17.1, 10.4, 6.5, 5.3 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 7.28–7.43 (m, 6H), 7.46–7.54 (m, 3H), 7.96–8.00 (m, 6H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 16.1, 55.3, 61.2, 65.2, 68.3, 69.3, 69.6, 70.7, 72.2, 73.0, 74.0, 77.4, 96.1, 98.6, 113.9, 113.9, 118.1, 128.5 (4C), 128.6 (2C), 129.0, 129.2, 129.3, 129.9 (6C), 130.0 (2C), 130.5, 133.5, 133.5, 133.7, 134.0, 159.4, 165.6, 165.6, 165.8; HRMS (ES): *m*/*z* calcd for $C_{43}H_{44}O_{13}$, $[M + Na]^+$: 791.2680; found: 791.2683.

4.3.26. Allyl 2-*O*-(*p*-methoxybenzyl)-3-*O*-(2-*O*-benzoyl-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-4-*O*-(2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl)-α-L-fucopyranoside (25). The title compound was prepared according to the general procedure 4.2.15; syrup (340 mg, 97% yield); $[\alpha]_{25}^{D}$ ($CHCl_3$, *c* 1.0): −62.5; IR (cm^{-1}, $CHCl_3$): 3068, 2927, 1715, 1610, 1440, 1247, 1108, 1027, 962, 718; ^1H NMR (400.31 MHz, $CDCl_3$): δ 1.20 (d, *J* = 6.5 Hz, 3H), 1.38 (d, *J* = 6.1 Hz, 3H), 3.45 (s, 3H), 3.51 (t, *J* = 9.5 Hz, 1H), 3.59 (dd, *J* = 12.3, 6.3 Hz, 1H), 3.71 (s, 3H), 3.72–3.74 (m, 1H), 3.76–3.83 (m, 2H), 3.90 (dd, *J* = 10.3, 3.7 Hz, 1H), 4.00 (dd, *J* = 12.9, 6.7 Hz, 1H), 4.12 (dd, *J* = 13.0, 5.2 Hz, 1H), 4.17–4.27 (m, 2H), 4.55 (d, *J* = 4.3 Hz, 1H), 4.58 (d, *J* = 4.3 Hz, 1H), 4.64 (d, *J* = 13.7 Hz, 1H), 4.68 (d, *J* = 13.7 Hz, 1H), 4.76 (d, *J* = 13.7 Hz, 1H), 4.89–4.92 (m, 2H), 5.16–5.24 (m, 2H), 5.24–5.29 (m, 1H), 5.32 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.38 (dd, *J* = 6.2, 4.7 Hz, 1H), 5.55 (dd, *J* = 2.9, 2.0 Hz, 1H), 5.67 (t, *J* = 6.4 Hz, 1H), 5.92 (dddd, *J* = 17.0, 10.3, 6.6, 5.3 Hz, 1H), 6.78 (d, *J* = 8.6 Hz, 2H), 7.19–7.24 (m, 4H), 7.25–7.39 (m, 9H), 7.40–7.50 (m, 4H), 7.51–7.60 (m, 2H), 7.84–7.87 (m, 2H), 7.99–8.07(m, 6H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 16.8, 18.5, 55.3, 57.6, 61.0, 66.3, 68.4, 68.5, 68.7, 69.2, 70.2, 71.1, 72.7, 74.6, 75.3, 75.3, 79.2, 79.8, 80.5, 96.0, 98.4, 99.7, 113.8, 113.8, 118.2, 127.7, 128.3–128.5 (12C), 129.4, 129.4, 129.5, 129.9–130.1 (11C), 130.3, 133.3, 133.3, 133.4, 133.4, 134.1, 138.8, 159.4, 165.0, 165.5, 165.6, 166.2; HRMS (ESI): *m*/*z* calcd for $C_{64}H_{66}O_{18}$, $[M + Na]^+$: 1145.4147; found: 1145.4142.

4.3.27. Allyl 3-*O*-(2-*O*-benzoyl-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-4-*O*-(2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl)-α-L-fucopyranoside (26). The title compound was prepared according to the general procedure 4.2.16; syrup (244 mg, 88% yield); $[\alpha]_{25}^{D}$ ($CHCl_3$, *c* 1.0): −98.2; IR (cm^{-1}, $CHCl_3$): 3039, 2935, 1730, 1622, 1430, 1235, 1095, 1014, 970, 709; ^1H NMR (400.31 MHz, $CDCl_3$): δ 1.24 (d, *J* = 6.2 Hz, 3H), 1.30 (d, *J* = 6.5 Hz, 3H), 2.61 (s, 1H), 3.34–3.49 (m, 1H), 3.42 (s, 3H), 3.71–3.84 (m, 3H), 3.91–3.99 (m, 1H), 3.99–4.14 (m, 4H), 4.22 (dd, *J* = 12.9, 5.4 Hz, 1H), 4.56–4.70 (m, 2H), 4.80–4.85 (m, 2H), 5.00 (s, 1H), 5.16 (d, *J* = 4.7 Hz, 1H), 5.20–5.30 (m, 2H), 5.30–5.39 (m, 2H), 5.48–5.53 (m, 1H), 5.74 (t, *J* = 6.4 Hz, 1H), 5.95 (dddd, *J* = 17.0, 10.3, 6.6, 5.3 Hz, 1H), 7.09–7.21 (m, 2H), 7.26–7.39 (m, 10H), 7.42–7.46 (m, 3H), 7.49–7.56 (m, 2H), 7.81–7.83 (m, 2H), 7.97–8.03 (m, 6H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 16.9, 18.0, 57.5, 61.1, 66.7, 67.6, 68.4, 68.5, 68.8, 69.2, 69.6, 70.0, 75.3, 77.1, 79.5, 79.7, 80.4, 97.7, 98.2, 99.9, 118.2, 127.7, 128.2–128.5 (11C), 129.2, 129.3, 129.8–130.1 (11C), 133.2, 133.4, 133.4, 133.4, 133.9, 138.6, 165.2, 165.4, 165.6, 166.1; HRMS (ESI): *m*/*z* calcd for $C_{56}H_{58}O_{17}$, $[M + Na]^+$: 1025.3572; found: 1025.3568.

4.3.28. Allyl 2-*O*-(2,3-di-*O*-benzyl-4-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl α-D-galactopyranosyl)-3-*O*-(2-*O*-benzoyl-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-4-*O*-(2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl)-α-L-fucopyranoside (2). The title compound was prepared according to the general procedure 4.2.15; syrup (285 mg, 91% from **5** and 320 mg, 94% yield from **26**); $[\alpha]_{25}^{D}$ ($CHCl_3$, *c* 1.0): −56.3; IR (cm^{-1}, $CHCl_3$): 3023, 2927, 2852, 1720, 1615, 1460, 1345, 1264, 1115, 952, 709; ^1H NMR (400.31 MHz, $CDCl_3$): δ 1.01–1.15 (m, 12H), 1.32 (d, *J* = 6.1 Hz, 3H), 1.89 (s, 3H), 3.40 (s, 3H), 3.43–3.56 (m, 3H), 3.57–3.65 (m, 2H), 3.66–3.73 (m, 2H), 3.77 (dd, *J* = 9.4, 3.1 Hz, 1H), 3.86–3.97 (m, 3H), 4.06–4.16 (m, 2H), 4.25 (t, *J* = 6.8 Hz, 1H), 4.31 (dd, *J* = 10.1, 2.5 Hz, 1H), 4.42 (dd, *J* = 12.4, 4.5 Hz, 1H), 4.59–4.75 (m, 4H), 4.80–4.94 (m, 4H), 4.97 (d, *J* = 3.4 Hz, 1H), 5.01 (d, *J* = 3.4 Hz, 1H), 5.15–5.18 (m, 2H), 5.28 (dd, *J* = 17.2, 1.1 Hz, 1H), 5.37 (dd, *J* = 8.2, 5.7 Hz, 1H), 5.50 (d, *J* = 5.7 Hz, 1H), 5.70 (t, *J* = 7.9 Hz, 1H), 5.77 (d, *J* = 5.7 Hz, 1H), 5.89 (dddd, *J* = 17.0, 10.3, 6.6, 5.3 Hz, 1H), 7.05–7.17 (m, 3H), 7.20–7.48 (m, 28H), 7.49–7.66 (m, 6H), 7.81–7.83 (m, 2H), 7.86–8.13 (m, 6H); ^{13}C NMR (100.67 MHz, $CDCl_3$): δ 16.5, 18.3, 19.2, 21.0, 27.0, 27.0, 27.0, 57.5, 61.6, 62.5, 66.0, 67.6, 68.5, 68.5, 69.3, 69.5, 70.2, 71.1,

72.0, 72.6, 73.4, 73.6, 75.1, 75.3, 76.1, 77.7, 79.4, 79.9, 80.3, 98.1, 98.8, 99.9, 101.2, 116.9, 127.6–127.8 (8C), 128.1–128.5 (22C), 129.3, 129.4, 129.5, 129.7–130.1 (10C), 132.8, 133.0, 133.2, 133.2, 133.2, 133.3, 134.4, 135.8, 136.0, 138.5, 138.5, 138.8, 165.0, 165.5, 165.6, 166.2, 170.1; HRMS (ESI): *m*/*z* calcd for $C_{94}H_{100}O_{23}Si$, $[M + Na]^+$: 1648.6356; found: 1648.6351.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

BM and MN acknowledge the research fellowship from CSIR-UGC-NET. SC and GW thanks IISER Pune for the fellowship. SM and SH acknowledge the financial assistance from DBT-New Delhi (BT/PR20820/MED/30/1875/2017). The authors thank Sandip Pasari for the fruitful discussion.

Notes and references

1 (*a*) F. Piacente, M. Gaglianone, M. E. Laugieri and M. G. Tonetti, *Int. J. Mol. Sci.*, 2015, **16**, 29315; (*b*) R. Danovaro, C. Corinaldesi, A. Dell'Anno, J. A. Fuhrman, J. J. Middelburg, R. T. Noble and C. A. Suttle, *FEMS Microbiol. Rev.*, 2011, **35**, 993; (*c*) S. Sharoni, M. Trainic, D. Schatz, Y. Lehahn, M. J. Flores, K. D. Bidle, S. Ben-Dor, Y. Rudich, I. Koren and A. Vardi, *Proc. Natl. Acad. Sci. U. S. A.*, 2015, **112**, 6643; (*d*) J. L. Van Etten, J. R. Gurnon, G. M. Yanai-Balser, D. D. Dunigan and M. V. Graves, *Biochim. Biophys. Acta*, 2010, **1800**, 152; (*e*) I. Barkia, N. Saari and S. R. Manning, *Mar. Drugs*, 2019, **17**, 304; (*f*) D. D. Dunigan, L. A. Fitzgerald and J. L. Van Etten, *Virus Res.*, 2006, **117**, 119; (*g*) J. L. Van Etten, I. Agarkova, D. D. Dunigan, M. Tonetti, M. C. De Castro and G. A. Duncan, *Viruses*, 2017, **9**, 88.

2 (*a*) C. De Castro, A. Molinaro, F. Piacente, J. R. Gurnon, L. Sturiale, A. Palmigiano, R. Lanzetta, M. Parrilli, D. Garozzo, M. G. Tonetti and J. L. Van Etten, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 13956; (*b*) R. H. Yolken, L. Jones-Brando, D. D. Dunigan, G. Kannan, F. Dickerson, E. Severance, S. Sabunciyan, C. C. Talbot Jr., E. Prandovszky, J. R. Gurnon, I. V. Agarkova, F. Leister, K. L. Gressitt, O. Chen, B. Deuber, F. Ma, M. V. Pletnikov and J. L. Van Etten, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, **111**, 16106; (*c*) M. S. Petro, I. V. Agarkova and T. M. Petro, *J. Neuroimmunol.*, 2016, **297**, 46.

3 (*a*) P. Spolaore, C. Joannis-Cassan, E. Duran and A. Isambert, *J. Biosci. Bioeng.*, 2006, **101**, 87–96; (*b*) S. Sasso, G. Pohnert, M. Lohr, M. Mittag and C. Hertweck, *FEMS Microbiol. Rev.*, 2012, **36**, 761; (*c*) S. S. Merchant, J. Kropat, B. Liu, J. Shaw and J. Warakanont, *Curr. Opin. Biotechnol.*, 2012, **23**, 352; (*d*) F. Hempel, A. S. Bozarth, N. Lindenkamp, A. Klingl, S. Zauner, U. Linne, A. Steinbüchel and U. G. Maier, *Microb. Cell Fact.*, 2011, **10**, 81; (*e*) G. Walsh, *Nat. Biotechnol.*, 2010, **28**, 917.

4 (*a*) C. De Castro, T. Klose, I. Speciale, R. Lanzett, A. Molinaro, J. L. Van Etten and M. G. Rossmann, *Proc. Natl. Acad. Sci. U. S. A.*, 2018, **118**, E44; (*b*) C. F. Quispe, A. Esmael, O. Sonderman, M. McQuinn, I. Agarkova, M. Battah, G. A. Duncan, D. D. Dunigan, T. P. Smith, C. De Castro, I. Speciale, F. Ma and J. L. Van Etter, *Virology*, 2017, **500**, 103; (*c*) C. De Castro, I. Speciale, G. Duncan, D. D. Dunigan, I. Agarkova, R. Lanzetta, L. Sturiale, A. Palmigiano, D. Garozzo, A. Molinaro, M. Tonetti and J. L. Van Etten, *Angew. Chem., Int. Ed.*, 2016, **55**, 654–658; (*d*) I. Speciale, R. Agarkova, D. D. Duncan, J. L. Van Etten and C. De Castro, *Antonie van Leeuwenhoek*, 2017, **110**, 1391.

5 (*a*) S. Lin and T. L. Lowary, *Chem. – Eur. J.*, 2018, **24**, 16992–16996; (*b*) Y.-S. Wang, Y. Wu, D.-C. Xiong and X.-S. Ye, *Chin. J. Chem.*, 2019, **37**, 42–48; (*c*) S. Lin and T. L. Lowary, *Org. Lett.*, 2020, **22**, 7645–7649.

6 (*a*) B. Mishra, M. Neralkar and S. Hotha, *Angew. Chem.*, 2016, **128**, 7917; (*b*) M. Rommel, A. Ernst and U. Koert, *Eur. J. Org. Chem.*, 2007, 4408.

7 (*a*) A. Imamura, A. Kimura, H. Ando, H. Ishida and M. Kiso, *Chem. – Eur. J.*, 2006, **12**, 8862; (*b*) S. S. Nigudkar and A. V. Demchenko, *Chem. Sci.*, 2015, **6**, 2687 and references therein; (*c*) A. V. Demchenko, *Curr. Org. Chem.*, 2003, **7**, 35; (*d*) A. V. Demchenko, *Synlett*, 2003, 1225; (*e*) D. Crich, *Acc. Chem. Res.*, 2010, **43**, 1144.

8 (*a*) A. Ishiwata, Y. Munemura and Y. Ito, *Tetrahedron*, 2008, **64**, 92; (*b*) G. Wulff and G. Rohle, *Angew. Chem., Int. Ed. Engl.*, 1974, **13**, 157; (*c*) A. V. Demchenko, T. Stauch and G. J. Boons, *Synlett*, 1997, 818; (*d*) C. S. Chao, C. Lin, Y. S. Mulani, W. C. Hung and K. K. Mong, *Chem. – Eur. J.*, 2011, **17**, 12193; (*e*) T. Shirahata, J.-I. Matsuo, S. Teruya, N. Hirata, T. Kurimoto, N. Akimoto, T. Sunazuka, E. Kaji and S. Omura, *Carbohydr. Res.*, 2010, **345**, 740; (*f*) G. Wasonga, Y. Zeng and X. Huang, *Sci. China: Chem.*, 2011, **54**, 66.

9 (*a*) F. Andersson, P. Fógedi, P. J. Garegg and M. Nashed, *Tetrahedron Lett.*, 1986, **27**, 3919; (*b*) S. Manabe, Y. Ito and T. Ogawa, *Synlett*, 1998, 628; (*c*) R. R. Schmidt and E. Rucker, *Tetrahedron Lett.*, 1980, **21**, 1421; (*d*) H. Dohi, Y. Nishida, H. Tanaka and K. Kobayashi, *Synlett*, 2001, 1446; (*e*) T. G. Frihed, M. Bols and C. M. Pedersen, *Chem. Rev.*, 2015, **115**, 4963.

10 P. Peng and R. R. Schmidt, *J. Am. Chem. Soc.*, 2015, **137**, 12653.

11 (*a*) J. Li, Y. Dai, W. Li, S. Laval, P. Xu and B. Yu, *Asian J. Org. Chem.*, 2015, **4**, 756; (*b*) P. Xu, W. Xu, Y. Dai, Y. Yang and B. Yu, *Org. Chem. Front.*, 2014, **1**, 405; (*c*) Y. Li, X. Yang, Y. Liu, C. Zhu, Y. Yang and B. Yu, *Chem. – Eur. J.*, 2010, **16**, 1871; (*d*) Y. Ma, G. Lian, Y. Li and B. Yu, *Chem. Commun.*, 2011, **47**, 7515; (*e*) Y. Zhu, Z. Shen, W. Li and B. Yu, *Org. Biomol. Chem.*, 2016, **14**, 1536.

12 (*a*) B. Fraser-Reid, K. N. Jayaprakash, J. C. López, A. M. Gómez and C. Uriel, in *ACS Symp. Ser. (Frontiers in Modern Carbohydrate Chemistry)*, ed. A. V. Demchenko, Oxford Univ. Press, 2007, vol. 960, pp. 91–117; (*b*) T. Ishikawa and H. G. Fletcher, *J. Org. Chem.*, 1969, **34**, 563; (*c*) R. Eby and C. Schuerch, *Carbohydr. Res.*, 1974, **34**, 79 and references therein; (*d*) T. Mukaiyama, M. Suenaga, H. Chiba and H. Jona, *Chem. Lett.*, 2002, 56; (*e*) A. V. Demchenko, E. Rousson and G. J. Boons, *Tetrahedron Lett.*, 1999, **40**, 6523; (*f*) M. Takatani, I. Matsuo and Y. Ito, *Carbohydr. Res.*, 2003, **338**, 1073; (*g*) N. Ustyuzhanina, B. Komarova, N. Zlotina, V. Krylov, A. G. Gerbst, Y. Tsvetkov and N. E. Nifantiev, *Synlett*, 2006, 921; (*h*) B. S. Komarova, M. V. Orekhova, Y. E. Tsvetkov and N. E. Nifantiev, *Carbohydr. Res.*, 2014, **384**, 70; (*i*) D. Crich and W. Cai, *J. Org. Chem.*, 1999, **64**, 4926; (*j*) D. Crich and N. S. Chandrasekera, *Angew. Chem., Int. Ed.*, 2004, **43**, 5386; (*k*) A. Imamura, H. Ando, H. Ishida and M. Kiso, *Org. Lett.*, 2005, **7**, 4415; (*l*) A. Imamura, N. Matsuzawa, S. Sakai, T. Udagawa, S. Nakashima, H. Ando, H. Ishida and M. Kiso, *J. Org. Chem.*, 2016, **81**, 9086.

13 (*a*) E. J. Corey and P. Carpino, *J. Am. Chem. Soc.*, 1989, **111**, 5472; (*b*) A. G. Gerbst, N. E. Ustuzhanina, A. A. Grachev, D. E. Tsvetkov, E. A. Khatuntseva and N. E. Nifantiev, *Mendeleev Commun.*, 1999, 114–116.

14 See the ESI.†