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# Toward Novel Glyconjugates: Efficient Synthesis of Glycosylated 4-Alkylidene-β-lactams

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*Dedicated to the memory of Prof. Gaspare Barone*

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A new class of glycoconjugated β-lactams was accessed by direct glycosidation of a suitable 4-alkylidene-azetidin-2-one acceptor with several perbenzylated (*N*-phenyl)trifluoroacetimidate donors activated by catalytic $Yb(OTf)_3$. Good stereocontrol was achieved by relying on the stereo directing effect of nitrile or ether solvents. Transfer hydrogenolysis under carefully controlled conditions enabled the removal of the benzyl group without affecting the β-lactam double bond. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

The β-lactam functionality plays a prominent role in organic chemistry because it is present in a variety of very important antibiotics such as penicillins and cephalosporins, and because recent observations have revealed the ability of some members of this class to act as inhibitors of prostate-specific antigens,[1] cholesterol absorption,[2] the human cytomegalovirus protease,[3] the human leukocyte elastase,[4] and even matrix-metallo proteases.[5] The ever-increasing bacterial resistance to β-lactam antibiotics represents a very serious concern, and active investigation is currently aimed at establishing the related chemical mechanisms.[6] In addition, the search for novel candidates with antibiotic activity remains another field of interest.

It is well known that glycoconjugation represents a frequent approach for improving the performance of bioactive molecules.[7] For instance, glycosidation can improve solubility in water and favourably alter pharmacodynamic properties. In the case of β-lactams, this concept may be further supported by recognizing that their antibiotic role is related to the inhibition of a transpeptidation reaction which involves, as substrates, linear oligosaccharides bearing lateral peptide chains.[6] Therefore the transpeptidase enzyme, namely the target of β-lactam antibiotics, should be able to accommodate saccharidic moieties in the course of the process. Moreover, very short peptidoglycan moieties were recently found to play an important role in activating catalysis for Penicillin-binding protein 2A from methicillin-resistant *Staphylococcus aureus* that is otherwise refractory to the action of available β-lactam antibiotics.[8]

A few reports describe the synthesis of β-lactams conjugated to carbohydrates, and in many cases the saccharidic moiety plays the role of chiral auxiliary for the stereocontrolled construction of the lactam ring.[9] Isolated examples focus on the biological properties of such conjugates; the attachment of glycolipids to a cephalosporin called cephalexine results in the enhancement of pharmacodynamic properties,[10] and the connection of oligosaccharides to β-lactams provides active compounds against *Helicobacter pylori*.[11]

Recently, some of us have reported an efficient and versatile approach for the synthesis of 4-alkylidene-β-lactams (4-alkylideneazetidin-2-ones), a class of derivatives featuring an increased electrophilic character of the carbonyl group resulting from the conjugation of the exocyclic double bond.[12] The promising reactivity towards serine proteases shown by some derivatives belonging to this class was actually demonstrated by the inhibition of leukocyte elastase and gelatinase.[5a]

The Lewis acid mediated reaction of 4-acetoxyazetidinones with α-diazo carbonyl groups represents the key step in the synthesis of 4-alkylidene-azetidinone precursors.[12] 4-Alkylidene-azetidin-2-one **4** can be obtained in excellent yield by the reaction of the *N*-trimethylsilyl derivative of commercially available (3*R*,4*R*)-4-acetoxy-3-[(1*R*)-1-(*tert*-butyldimethylsilyloxy)ethyl]azetidin-2-one (**1**) and ethyl diazoacetate in the presence of $TiCl_4$ (Scheme 1). The reaction proceeds smoothly to yield an 85:15 mixture of the *Z*

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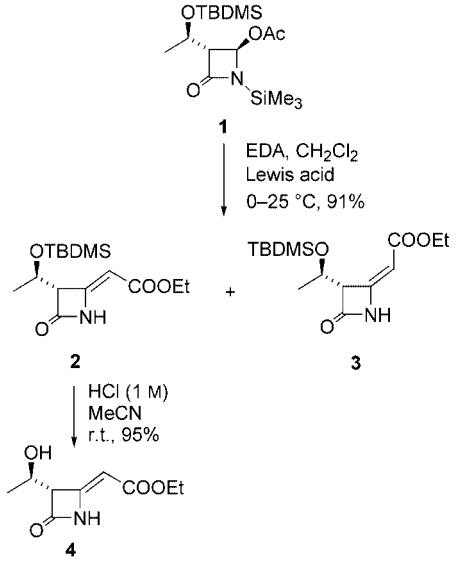
and *E* isomers **2** and **3**. Critical to the success of the reaction is a stoichiometric amount of $TiCl_4$ and an excess of the diazo compound associated with a requirement of trimethylsilyl protection for the β-lactam nitrogen atom. The diastereomeric products *E* and *Z* were easily separated by column chromatography, allowing access to stereochemically pure **2**. Treatment of **2** with HCl in acetonitrile produced the deprotected derivative **4**.




Scheme 1.

The presence of a free hydroxy group in compound **4** and the positive inhibitory effects associated with its functionalization[5] prompted us to explore an initial strategy for glycoconjugation based on a direct connection mediated by a glycosidic bond. The sensitivity of **4** toward both acidic and basic conditions posed some concerns in the choice of a suitable glycosidation approach and of the protecting groups to be installed on the saccharidic moiety, since the final deprotection step had to be compatible with the whole structure of the glycosylated β-lactam. As the extreme lability of **4** in mild basic conditions was known from preliminary tests, acyl protection for the saccharidic moiety was ruled out. On the other hand, the observed survival of the alkylidene-β-lactams under mild hydrogenation conditions drove our choice toward benzyl groups.[13]

As for the glycosidation approach, the choice was the catalytic activation of glycosyl (*N*-phenyl)trifluoroacetimidates[14] with $Yb(OTf)_3$, which proved tolerant of a wide range of functional groups[15] including extremely acid-labile ones.[16] The unviability of using acyl groups also led to the necessity of controlling the stereochemical outcome with a mechanism other than the neighbouring participation that typically operates when 2-*O*-acylated donors are used. In previous reports, the suitable choice of the solvent was shown to tune the anomeric selectivity of ytterbium(III) triflate promoted glycosidations with (*N*-phenyl)trifluoroacetimidates (nitrile solvents favour β-selectivity, whereas ether mixtures display α-selectivity).[15,17]

For this investigation (*N*-phenyl)trifluoroacetimidates **5**–**7** (Figure 1) of perbenzylated D-glucose, D-galactose and L-fucose were prepared as previously reported [treatment of the commercially available hemiacetals in anhydrous dichloromethane with (*N*-phenyl)trifluoroacetimidoyl chloride and sodium hydride as the base].[15,17] Under these conditions, all the donors were obtained with a large predominance of the β-anomer and were used in the ensuing glycosidation step as anomeric mixtures. In the first attempts, the syntheses of α-linked glycosides of glucose and galactose were investigated by taking advantage of the α-directing ability of dimethoxyethane/dioxane solvent mixtures.[17a] In both cases, the glycosidation produced the desired glycosides in high yield (70 and 90%, respectively) and satisfying stereocontrol (α/β ≈ 4:1 in both cases; see Table 1). The anomers could be separated by silica-gel chromatography and characterized by NMR spectroscopy, which also clearly indicated the integrity of the alkylidene-β-lactam skeleton. Glycoconjugation of compound **4** was also attempted through a α-L-fucosidation reaction which represents an important task in oligosaccharide synthesis because of the frequent occurence of α-L-fucosyl residues in important antigen sequences.[17b] In the present study, the reaction might have allowed access to glycosyl-conjugated products of reduced polarity. Owing to the high reactivity of fucosyl donors, this glycosidation with **7** could be conducted at low temperature. Consistently with previous findings,[17b,17c] a solvent mixture containing dioxane and diethyl ether led to the desired product in very good yield and α-selectivity (88%, α/β ≈ 7.5:1).

β-Selective glycosidations of **4** with the donors **5** and **6** were then attempted by catalytic activation with ytterbium(III) triflate in nitrile solvents. In both cases, the reactions proceeded in lower yields and selectivities than previously observed in the ether solvents (Table 1, Entries 2 and 4). Nevertheless, the obtained β-glycosides **8β** and **9β** were easily separated from the corresponding α-anomers by chromatography. It should be noted that acceptors bearing hydroxy groups adjacent to rigid cyclic structures appear to be glycosylated in lower yield and β-selectivity in reactions conducted in nitrile solvents.[15,18] The origin of such behaviour will be further explored.

α-Glycosides **8α**, **9α** and **10α** were deprotected by a transfer-hydrogenolysis reaction conducted in methanol/formic acid (9:1) under sonication.[19] Careful control of temperature was found to play a decisive role in obtaining the desired products **11α**–**13α** in high yields (>90%). It is worthy of note that the exocyclic double bond on the β-lactam skeleton appeared to be completely unaffected by this reaction.

In conclusion, the glycosylation of the sensitive β-lactam acceptor **4** has been performed taking advantage of the mild activation of (*N*-phenyl)trifluoroacetimidate donors with ytterbium(III) triflate. Satisfying yields were obtained in the synthesis of both α- and β-linked glycosides, the best results being registered in the former case. The hydrogenolytic deprotection of the saccharidic moieties can be accomplished without affecting the β-lactam moiety. Evaluation of these unprecedented derivatives for antibiotic activity against re-

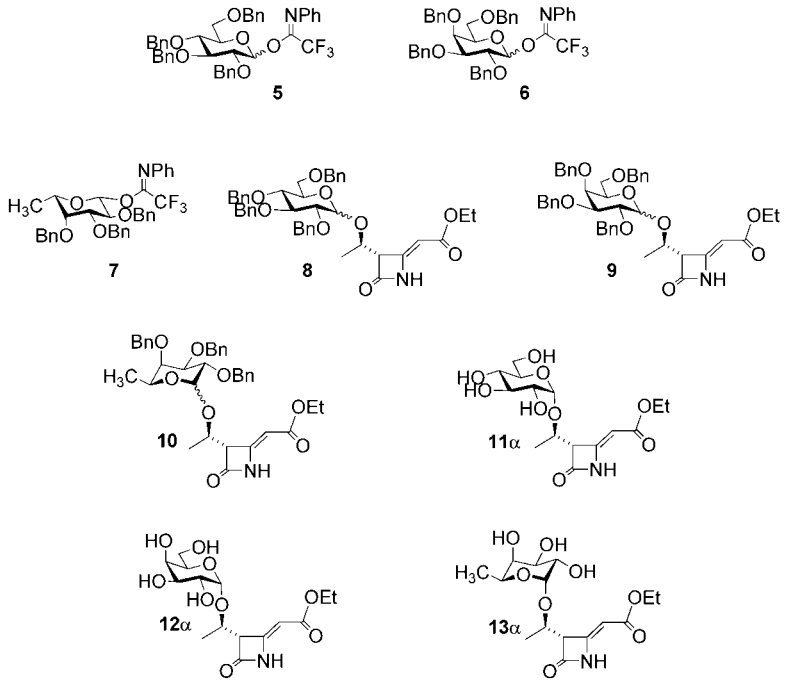



Figure 1. Reagents and products of the glycosidations.

Table 1. $Yb(OTf)_3$-promoted glycosidations of acceptor **4**.

| Entry[a] | Donor | Solvent | Temperature [°C] | Product | Yield [%] (α:β) |
|---|---|---|---|---|---|
| 1 | **5** | 1:1 DME/dioxane | 0 to r.t. | **8** | 70 (3.9:1) |
| 2 | **5** | $CH_3CN$ | –15 to r.t. | **8** | 73 (1:2.4) |
| 3 | **6** | 1:1 DME/dioxane | 0 to r.t. | **9** | 90 (4.3:1) |
| 4 | **6** | $CH_3CN$ | –15 to r.t. | **9** | 55 (1:1.4) |
| 5 | **7** | 4:1:1 dichloromethane/$Et_2O$/dioxane | –30 to r.t. | **10** | 88 (7.4:1) |

[a] General conditions for Entries 1–4: donor (1.3–1.5 equiv.), acceptor (1 equiv.), $Yb(OTf)_3$ (0.1 equiv., added as a solution in DME or $CH_3CN$), 4 Å acid-washed molecular sieves (AW MS). For Entry 5: donor (2.5 equiv.), acceptor (1 equiv.), $Yb(OTf)_3$ (0.05 equiv., added as a solution in dioxane).

sistant bacteria and for inhibitory activity against serine- and metallo-dependent enzymes is under investigation.

Furthermore, the approach described here discloses the possibility of using the 4-alkylidene-azetidinone moiety as a useful reactive scaffold to mediate the attachment of sugars to appropriate nucleophilic functionalities, thus providing a novel tethering approach in the active field of glycoconjugates.

## Experimental Section

**General:** $^1H$- and $^{13}C$ NMR spectra were recorded in $CDCl_3$ (internal standard $CHCl_3$ at $\delta$ = 7.26 ppm) or $D_2O$. The assignment of proton chemical shifts was based on decoupling experiments. Analytical thin layer chromatography (TLC) was performed on aluminium plates precoated with Silica Gel 60 $F_{254}$ as the adsorbent. Column chromatography was performed on Kieselgel 60 (63–200 mesh). Mass spectra were recorded in a reflection positive mode with a MALDI-TOF spectrometer. Acid-washed molecular sieves and ytterbium(III) triflate were dried by heating at 200 °C overnight under vacuum before their use in glycosidations.

**Starting Materials:** Compounds **2**, **3** and **4** were prepared according to ref.[12] (*N*-Phenyl)trifluoroacetimidates **5**, **6** and **7** were prepared from the corresponding commercially available hemiacetals as reported in refs.[15,17]

**General Procedure for Glycosidations:** A mixture of **4** (0.10 mmol) and the glycosyl donor (0.14 mmol) was dissolved in anhydrous 1,2-dimethoxyethane (0.75 mL) and dioxane (1 mL) under argon in the presence of freshly activated 4-Å acid-washed molecular sieves (AW 300 MS). A solution of $Yb(OTf)_3$ (6.2 mg, 0.01 mmol) in DME (0.25 mL) was then added at 0 °C. The mixture was gradually warmed to room temperature. After consumption of the donor (TLC analysis, generally ca 5 hours) a few drops of pyridine were added, and the mixture was filtered through a short plug of silica gel eluted with dichloromethane/methanol, 9:1. The residue was then purified on a short silica gel column eluted with toluene/ethyl acetate mixtures.

**8α:** (40 mg, yield 56%) $[\alpha]_D$ = +40.3 ($c$ = 1, $CH_2Cl_2$). $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 8.39 (br. s, 1 H, NH), 7.40–7.05 (aromatic protons), 5.55 (br. s, 1 H, –C=C*H*–$CO_2$Et), 4.96 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H Glc), 5.00–4.42 (4×AB, 8 H, 4×$CH_2$ benzyl protons), 4.13 (q, $J$ = 7.0 Hz, 2 H, –O*C*$H_2$$CH_3$), 4.00 [m, 1 H, $CH_3$–C*H*(OGlc)CH–], 3.96 (t, $J_{2,3}$ = $J_{3,4}$ = 9.8 Hz, 1 H, 3-H Glc), 3.88 (m, 1 H, 5-H Glc), 3.75 [br. d, $J$ = 7.0 Hz, 1 H, $CH_3$CH(OGlc)C*H*–], 3.75–3.55 (overlapping signals, 3 H, 4-H and $CH_2$-6 Glc), 3.51 (dd, 1 H, 2-H Glc), 1.42 [d, $J$ = 6.4 Hz, 3 H, C*H*$_3$CH(OGlc)CH–], 1.21 (t, $J$ = 7.2 Hz, 3 H, –O$CH_2$C*H*$_3$) ppm. $^{13}C$ NMR

(50 MHz, $CDCl_3$): $\delta$ = 167.3, 165.6, 152.3, 138.8, 138.3, 138.2, 138.0, 128.4–127.7, 98.7 (C-1, Glc), 91.4, 81.7, 79.5, 75.5, 75.1, 73.8, 73.5, 73.1, 70.9, 68.4, 62.6, 60.0, 17.0, 14.3 ppm. MALDI-TOF MS: for $C_{43}H_{47}NO_9$ (721.3) *m*/*z* = 744.4 $[M + Na]^+$.

**8β:** (37 mg, yield 51%) $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 8.45 (br. s, 1 H, NH), 7.40–7.05 (aromatic protons), 5.31 (br. s, 1 H, –C=CH–$CO_2$Et), 4.95–4.52 (4× AB, 8 H, 4× $CH_2$ benzyl protons), 4.47 (d, $J_{1,2}$ = 7.6 Hz, 1 H, 1-H Glc), 4.31 [quintuplet, $J$ = 6.2 Hz, 1 H, $CH_3CH$(OGlc)CH–], 4.20–4.05 (m, 2 H, –O$CH_2CH_3$), 3.87 [br. d, $J$ = 5.8 Hz, 1 H, $CH_3CH$(OGlc)C*H*–], 3.80–3.53 (overlapping signals, 4 H, 3-H, 4-H and $CH_2$-6 Glc), 3.50–3.38 (overlapping signals, 2 H, 2-H and 5-H Glc), 1.37 [d, $J$ = 6.4 Hz, 3 H, $CH_3$CH(OGlc)-CH–], 1.22 (t, $J$ = 7.2 Hz, 3 H, –O$CH_2CH_3$) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 167.2, 165.5, 152.5, 138.6, 138.4, 138.3, 138.1, 128.4–127.7, 100.6 (C-1, Glc), 90.7, 84.7, 81.9, 75.3, 75.1, 75.0, 73.5, 70.1, 69.0, 62.8, 60.1, 17.5, 14.2 ppm. MALDI-TOF MS: for $C_{43}H_{47}NO_9$ (721.3) *m*/*z* = 744.3 $[M + Na]^+$.

**9α:** (58 mg, yield 81%) $[\alpha]_D$ = +54.9 (*c* = 1, $CH_2Cl_2$). $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ = 8.37 (br. s, 1 H, NH), 7.40–7.20 (aromatic protons), 5.57 (br. s, 1 H, –C=C*H*–$CO_2$Et), 4.98 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H Glc), 4.95–4.36 (4× AB, 8 H, 4× $CH_2$ benzyl protons), 4.14 (q, $J$ = 7.2 Hz, 2 H, –O$CH_2CH_3$), 4.04–3.95 [overlapping signals, 4 H, 2-H, 4-H, 5-H Gal and $CH_3CH$(OGal)CH–], 3.75 [br. d, $J$ = 8.0 Hz, 1 H, $CH_3CH$(OGal)C*H*–], 3.56–3.42 (m, 2 H, $CH_2$-6 Gal), 1.41 [d, $J$ = 6.2 Hz, 3 H, $CH_3CH$(OGal)CH–], 1.23 (t, $J$ = 7.2 Hz, 3 H, –O$CH_2CH_3$) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 167.3, 165.6, 152.5, 138.6, 138.5, 137.9, 128.4–127.4, 99.2 (C-1, Gal), 91.3, 79.0, 75.6, 74.9, 74.7, 73.5, 73.4, 72.7, 69.9, 69.0, 62.7, 60.0, 20.2, 14.3 ppm. MALDI-TOF MS: for $C_{43}H_{47}NO_9$ (721.3) *m*/*z* = 744.4 $[M + Na]^+$.

**9β:** (23 mg, yield 32%) $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.41 (br. s, 1 H, NH), 7.40–7.20 (aromatic protons), 5.31 (br. s, 1 H, –C=CH–$CO_2$Et), 4.97–4.36 (4× AB, 8 H, 4× $CH_2$ benzyl protons), 4.42 (d, $J_{1,2}$ = 7.8 Hz, 1 H, 1-H Gal), 4.25 [quintuplet, $J$ = 6.4 Hz, 1 H, $CH_3CH$(OGal)CH–], 4.15–4.10 (m, 2 H, –O$CH_2CH_3$), 3.87–3.84 [overlapping signals, 2 H, 4-H Gal and $CH_3CH$(OGal)C*H*–], 3.78 (dd, $J_{2,3}$ = 9.6 Hz, 1 H, 2-H Gal), 3.60–3.48 (overlapping signals, 4 H, 3-H, 5-H and $CH_2$-6 Gal), 1.34 [d, $J$ = 7.2 Hz, 3 H, $CH_3CH$(OGal)CH–], 1.23 (t, $J$ = 7.2 Hz, 3 H, –O$CH_2CH_3$) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 167.2, 165.5, 152.4, 138.7, 138.6, 138.5, 138.0, 128.4–127.5, 101.2 (C-1 Gal), 90.8, 82.2, 79.3, 77.1, 75.2, 74.5, 73.7, 73.5, 73.1, 70.5, 68.9, 62.8, 60.0, 17.4, 14.3 ppm. MALDI-TOF MS: for $C_{43}H_{47}NO_9$ (721.3) *m*/*z* = 744.3 $[M + Na]^+$.

**10α:** (48 mg, yield 78%) $[\alpha]_D$ = –94.6 (*c* = 1, $CH_2Cl_2$). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 8.43 (br. s, 1 H, NH), 7.40–7.20 (aromatic protons), 5.21 (br. s, 1 H, –C=C*H*–$CO_2$Et), 4.95 (d, $J_{1,2}$ = 3.8 Hz, 1 H, 1-H Fuc), 5.00–4.59 (3× AB, 6 H, 3× $CH_2$ benzyl protons), 4.18 (q, $J$ = 7.2 Hz, 2 H, –O$CH_2CH_3$), 4.15–4.05 [overlapping signals, 2 H, 2-H Fuc and $CH_3CH$(OFuc)CH–], 3.93 (br. q, $J_{5,6}$ = 6.6 Hz, 1 H, 5-H Fuc), 3.90–3.85 [overlapping signals, 2 H, 3-H Fuc and $CH_3CH$(OFuc)C*H*–], 3.66 (br. d, $J_{3,4}$ = 2.4 Hz, 1 H, 4-H Fuc), 1.32 [d, $J$ = 6.2 Hz, 3 H, $CH_3CH$(OFuc)CH–], 1.29 (t, 3 H, –O$CH_2CH_3$), 1.10 (d, 3 H, $CH_3$-6 Fuc) ppm. $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$ = 167.0, 165.8, 152.6, 138.8, 138.6, 128.5–127.5, 94.8 (C-1, Fuc), 90.7, 78.9, 76.1, 74.8, 73.1, 72.9, 68.5, 67.0, 62.7, 60.1, 16.8, 16.6, 14.3 ppm. MALDI-TOF MS: for $C_{36}H_{41}NO_8$ (615.3) *m*/*z* = 638.3 $[M + Na]^+$.

**11α:** (13 mg, yield 92%) $[\alpha]_D$ = +49.6 (*c* = 1, $CH_3OH$).$^1H$ NMR (200 MHz, $D_2O$): $\delta$ = 5.40 (br. s, 1 H, –C=C*H*–$CO_2$Et), 5.04 (d, $J_{1,2}$ = 3.8 Hz, 1 H, 1-H Glc), 4.26 [m, 1 H, $CH_3CH$(OGlc)CH–], 4.21 (q, $J$ = 7.2 Hz, 2 H, –O$CH_2CH_3$), 4.07 [d, $J$ = 5.4 Hz, 1 H, $CH_3CH$(OGlc)C*H*–], 3.87–3.62 (overlapping signals, 4 H, 3-H, 5-H and $CH_2$-6 Glc), 3.49 (dd, $J_{2,3}$ = 10.0 Hz, 1 H, 2-H Glc), 3.37 (t, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, 1 H, 4-H Glc), 1.38 [d, $J$ = 6.4 Hz, 3 H, $CH_3CH$(OGlc)CH–], 1.27 (t, 3 H, –O$CH_2CH_3$) ppm. $^{13}C$ NMR (50 MHz, $D_2O$): $\delta$ = 167.7, 167.7, 150.4, 96.5 (C-1, Glc), 89.1, 70.6, 69.9, 69.6, 69.2, 67.4, 59.2, 59.0, 58.3, 16.2, 11.3 ppm. MALDI-TOF MS: for $C_{15}H_{23}NO_9$ (361.2) *m*/*z* = 384.3 $[M + Na]^+$.

**12α:** (15 mg, yield 94%) $[\alpha]_D$ +60.7 (*c* = 1, $CH_3OH$). $^1H$ NMR (200 MHz, $D_2O$): $\delta$ = 5.38 (br. s, 1 H, –C=C*H*–$CO_2$Et), 5.03 (d, $J_{1,2}$ = 3.2 Hz, 1 H, 1-H Glc), 4.23 [m, 1 H, $CH_3CH$(OGal)CH–], 4.17 (q, $J$ = 7.0 Hz, 2 H, –O$CH_2CH_3$), 4.12–3.90 [overlapping signals, 4 H, 3-H, 4-H, 5-H Gal and $CH_3CH$(OGal)C*H*–], 3.80–3.65 (overlapping signals, 3 H, 2-H and $CH_2$-6 Gal), 1.36 [d, $J$ = 6.4 Hz, 3 H, $CH_3CH$(OGlc)CH–], 1.24 (t, $J$ = 7.2 Hz, 3 H, –O$CH_2CH_3$) ppm. $^{13}C$ NMR (50 MHz, $D_2O$): $\delta$ = 168.0, 166.3, 150.5, 96.9 (C-1, Gal), 89.2, 69.5, 69.0, 67.1, 66.2, 59.4, 59.1, 16.2, 13.4 ppm. MALDI-TOF MS: for $C_{15}H_{23}NO_9$ (361.2) *m*/*z* = 384.2 $[M + Na]^+$.

**13α:** (15 mg, yield 91%) $^1H$ NMR (500 MHz, $D_2O$): $\delta$ = 5.38 (s, 1 H, –C=CH–$CO_2$Et), 5.02 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1-H Fuc), 4.25 (q, $J$ = 7.0 Hz, 2 H, –O$CH_2CH_3$), 4.12 [d, $J$ = 7.0 Hz, 1 H, $CH_3CH$(O-Fuc)C*H*–], 4.05 (br. d, $J_{5,6}$ = 6.5 Hz, 1 H, 5-H Fuc), 3.85–3.75 (overlapping signals, 3 H, 2-H, 3-H and 4-H Fuc), 1.35 [d, $J$ = 6.0 Hz, 3 H, $CH_3CH$(OFuc)CH–], 1.31 (t, 3 H, –O$CH_2CH_3$), 1.21 (3 H, $CH_3$-6 Fuc) ppm. $^{13}C$ NMR (50 MHz, $D_2O$): $\delta$ = 168.4, 166.2, 150.4, 94.1 (C-1, Fuc), 90.7, 89.2, 69.7, 68.7, 67.4, 66.8, 65.6, 65.0, 59.7, 59.1, 14.0, 13.1, 11.4 ppm. MALDI-TOF MS: for $C_{15}H_{23}NO_8$ (345.1) *m*/*z* = 368.2 $[M + Na]^+$.

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