Carbohydrate Research 346 (2011) 465–471

Contents lists available at ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Stereoselective synthesis of *N*-galactofuranosyl amides

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ARTICLE INFO

Article history:
Received 29 November 2010
Received in revised form 23 December 2010
Accepted 23 December 2010
Available online 31 December 2010

Keywords:
Glycosyl amides
Glycosyl azides
Glycomimetics
Neoglycoconjugates
Staudinger ligation
Stereoselective synthesis

ABSTRACT

α- or β-Galactofuranosyl (Gal*f*) amides can be synthesized with high stereoselectivity by traceless Staudinger ligation starting from unprotected β-galactofuranosyl azide or tetra-*O*-acetyl-β-galactofuranosyl azide, respectively. The resulting Gal*f* amides are hitherto unknown molecules, with interesting potential as inhibitors of mycobacterial growth.

1. Introduction

The arabinogalactan constituent of mycobacterial cell walls contains a galactan polymer made of galactose residues in the furanose form, Gal*f*. The Gal*f* residues are created by bacterial mutases which convert UDP-galactopyranose into UDP-galactofuranose and are essential for the viability of mycobacteria.[1] The furanose form of D-galactose is unknown in mammals and UDP-galactopyranose (UDPG) mutase has become an interesting target for the development of drugs against the many pathogens which contain Gal*f*, most prominently *Mycobacterium tuberculosis*. UDPG mutase inhibitors have been reported and shown to block mycobacterial growth.[2–8] Furthermore, simple galactofuranosyl derivatives in low micromolar concentration have been shown to inhibit bacterial growth[9,10] with a mechanism which has not been fully elucidated.

We have been interested for some time in the opportunities offered by glycosyl amides as mimics of natural glycosides[11,12] and have been developing synthetic methodologies for the preparation of glycosyl amides from glycosyl azides based on the traceless Staudinger ligation.[13–15] In this paper, we describe a simple stereoselective synthesis of Gal*f* amides in both anomeric configurations starting from a common azide precursor. The resulting compounds may be of interest in the generation of new antibacterial leads, or as inhibitors of galactofuranosidases and galactofuranosyltransferases.[1,16]

2. Results and discussion

The starting galactofuranosyl azide **2** was prepared in 90% yield from known penta-*O*-acetyl-galactofuranose **1**[17] using $TMSN_3$ and $SnCl_4$ (Scheme 1). Zemplén deacetylation afforded the unprotected Gal*f*-azide **3**, whose anomeric β configuration was established by NOE difference experiments, which showed a clear correlation between protons H1 and H3.[†]

Initial studies focused on the functionalization of **2** using standard methodology, such as catalytic hydrogenation followed by in situ acetylation (Scheme 2). However, anomerization of the intermediate glycosyl amine is fast and a mixture of epimers was obtained. Similarly, reaction of **2** and Ph_3P generated an iminophosphorane that epimerized at the anomeric position before reacting with acylating agents, such as pentafluorophenyl valerate (C_4H_9COPFP, Scheme 2).[18] These results are consistent with previous observations by our group[13–15,18] and others[19] working on pyranosyl azides.

On the contrary, following our previously established protocol,[13–15] traceless Staudinger ligation of **2** with 2-diphenylphosphanyl-phenyl valeroate (**4a**) in a 98:2 *N*,*N*-dimethylacetamide (DMA)–1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) solvent mixture (4 h, 70 °C) followed by treatment with water afforded the corresponding galactofuranosyl amide **5a** in 60% yield as a single anomer (Scheme 3). The structure and anomeric

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[†] One Referee remarked that many physical and spectral data of the compounds described in this paper are also indicative of their anomeric configuration. All the Referee's observations are reported in the Supplementary data. We are grateful to this reviewer for his/her comments.

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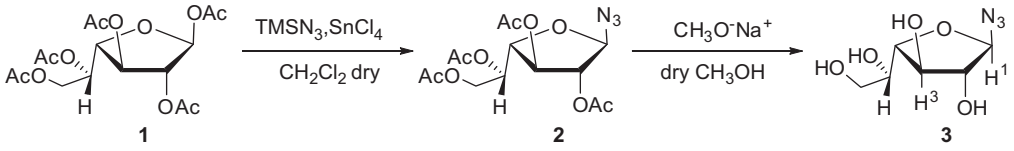
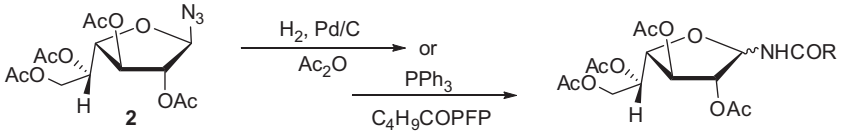
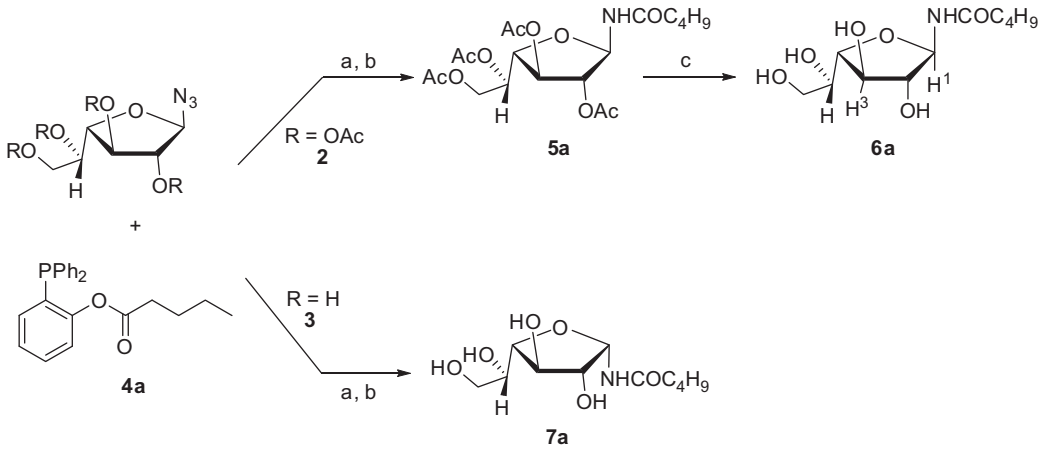
doi:10.1016/j.carres.2010.12.020



Scheme 1. Synthesis of Gal*f*-azide **2** and **3**.



Scheme 2. Derivatization of **2** with conventional methods leads to mixtures of epimers at the anomeric position.



a) 70°C, 4h, DMA:DMPU 98:2; b) H_2O, 2 h, 70°C; c) 0.05M MeO^-Na^+, MeOH.

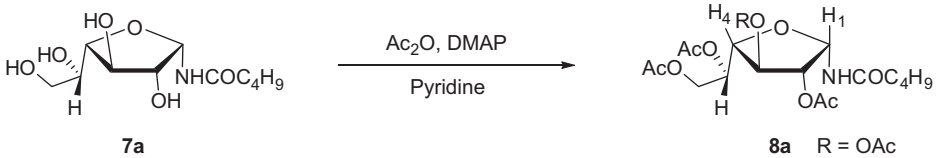
Scheme 3. Stereodivergent synthesis of furanosyl amides **5a** and **7a** by ligation of **2** and **3**.

configuration of **5a** were confirmed by NMR after deacetylation (cat. NaOMe in MeOH) to yield the unprotected amide **6a** (Scheme 4). The chemical shift of C4 in **6a** at 83.6 ppm is diagnostic for the furanose form, and NOESY experiments (CD_3OD at 400 MHz) showed the expected crosspeak between protons H1 and H3.

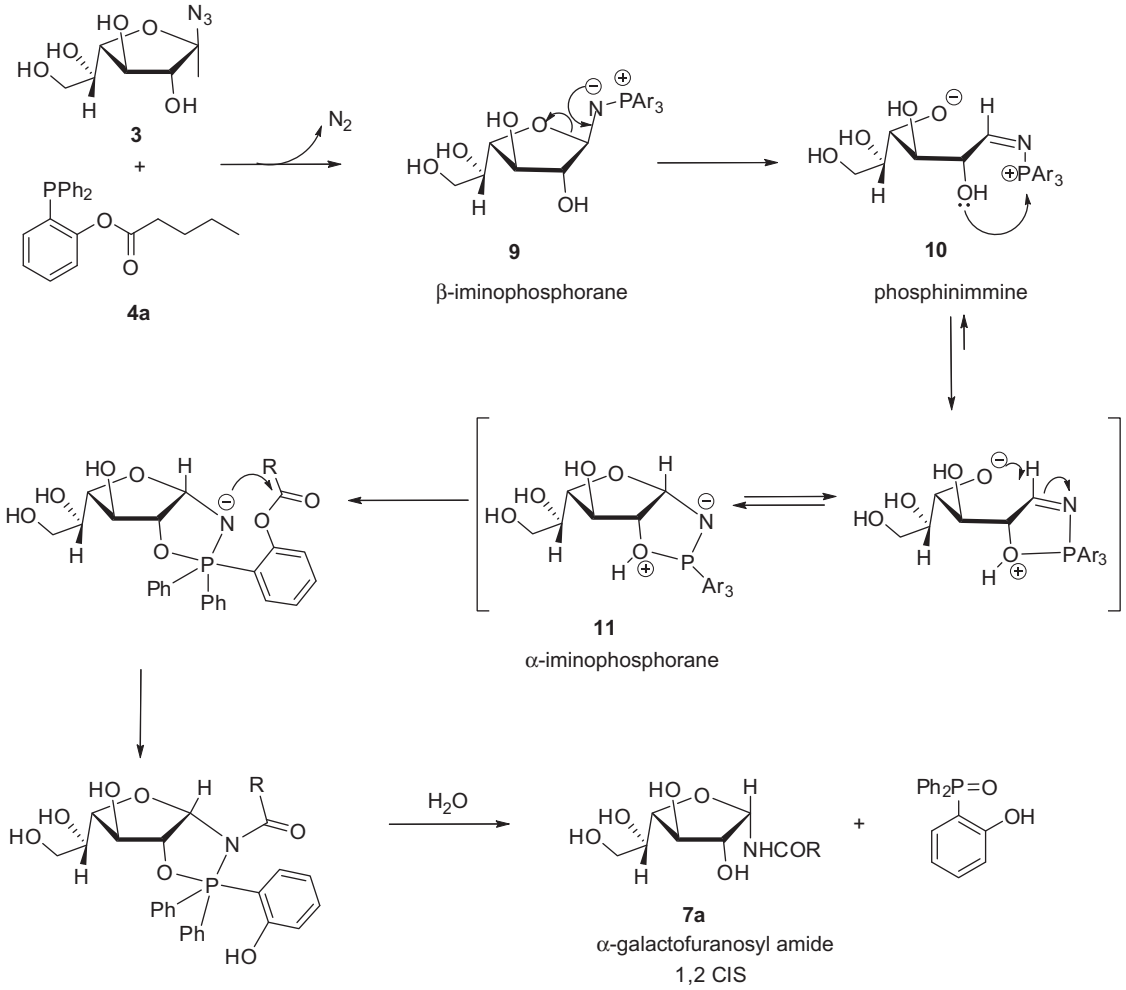
Surprisingly, ligation of unprotected Gal*f*-azide **3** with **4a** afforded, under similar conditions, amide **7a** with *the opposite* anomeric configuration (Scheme 3). The structure of **7a** was confirmed by the C4 chemical shift (84.4 ppm) and by the absence of crosspeaks between protons H1 and H3 in the NOESY spectrum (CD_3OD; H1, and H3 of **7a** are isochronous in D_2O at 400 MHz).

Compound **7a** was fully characterized as the 1,2-cis isomer after acetylation to **8a** (Scheme 4), by the presence of crosspeaks between protons H1 and H4 in the NOESY spectrum ($CDCl_3$ at 400 MHz).

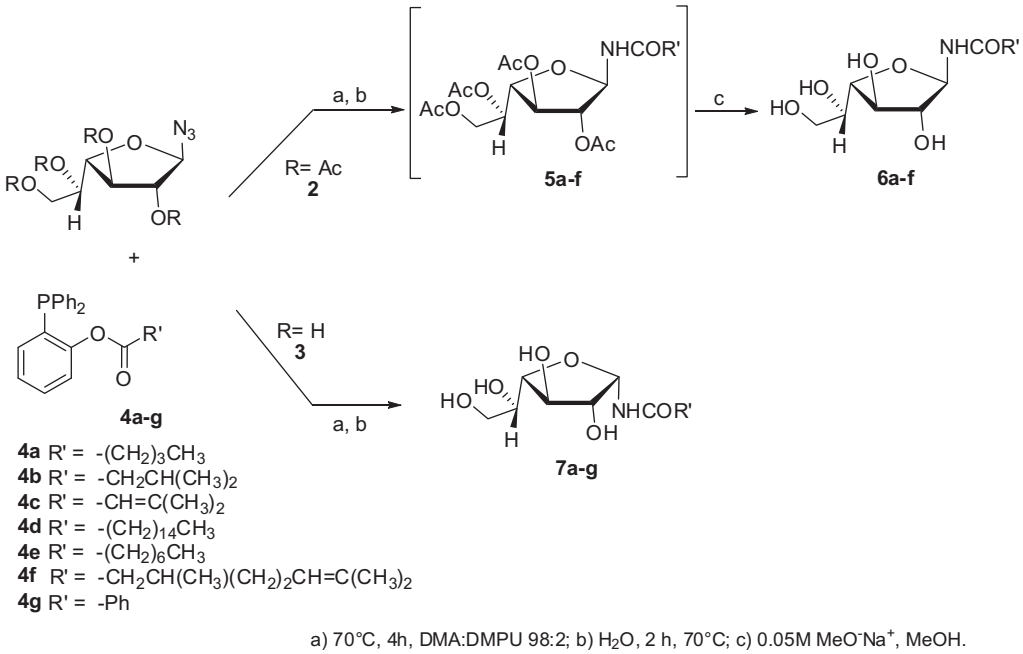
The reason for this selectivity switch is not completely understood at present, but the anomeric inversion must derive from a ring-opening process occurring after the azide reduction step, presumably from the β-iminophosphorane **9** to afford the phosphinimmine **10** (Scheme 5). From this open-chain intermediate, the ring closure step could be biased by the unprotected hydroxy group at position 2, which can trap the α-iminophosphorane **11** and enforce formation of the (1,2-cis) α-anomers. This result is consistent with our previous observation that α-*N*-glucofuranosylamides are formed as by-products in the ligation of unprotected α-glucopyranosyl azide with phosphines **4a**, and that the amount of furanose by-product increases with the reaction temperature.[14] In this case, ring opening of the intermediate iminophosphorane, which is favored at high temperatures, leads to an open-chain 2-hydroxy phosphinimine, which follows the same path as **10**. If this is the case, the retention of configuration observed with the tetra-*O*-acetyl azide **2** is even more puzzling. Indeed, as it was observed for pyranosyl azides,[15] the acetylated substrate is expected to undergo ring-opening even more easily than **3**, due to the electron withdrawing property of the protecting groups, and thus to afford



Scheme 4. Acetylation of **7a** and NOESY characterization of **8a**.



Scheme 5. Proposed mechanism for the anomeric epimerization of **3**.



Scheme 6. Traceless Staudinger ligation of **2** and **3** with phosphines **4a–g**.

at least partial racemization. The exclusive formation of the α-(1,2-trans) anomer may indicate that, in the absence of a directing effect of a free 2-OH group, trans ring closure of the phosphinimine is favored, possibly for steric reasons.

To explore the scope of this reaction and confirm its stereochemical outcome, **2** and **3** were subjected to traceless ligation with a series of phosphines **4a**–**g** (Scheme 6). To facilitate purification from the phosphinoxide byproduct, amides **5a**–**f** obtained from tetra-*O*-acetyl azide **2** were not directly isolated. Anomeric configurations and diastereomeric distributions were analyzed by ^{1}H NMR spectroscopy on the crude reaction mixtures, which were then deacetylated to afford the corresponding deprotected amides **6a**–**f.** The latter were finally isolated and purified by flash chromatography on silica gel. The deprotection step was found to be critical to preserve configurational integrity of the anomeric carbon. Although 0.05 M NaOMe in MeOH solutions and short contact times (45 min) were used successfully, the use of more concentrated (0.1 M) solutions caused anomeric epimerization. This process likely occurs via NaOMe-induced deprotonation of the amide nitrogen, which allows ring opening to occur with a process similar to that described in Scheme 5 for iminophosphorane **9**. Longer chain amides, such as **4d**–**f**, appeared to be more stable to basic conditions. Products from the Staudinger ligation of the unprotected Gal*f*-azide **3** were isolated by water extraction from the crude reaction mixtures and purified by silica gel chromatography. Anomeric ratios were evaluated on the crude by ^{1}H NMR spectroscopy.

The results of this screening are collected in Table 1. Transfer of linear aliphatic (**4a,d,e**), branched aliphatic (**4b,f**), unsaturated (**4c,f**), and aromatic (**4g**) amide chains was performed with uniform results. All reactions gave the expected products in moderate yields. As previously reported for unprotected glycopyranosyl azides,[14] microwave irradiation was found to accelerate the ligation of **3** (entries 7 and 11). The stereoselectivity was complete, as determined by the ^{1}H NMR spectra of the crude reaction mixtures. In all cases, β-anomers were obtained from the tetra-*O*-acetyl azide **2** and α-anomers from the unprotected azide **3**.

While further studies are clearly needed to clarify the mechanism of this intriguing reaction, the results described herein represent the first reported synthesis of Gal*f* amides. Notably, both isomers can be obtained with excellent selectivity from a common, easily available precursor. The chemical synthesis of Gal*f* derivatives has been recently reviewed[1,16,20] and the interest in these molecules is currently increasing for their potential as antibacterial agents and as useful core structures for targeting Gal*f* recognizing enzymes.[1,16] Further studies are in progress to analyze the activity of galactofuranosyl amides against Gal*f*-containing pathogens.

3. Experimental

3.1. General

Solvents were dried by standard procedures: dichloromethane, methanol, *N*,*N*-diisopropylethylamine, and triethylamine were dried over calcium hydride; *N*,*N*-dimethylacetamide (DMA), 1,3-dimethyltetrahydro-2(1*H*)pyrimidinone (DMPU), chloroform, and pyridine were dried over activated molecular sieves. Reactions requiring anhydrous conditions were performed under nitrogen. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at 400 MHz on a Bruker AVANCE-400 instrument. Chemical shifts (δ) for ^{1}H and ^{13}C spectra are expressed in ppm relative to internal Me_4Si as standard. Signals were abbreviated as s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra were obtained with a Bruker ion-trap Esquire 3000 apparatus (ESI ionization) and FT-ICR Mass Spectrometer APEX II & Xmass software (Bruker Daltonics)—4.7 Magnet. Thin layer chromatography (TLC) was carried out with pre-coated Merck F_{254} silica gel plates. Flash chromatography (FC) was carried out with Macherey-Nagel Silica Gel 60 (230–400 mesh). The syntheses of *o*-diphenylphosphinophenol and of phosphines **4a–c** have been described.[13]

3.2. 2-Diphenylphosphanylphenyl palmitate (4d)

Dry triethylamine (1.1 equiv) and palmitoyl chloride (1.1 equiv) were added, at room temperature and under nitrogen, to a solution of *o*-diphenylphosphinophenol (1 equiv) in dry CH_2Cl_2 (0.1 M). The reaction mixture was stirred at room temperature and monitored by TLC (90:10 hexane–EtOAc) until disappearance of the *o*-diphenylphosphinophenol (ca. 1 h). The solvent was then evaporated under reduced pressure and the residue was diluted with EtOAc and washed with 5% aqueous $NaHCO_3$ and water. The organic layer was dried over Na_2SO_4 and concentrated. The compound was purified by flash chromatography (hexane–EtOAc 95:5) yield = 85%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.42–7.28 (m, 11H, Ph), 7.18–7.08 (m, 2H), 6.82–6.76 (m, 1H), 2.23 (t, J = 7.2, J = 8 Hz, 2H, CH_2), 1.48 (t, J = 7.2, J = 6.8 Hz, 2H, CH_2), 1.41–1.17 (m, 24H, 12 × CH_2), 0.88 (t, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 171.8, 134.3, 134.1, 133.9, 129.2, 126.2, 122.8, 35.2, 34.3, 32.2, 29.9, 29.8, 29.6, 29.4, 29.3, 29.1, 24.7, 22.9, 14.3; ^{31}P NMR (161 MHz, $CDCl_3$): δ = −14.3 ppm [oxide ^{31}P = +27.3 ppm].

Table 1
Ligation of **2** and **3** with phosphines **4a–g**[a]

Entry	Azide	Phosphine	R	Product	α/β[b]	Yields
1	**2**	**4a**	$-(CH_2)_3CH_3$	**6a**	2:98	60
2	**2**	**4b**	$-CH_2CH(CH_3)_2$	**6b**	⩾1:99	53
3	**2**	**4c**	$-CH{=}C(CH_3)_2$	**6c**	2:98	48
4	**2**	**4d**	$-(CH_2)_{14}CH_3$	**6d**	⩾1:99	60
5	**2**	**4e**	$-(CH_2)_6CH_3$	**6e**	⩾1:99	56
6	**2**	**4f**	$-CH_2CH(CH_3)(CH_2)_2CH{=}C(CH_3)_2$	**6f**	⩾1:99	51
7	**3**	**4a**	$-(CH_2)_3CH_3$	**7a**	⩾99:1[c]	60
8	**3**	**4b**	$-CH_2CH(CH_3)_2$	**7b**	⩾99:1	57
9	**3**	**4c**	$-CH{=}C(CH_3)_2$	**7c**	⩾99:1	51
10	**3**	**4d**	$-(CH_2)_{14}CH_3$	**7d**	⩾99:1	55
11	**3**	**4e**	$-(CH_2)_6CH_3$	**7e**	⩾99:1[c]	63
12	**3**	**4f**	$-CH_2CH(CH_3)(CH_2)_2CH{=}C(CH_3)_2$	**7f**	⩾99:1	56
13	**3**	**4g**	–Ph	**7g**	⩾99:1	62

[a] Unless otherwise stated, all reactions were performed in 98:2 DMA–DMPU mixtures for 4 h at 70 °C. Water was then added and the solution was stirred for additional 2 h at 70 °C before work up.
[b] ^{1}H NMR spectroscopic ratio of the anomeric protons in the crude.
[c] Reaction performed under microwave irradiation: 30 min, 70 °C.

3.3. 2-Diphenylphosphanylphenyl caprylate (4e)

A solution of *o*-diphenylphosphinophenol (126.2 mg, 0.45 mmol, 1 equiv), caprylic acid (77.9 mg, 0.54 mmol, 1.2 equiv) and *N,N*-dimethylaminopyridine (5.5 mg, 0.045 mmol, 0.1 equiv) in dry CH_2Cl_2 was added, at room temperature and under argon, to a solution of *N,N′*-dicyclohexylcarbodiimide (130.1 mg, 0.63 mmol, 1.4 equiv) in dry CH_2Cl_2 (total volume: 4.5 mL, 0.1 M). The mixture was stirred at room temperature for 1 h, monitoring by TLC (90:10 hexane–EtOAc). The reaction mixture was filtered and washed with CH_2Cl_2. The crude product was purified by flash chromatography using 90:10 hexane–EtOAc as the eluent to afford the product in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.45–7.26 (m, 11H, Ph), 7.20–7.07 (m, 2H), 6.83–6.78 (m, 1H), 2.25 (t, J = 7.6 Hz, 2H, CH_2), 1.49 (t, J = 7.2 Hz, 2H, CH_2), 1.36–1.19 (m, 8H, 4 × CH_2), 0.89 (t, J = 6.8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 171.8, 135.9, 134.7, 134.3, 134.1, 130.1, 129.2, 128.8, 128.7, 126.2, 122.8, 34.2, 33.8, 31.8, 29.2, 29.1, 24.7, 22.8, 14.3 (CH_3).

3.4. 2-Diphenylphosphanylphenyl citronellate (4f)

A solution of the *o*-diphenylphosphinophenol (127.8 mg, 0.46 mmol, 1 equiv), the citronellic acid (93.6 mg, 0.55 mmol, 1.2 equiv) and *N,N*-dimethylaminopyridine (5.5 mg, 0.046 mmol, 0.1 equiv) in dry CH_2Cl_2 was added, at room temperature and under argon, to a solution of *N,N′*-dicyclohexylcarbodiimide (132.1 mg, 0.64 mmol, 1.4 equiv) in dry CH_2Cl_2 (total volume: 4.6 mL, 0.1 M). The mixture was stirred at room temperature for 1 h, monitoring by TLC (90:10 hexane–EtOAc). The reaction mixture was filtered and washed with CH_2Cl_2. The crude product was purified by flash chromatography using 95:5 hexane–EtOAc as the eluent to afford the product in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.45–7.27 (m, 11H, Ph), 7.21–7.08 (m, 2H), 6.84–6.78 (m, 1H), 5.07 (t, J = 7.2, J = 6.8 Hz, 1H, CH), 2.25 (dd, J = 5.6, J_{Ha-Hb} = 15.3 Hz, 1H, Ha, CH_2), 2.06 (dd, J = 8.4, J_{Ha-Hb} = 15.3 Hz, 1H, Hb, CH_2), 1.99–1.79 (m, 3H, CH–CH_2), 1.68 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.27–1.12 (m, 2H, CH_2), 0.89 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 171.2, 153.2, 153.1, 136, 135.9, 134.3, 134.1, 133.9, 131.9, 131.8, 131.7, 130.1, 129.2, 128.8, 128.7, 126.2, 124.5, 122.7, 41.5, 36.9, 29.9, 25.6, 19.8, 17.9; ^{31}P NMR (161 MHz, $CDCl_3$): δ = −14.9 ppm [oxide ^{31}P = +27.3 ppm].

3.5. 2-Diphenylphosphanylphenyl benzoate (4g)

Dry pyridine (27 μL, 0.34 mmol, 1.2 equiv), benzoic anhydride (76.6 mg, 0.34 mmol, 1.2 equiv), and *N,N*-dimethylaminopyridine (3.4 mg, 0.028 mmol, 0.1 equiv) were added, at room temperature and under argon, to a solution of *o*-diphenylphosphinophenol (78.6 mg, 0.28 mmol, 1 equiv) in dry CH_2Cl_2 (1.87 mL, 0.15 M). The solution was stirred for 3 h and then concentrated in vacuo. The residue was dissolved in EtOAc and washed with 5% aqueous $NaHCO_3$ and water. The organic layer was dried over Na_2SO_4 and concentrated. The product was purified by flash chromatography using 95:5 hexane–EtOAc as the eluant. Quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.81–7.78 (m, 2H), 7.46 (m, 1H), 7.37 (td, J = 7.6, 1.5 Hz, 1H), 7.32–7.23 (m, 13H, Ph), 7.12 (dd, J = 7.6 Hz, 1H), 6.82 (ddd, J = 9.8, 4.2, 2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 164.3, 152.9 (d, J = 17 Hz), 135.5 (d, J = 10 Hz), 134.6, 134.2, 133.6, 133.4, 131.7 (d, J = 11 Hz), 130.7 (d, J = 15 Hz), 130.2, 129.9, 129.2, 129.1, 128.6, 128.5, 128.3, 128.1, 126.2, 122.6; ^{31}P NMR (161 MHz, $CDCl_3$): δ = −14.3 ppm [oxide ^{31}P = +27.3 ppm].

3.6. 2,3,5,6-Tetra-*O*-acetyl-β-D-galactofuranosyl azide (2)

Trimethylsilyl azide (238 μL, 1.79 mmol, 1.4 equiv) and $SnCl_4$ (45 μL, 0.384 mmol, 0.3 equiv) were added in sequence, at room temperature and under argon, to a solution of 1,2,3,5,6-penta-*O*-acetyl-β-D-galactofuranose **1** (500 mg, 1.28 mmol, 1 equiv) in dry CH_2Cl_2 (2.56 mL, 0.5 M). The reaction mixture was stirred at room temperature and the reaction was monitored by TLC (6:4 hexane–EtOAc). After 24 h CH_2Cl_2 was added and the solution was washed with saturated Na_2CO_3 and then with water. The organic layer was dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The crude product was purified by flash chromatography using 60:40 hexane–EtOAc as the eluent to afford the product in 90% yield. $[\alpha]_D^{25}$ −11.5 (*c* 1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 5.42 (s, 1H, H-1), 5.40–5.35 (m, 1H, H-5), 5.05 (dd, $J_{2,3}$ = 5.2, $J_{3,4}$ = 2.8 Hz, 1H, H-3), 4.95 (t, $J_{3,4}$ = 2.8 Hz, 1H, H-4), 4.39–4.32 (m, 2H, H-2, H-6), 4.19 (dd, $J_{5,6'}$ = 6.8, $J_{6,6'}$ = 11.6 Hz, 1H, H-6′), 2.16 (s, 3H, OAc), 2.14 (s, 3H, OAc), 2.12 (s, 3H, OAc), 2.06 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 170.6, 170.1, 169.9, 169.7, 94.3 (C-1), 82.2 (C-2), 81.1 (C-4), 76.5 (C-3), 69.4 (C-5), 62.5 (C-6), 20.9–20.7 (4 × OAc). ESI-MS: *m/z* 396.2 $[M+Na]^+$.

3.7. Synthesis of β-D-galactofuranosyl azide (3)

A solution of NaOMe 0.1 M in dry methanol (320 μL, 0.32 mmol, 0.5 equiv) was added, at room temperature and under nitrogen, to a solution of 2,3,5,6-tetra-*O*-acetyl-β-D-galacto-furanosyl azide **2** (238 mg, 0.64 mmol, 1 equiv) in dry MeOH (6.4 mL, 0.1 M). The mixture was stirred at room temperature. After 1 h TLC monitoring (eluents: hexane–EtOAc 50:50 and $CHCl_3$–MeOH 80:20) showed total consumption of the starting material, Amberlyst IRA 120 H^+ resin was added. The mixture was stirred for 30 min (pH 3). The resin was filtered and washed with MeOH, the solvent was removed under reduced pressure. The product, isolated in quantitative yield, was used without further purification. $[\alpha]_D^{25}$ −153 (*c* 1, MeOH). ^{1}H NMR (400 MHz, D_2O, 25 °C): δ = 5.31 (d, $J_{1,2}$ = 2.8 Hz, 1H, H-1), 4.06 (ABX system, part A dd, $J_{2,3}$ = 4, $J_{3,4}$ = 10 Hz 1H, H-3), 4.01 (ABX system, part B, dd, $J_{3,4}$ = 10.4, $J_{4,5}$ = 4.4 Hz, 1H, H-4), 3.94 (ABX system, part X, dd, $J_{1,2}$ = 2.8, $J_{2,3}$ = 3.6 Hz, 1H, H-2), 3.80–3.73 (ddd, $J_{4,5}$ = 4.4, $J_{5,6'}$ = 7.2, $J_{5,6}$ = 4.8 Hz, 1H, H-5), 3.64 (dd, $J_{5,6}$ = 4.8, $J_{6,6'}$ = 11.6 Hz, 1H, H-6), 3.57 (dd, $J_{5,6'}$ = 7.2, $J_{6,6'}$ = 11.6 Hz, 1H, H-6′); ^{13}C NMR (100 MHz, D_2O, 25 °C): δ = 95.3 (C-1), 84.2 (C-4), 80.6 (C-2), 76.4 (C-3), 70.7 (C-5), 62.6 (C-6). ESI-MS: *m/z* 228.07 $[M+Na]^+$. NOESY (400 MHz, D_2O, 25 °C): contact between H-1/H-3.

3.8. General procedure for stereoselective ligation of 2 and 3 in DMA:DMPU mixtures

The phosphine (1.2 equiv) was added, at room temperature, to a 0.1 M solution of azide **2** or **3** (1 equiv) in 98:2 *N,N*-dimethylacetamide–DMPU. The solution was stirred for 4 h at 70 °C, then water was added and the mixture was stirred for an additional 2 h at the same temperature. The solvent was evaporated under reduced pressure, and the residue was purified as indicated below for each compound.

3.8.1. *N*-Pentanoyl-β-D-galactofuranosylamide (6a)

The compound was purified by flash chromatography ($CHCl_3$–MeOH 80:20) yield = 60%. $[\alpha]_D^{25}$ −17.9 (*c* 0.2, MeOH). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 5.38 (d, $J_{1,2}$ = 5.2 Hz, 1H, H-1), 4.14 (t, $J_{2,3}$ = 5.8, $J_{3,4}$ = 6.4 Hz, 1H, H-3), 3.95 (t, $J_{1,2}$ = 5.2, $J_{2,3}$ = 5.8 Hz, 1H, H-2), 3.90 (dd, $J_{3,4}$ = 6.4, $J_{4,5}$ = 2.8 Hz, 1H, H-4), 3.68–3.63 (m, 1H, H-5), 3.62–3.57 (m, 2H, H-6, H-6′), 2.22 (t, J = 7.4 Hz, 2H, CH_2), 1.71–1.54 (m, 2H, CH_2), 1.48–1.32 (m, 2H, CH_2), 0.95 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 177.4, 85.5 (C-1), 83.6 (C-4), 81.1 (C-2), 77.5 (C-3), 72.7 (C-5), 64.4 (C-6), 37.1 (CH_2), 28.9 (CH_2), 23.5 (CH_2), 14.3 (CH_3). FT-ICR (ESI) calcd for $C_{11}H_{21}N_1O_6$ $[M+Na]^+$ 286.12611, found 286.12586. NOESY (400 MHz, D_2O, 25 °C): contact between H-1/H-3.

3.8.2. *N*-(3-Methylbutanoyl)-β-D-galactofuranosylamide (6b)

The compound was purified by flash chromatography ($CHCl_3$–MeOH 85:15) yield = 53%. $[\alpha]_D^{25}$ −24.5 (*c* 1, MeOH). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 5.40 (d, $J_{1,2}$ = 5.2 Hz, 1H, H-1), 4.15 (t, $J_{2,3}$ = 5.8, $J_{3,4}$ = 6.4 Hz, 1H, H-3), 3.97 (t, $J_{1,2}$ = 5.2, $J_{2,3}$ = 5.8 Hz, 1H, H-2), 3.92 (dd, $J_{3,4}$ = 6.4, $J_{4,5}$ = 2.8 Hz, 1H, H-4), 3.71–3.65 (m, 1H, H-5), 3.63–3.58 (m, 2H, H-6, H-6′), 2.35 (d, *J* = 7.2 Hz, 2H, CH_2), 1.01 (d, *J* = 6.4 Hz, 3H, CH_3), 0.97 (d, *J* = 6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 176.6, 85.6 (C-1), 83.7 (C-4), 81.2 (C-2), 77.5 (C-3), 72.7 (C-5), 64.4 (C-6), 46.5 (CH_2), 22.9 (CH_3), 22.7 (CH_3). FT-ICR (ESI) calcd for $C_{11}H_{21}N_1O_6$ $[M+Na]^+$ 286.12611, found 286.12584.

3.8.3. *N*-3-Methyl-2-butenoyl-β-D-galactofuranosylamide (6c)

The compound was purified by flash chromatography ($CHCl_3$–MeOH 85:15) yield = 48%. $[\alpha]_D^{25}$ −27.8 (*c* 0.2, MeOH). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 5.74 (s, 1H, CH), 5.41 (d, $J_{1,2}$ = 5.6 Hz, 1H, H-1), 4.15 (t, $J_{2,3}$ = 5.8, $J_{3,4}$ = 6.4 Hz, 1H, H-3), 3.96 (t, $J_{1,2}$ = 5.6, $J_{2,3}$ = 5.8 Hz, 1H, H-2), 3.90 (dd, $J_{3,4}$ = 6.4, $J_{4,5}$ = 2.8 Hz, 1H, H-4), 3.68–3.63 (m, 1H, H-5), 3.61–3.57 (m, 2H, H-6, H-6′), 2.15 (s, 3H, CH_3), 1.89 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 170.2, 154.3, 119.3 (CH), 85.4 (C-1), 83.4 (C-4), 81.1 (C-2), 77.5 (C-3), 72.8 (C-5), 64.4 (C-6), 27.5 (CH_3), 20.3 (CH_3). FT-ICR (ESI) calcd for $C_{11}H_{21}N_1O_6$ $[M+Na]^+$ 284.11046, found 284.11027.

3.8.4. *N*-Palmitoyl-β-D-galactofuranosylamide (6d)

The compound was purified by flash chromatography ($CHCl_3$–MeOH 90:10) yield = 60%. $[\alpha]_D^{25}$ −37.3 (*c* 1, MeOH). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 5.40 (d, $J_{1,2}$ = 5.2 Hz, 1H, H-1), 4.15 (t, $J_{2,3}$ = 6, $J_{3,4}$ = 6 Hz, 1H, H-3), 3.96 (t, $J_{1,2}$ = 5.2, $J_{2,3}$ = 5.6 Hz, 1H, H-2), 3.93 (dd, $J_{3,4}$ = 6.4, $J_{4,5}$ = 2.8 Hz, 1H, H-4), 3.70–3.65 (m, 1H, H-5), 3.63–3.58 (m, 2H, H-6, H-6′), 2.24 (t, *J* = 8 Hz, 2H, CH_2), 1.63 (m, 2H, CH_2), 1.41–1.25 (m, 24H, 12 × CH_2), 0.92 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 177.1, 85.7 (C-1), 83.8 (C-4), 81.2 (C-2), 77.6 (C-3), 72.8 (C-5), 64.4 (C-6), 37.4, 33.2, 30.9, 30.7, 30.6, 30.4, 26.8, 23.8, 14.6 (CH_3). FT-ICR (ESI) calcd for $C_{22}H_{43}N_1O_6$ $[M+Na]^+$ 440.29826; found 440.29844.

3.8.5. *N*-Capryloyl-β-D-galactofuranosylamide (6e)

The compound was purified by flash chromatography ($CHCl_3$–MeOH 85:15) yield = 56%. $[\alpha]_D^{25}$ −50.4 (*c* 0.9, MeOH). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 5.42 (d, $J_{1,2}$ = 5.2 Hz, 1H, H-1), 4.17 (t, $J_{2,3}$ = 5.8, $J_{3,4}$ = 6.4 Hz, 1H, H-3), 3.98 (t, $J_{1,2}$ = 5.2, $J_{2,3}$ = 5.8 Hz, 1H, H-2), 3.95 (dd, $J_{3,4}$ = 6.4, $J_{4,5}$ = 2.8 Hz, 1H, H-4), 3.73–3.68 (m, 1H, H-5), 3.65–3.59 (m, 2H, H-6, H-6′), 2.28 (t, *J* = 7.2, *J* = 8 Hz, 2H, CH_2), 1.65 (m, 2H, CH_2), 1.47–1.27 (m, 8H, 4 × CH_2), 0.94 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 177.1, 85.4 (C-1), 83.6 (C-4), 81 (C-2), 77.3 (C-3), 72.6 (C-5), 64.2 (C-6), 37.2, 32.8, 30.2, 30.1, 26.7, 23.6, 14.4 (CH_3). FT-ICR (ESI) calcd for $C_{14}H_{27}N_1O_6$ $[M+Na]^+$ 328.17306, found 328.17317.

3.8.6. *N*-Citronelloyl-β-D-galactofuranosylamide (6f)

The compound was purified by flash chromatography ($CHCl_3$–MeOH 90:10) yield = 51%. $[\alpha]_D^{25}$ −55.8 (*c* 0.9, MeOH). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 5.45 (d, $J_{1,2}$ = 5.2 Hz, 1H, H-1), 5.16 (t, *J* = 6.8 Hz, 1H, CH) 4.20 (t, $J_{2,3}$ = 5.6, $J_{3,4}$ = 6.2 Hz, 1H, H-3), 4.01 (t, $J_{1,2}$ = 5.2, $J_{2,3}$ = 5.6 Hz, 1H, H-2), 3.97 (dd, $J_{3,4}$ = 6.2, $J_{4,5}$ = 2.8 Hz, 1H, H-4), 3.71 (ddd, $J_{4,5}$ = 2.8, *J* = 6, *J* = 6.8 Hz, 1H, H-5), 3.68–3.63 (m, 2H, H-6, H-6′), 2.29 (dd, *J* = 13.6, *J* = 6 Hz, 1H, Ha, CH_2), 2.18–1.98 (m, 4H), 1.73 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 1.48–1.40 (m, 1H), 1.33–1.22 (m, 1H), 1.01 (d, *J* = 6.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 176.6, 132.4, 125.7, 85.7 (C-1), 83.8 (C-4), 81.2 (C-2), 77.6 (C-3), 72.8 (C-5), 64.4 (C-6), 44.9, 38.1, 30.9, 26.6, 26, 19.9, 17.9. FT-ICR (ESI) calcd for $C_{16}H_{29}N_1O_6$ $[M+Na]^+$ 354.18871, found 354.18866.

3.8.7. *N*-Pentanoyl-α-D-galactofuranosylamide (7a)

The compound was purified by flash chromatography ($CHCl_3$–MeOH 80:20) yield = 60%. $[\alpha]_D^{25}$ +18.1 (*c* 1, MeOH). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 5.69 (d, $J_{1,2}$ = 4.4 Hz, 1H, H-1), 4.13 (t, $J_{2,3}$ = 3.4, $J_{3,4}$ = 3.6 Hz, 1H, H-3), 3.88 (dd, $J_{1,2}$ = 4.4, $J_{2,3}$ = 3.4 Hz, 1H, H-2), 3.80 (dd, $J_{3,4}$ = 3.6, $J_{4,5}$ = 3 Hz, 1H, H-4), 3.74 (ddd, $J_{4,5}$ = 3, $J_{5,6}$ = 6, $J_{5,6'}$ = 6.8 Hz, 1H, H-5), 3.62 (dd, $J_{5,6}$ = 6, $J_{6,6'}$ = 11.6 Hz, 1H, H-6), 3.57 (dd, $J_{5,6'}$ = 6.8, $J_{6,6'}$ = 11.6 Hz, 1H, H-6′), 2.29 (t, *J* = 7.6 Hz, 2H, CH_2), 1.64–1.56 (m, 2H, CH_2), 1.43–1.32 (m, 2H, CH_2), 0.95 (t, *J* = 7.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 176.7, 84.4 (C-4), 82.2 (C-1), 78.5 (C-3), 77.4 (C-2), 73 (C-5), 64.3 (C-6), 37 (CH_2), 28.9 (CH_2), 23.5 (CH_2), 14.3 (CH_3). FT-ICR (ESI) calcd for $C_{11}H_{21}N_1O_6$ $[M+Na]^+$ 286.12611, found 286.12597.

3.8.8. *N*-(3-Methylbutanoyl)-α-D-galactofuranosylamide (7b)

The compound was purified by flash chromatography ($CHCl_3$/MeOH 80:20) yield = 57%. $[\alpha]_D^{25}$ +33.4 (*c* 1, MeOH). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 5.72 (d, $J_{1,2}$ = 4.4 Hz, 1H, H-1), 4.16 (t, $J_{2,3}$ = 3.2, $J_{3,4}$ = 3.6 Hz, 1H, H-3), 3.92 (dd, $J_{1,2}$ = 4.4, $J_{2,3}$ = 3.2 Hz, 1H, H-2), 3.84 (dd, $J_{3,4}$ = 3.6, $J_{4,5}$ = 3.2 Hz, 1H, H-4), 3.78 (ddd, $J_{4,5}$ = 3.2, $J_{5,6}$ = 5.6, $J_{5,6'}$ = 6.8 Hz, 1H, H-5), 3.65 (dd, $J_{5,6}$ = 5.6, $J_{6,6'}$ = 11.2 Hz, 1H, H-6), 3.61 (dd, $J_{5,6'}$ = 6.8, $J_{6,6'}$ = 11.2 Hz, 1H, H-6′), 2.18 (d, *J* = 6.4 Hz, 2H, CH_2), 2.16–2.08 (m, 1H, CH), 1.01 (d, *J* = 2.4 Hz, 3H, CH_3), 0.99 (d, *J* = 2.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 176, 85.6 (C-4), 84.5 (C-1), 82.2 (C-3), 77.4 (C-2), 73 (C-5), 64.3 (C-6), 46.5 (CH_2), 27.3 (CH), 22.9 (CH_3). FT-ICR (ESI) calcd for $C_{11}H_{21}N_1O_6$ $[M+Na]^+$ 286.12611, found 286.12591.

3.8.9. *N*-(3-Methyl-2-butenoyl)-α-D-galactofuranosylamide (7c)

The compound was purified by flash chromatography ($CHCl_3$–MeOH 85:15) yield = 51%. $[\alpha]_D^{25}$ +30.2 (*c* 0.8, MeOH). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 5.86 (s, 1H, CH), 5.77 (d, $J_{1,2}$ = 4 Hz, 1H, H-1), 4.17 (t, $J_{2,3}$ = 3.2, $J_{3,4}$ = 3.6 Hz, 1H, H-3), 3.94 (dd, $J_{1,2}$ = 4, $J_{2,3}$ = 3.2 Hz, 1H, H-2), 3.85 (br t, $J_{3,4}$ = 3.6, $J_{4,5}$ = 3.2 Hz, 1H, H-4), 3.79 (ddd, $J_{4,5}$ = 3.2, $J_{5,6}$ = 6, $J_{5,6'}$ = 6.8 Hz, 1H, H-5), 3.68 (dd, $J_{5,6}$ = 6, $J_{6,6'}$ = 11.2 Hz, 1H, H-6), 3.62 (dd, $J_{5,6'}$ = 6.8, $J_{6,6'}$ = 11.2 Hz, 1H, H-6′), 2.20 (s, 3H, CH_3), 1.94 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 169.5, 154.2, 119.4 (CH), 84.4 (C-4), 82.1 (C-1), 78.7 (C-3), 77.5 (C-2), 73.1 (C-5), 64.4 (C-6), 27.4 (CH_3), 20.3 (CH_3). FT-ICR (ESI) calcd for $C_{11}H_{21}N_1O_6$ $[M+Na]^+$ 284.11046; found 284.11044.

3.8.10. *N*-Palmitoyl-α-D-galactofuranosylamide (7d)

The compound was purified by flash chromatography ($CHCl_3$/MeOH 90:10) yield = 55%. $[\alpha]_D^{25}$ +9 (*c* 1, MeOH). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 5.74 (d, $J_{1,2}$ = 4 Hz, 1H, H-1), 4.18 (t, $J_{2,3}$ = 3.2, $J_{3,4}$ = 3.6 Hz, 1H, H-3), 3.94 (dd, $J_{1,2}$ = 4, $J_{2,3}$ = 3.2 Hz, 1H, H-2), 3.85 (br t, $J_{3,4}$ = 3.6, $J_{4,5}$ = 2.8 Hz, 1H, H-4), 3.79 (ddd, $J_{4,5}$ = 2.8, $J_{5,6}$ = 6, $J_{5,6'}$ = 6.8 Hz, 1H, H-5), 3.67 (dd, $J_{5,6}$ = 6, $J_{6,6'}$ = 11.2 Hz, 1H, H-6), 3.63 (dd, $J_{5,6'}$ = 6.8, $J_{6,6'}$ = 11.2 Hz, 1H, H-6′), 2.33 (t, *J* = 7.2 Hz, 2H, CH_2), 1.68 (br t, *J* = 7.2 Hz, 2H, CH_2), 1.44–1.28 (m, 24H), 0.96 (t, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 176.7, 84.4 (C-4), 82.2 (C-1), 78.5 (C-3), 77.4 (C-2), 73 (C-5), 64.4 (C-6), 37.3, 33.2, 30.9, 30.8, 30.6, 30.4, 26.8, 23.9, 14.6 (CH_3). FT-ICR (ESI) calcd for $C_{22}H_{43}N_1O_6$ $[M+Na]^+$ 440.29826, found 440.29797.

3.8.11. *N*-Capryloyl-α-D-galactofuranosylamide (7e)

The compound was purified by flash chromatography ($CHCl_3$–MeOH 85:15) yield = 63%. $[\alpha]_D^{25}$ +12.2 (*c* 1, MeOH). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 5.68 (d, $J_{1,2}$ = 4.4 Hz, 1H, H-1), 4.12 (t, $J_{2,3}$ = 3.6, $J_{3,4}$ = 3.2 Hz, 1H, H-3), 3.87 (dd, $J_{1,2}$ = 4.4, $J_{2,3}$ = 3.6 Hz, 1H, H-2), 3.79 (t, $J_{3,4}$ = 3.2, $J_{4,5}$ = 2.8 Hz, 1H, H-4), 3.73 (ddd, $J_{4,5}$ = 2.8, $J_{5,6}$ = 6, $J_{5,6'}$ = 6.8 Hz, 1H, H-5), 3.61 (dd, $J_{5,6}$ = 6,

$J_{6,6'}$ = 11.2 Hz, 1H, H-6), 3.57 (dd, $J_{5,6'}$ = 6.8, $J_{6,6'}$ = 11.2 Hz, 1H, H-6′), 2.27 (t, J = 7.2 Hz, 2H, CH_2), 1.62 (br t, J = 7.2 Hz, 2H, CH_2), 1.40–1.24 (m, 8H, 4 × CH_2), 0.91 (t, J = 6.4, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 176.7, 84.4 (C-4), 82.2 (C-1), 78.5 (C-3), 77.3 (C-2), 72.9 (C-5), 64.3 (C-6), 37.3 (CH_2), 33.0, 30.4, 30.3 (3 × CH_2), 26.8 (CH_2), 23.8 (1 × CH_2), 14.6 (CH_3). FT-ICR (ESI) calcd for $C_{14}H_{27}N_1O_6$ $[M+Na]^+$ 328.17306, found 328.17314.

3.8.12. *N*-Citronelloyl-α-D-galactofuranosylamide (7f)

The compound was purified by flash chromatography ($CHCl_3$–MeOH 90:10) yield = 56%. $[\alpha]_D^{25}$ +13.2 (*c* 1, MeOH). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 5.74 (d, $J_{1,2}$ = 4 Hz, 1H, H-1), 5.17 (t, J = 5.8 Hz, 1H, CH) 4.18 (t, $J_{2,3}$ = 3.4, $J_{3,4}$ = 3.6 Hz, 1H, H-3), 3.93 (dd, $J_{1,2}$ = 4, $J_{2,3}$ = 3.4 Hz, 1H, H-2), 3.85 (dd, $J_{3,4}$ = 3.6, $J_{4,5}$ = 3.2 Hz, 1H, H-4), 3.79 (ddd, $J_{4,5}$ = 3.2, $J_{5,6}$ = 5.6, $J_{5,6'}$ = 6.8 Hz, 1H, H-5), 3.68 (dd, $J_{5,6}$ = 5.6, $J_{6,6'}$ = 11.2 Hz, 1H, H-6), 3.63 (dd, $J_{5,6'}$ = 6.8, $J_{6,6'}$ = 11.2 Hz, 1H, H-6′), 2.34 (dd, J = 13.6, J = 6 Hz, 1H, Ha, CH_2), 2.18–1.98 (m, 4H), 1.73 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 1.48–1.40 (m, 1H), 1.33–1.22 (m, 1H), 0.95 (d, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 175.9, 132.4, 125.7 (CH), 84.5 (C-4), 82.3 (C-1), 78.5 (C-3), 77.4 (C-2), 73 (C-5), 64.4 (C-6), 44.9, 38.1, 31.7, 26.6, 26, 19.9, 17.9. FT-ICR (ESI) calcd for $C_{16}H_{29}N_1O_6$ $[M+Na]^+$ 354.18871, found 354.18864.

3.8.13. *N*-Benzoyl-α-D-galactofuranosylamide (7g)

The compound was purified by flash chromatography ($CHCl_3$/MeOH 85:15) yield = 62%. $[\alpha]_D^{25}$ +7.9 (*c* 1, MeOH). ^{1}H NMR (400 MHz, CD_3OD, 25 °C): δ = 7.91 (m, 2H, H_{ortho}), 7.60 (m, 1H, H_{para}), 7.53 (m, 2H, H_{meta}), 5.94 (d, $J_{1,2}$ = 4.8 Hz, 1H, H-1), 4.27 (t, $J_{2,3}$ = 4.2, $J_{3,4}$ = 4.4 Hz, 1H, H-3), 4.13 (t, $J_{1,2}$ = 4.8, $J_{2,3}$ = 4.2 Hz, 1H, H-2), 3.93 (dd, $J_{3,4}$ = 3.6, $J_{4,5}$ = 2.8 Hz, 1H, H-4), 3.84 (ddd, $J_{4,5}$ = 2.8, $J_{5,6}$ = 5.4, $J_{5,6'}$ = 6.8 Hz, 1H, H-5), 3.70 (dd, $J_{5,6}$ = 5.6, $J_{6,6'}$ = 11.2 Hz, 1H, H-6), 3.66 (dd, $J_{5,6'}$ = 6.8, $J_{6,6'}$ = 11.2 Hz, 1H, H-6′); ^{13}C NMR (100 MHz, CD_3OD, 25 °C): δ = 169.8, 135.4, 133.2, 129.8, 128.6, 84.5 (C-4), 82.7 (C-1), 78.2 (C-3), 77.9 (C-2), 72.7 (C-5), 64.4 (C-6). FT-ICR (ESI) calcd for $C_{13}H_{17}N_1O_6$ $[M+Na]^+$ 306.09481, found 306.09465.

3.8.14. 2,3,5,6-Tetra-*O*-acetyl-*N*-pentanoyl-α-D-galactofuranosylamide (8a)

Acetic anhydride (10 equiv) and a catalytic amount of *N,N*-dimethylaminopyridine were added, at room temperature, to a solution of **7a** (1 equiv) in pyridine dried on molecular sieves (0.1 M). The solution was stirred for 24 h and then was concentrated in vacuo. The residue was dissolved in EtOAc and washed with aqueous 5% HCl, aqueous 5% $NaHCO_3$ and water. The organic layer was dried over Na_2SO_4 and concentrated to give **8a** in quantitative yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.14 (d, $J_{NH,1}$ = 10 Hz, 1H, NH), 6.06 (d, $J_{1,2}$ = 4.4 Hz, $J_{NH,1}$ = 10, 1H, H-1), 5.34 (ddd, $J_{4,5}$ = 6.8, $J_{5,6}$ = 3.6, $J_{5,6'}$ = 6.8 Hz, 1H, H-5), 5.21 (dd, $J_{1,2}$ = 4.4, $J_{2,3}$ = 1.8 Hz, 1H, H-2), 5.07 (dd, $J_{2,3}$ = 1.8, $J_{3,4}$ = 3.2 Hz, 1H, H-3), 4.38 (dd, $J_{5,6}$ = 3.6, $J_{6,6'}$ = 12 Hz, 1H, H-6), 4.09 (dd, $J_{5,6'}$ = 6.8, $J_{6,6'}$ = 12 Hz, 1H, H-6′), 3.92 (dd, $J_{3,4}$ = 3.2, $J_{4,5}$ = 6.8 Hz, 1H, H-4), 2.23 (t, J = 7.6 Hz, 2H, CH_2), 2.18 (s, 3H, OAc), 2.12 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.61–1.56 (m, 2H, CH_2), 1.41–1.32 (m, 2H, CH_2), 0.92 (t, J = 7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 176.7, 173, 170.7, 169.8, 169.1, 79.9 (C-1), 79.7 (C-4), 76.7 (C-3), 75.1 (C-2), 70.3 (C-5), 62.9 (C-6), 36.7 (CH_2), 29.9 (CH_2), 22.5 (CH_2), 21.1–20.8 (4 × OAc), 14.3 (CH_3). NOESY (400 MHz, $CDCl_3$, 25 °C): contact between H-1/H-4.

Acknowledgments

This work was supported by Universita' degli Studi di Milano (PUR2008) and by Comune di Milano (Convenzione 55/2008). The HRMS spectra have been obtained from CIGA (Centro Interdipartimentale Grandi Apparecchiature, Universita' degli Studi di Milano).

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2010.12.020.

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