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Practical Gram-Scale Synthesis of Either α- or β-Anomer of *C*-Vinyl Glycosides

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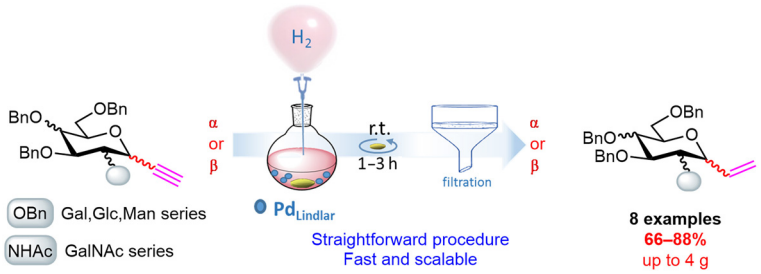

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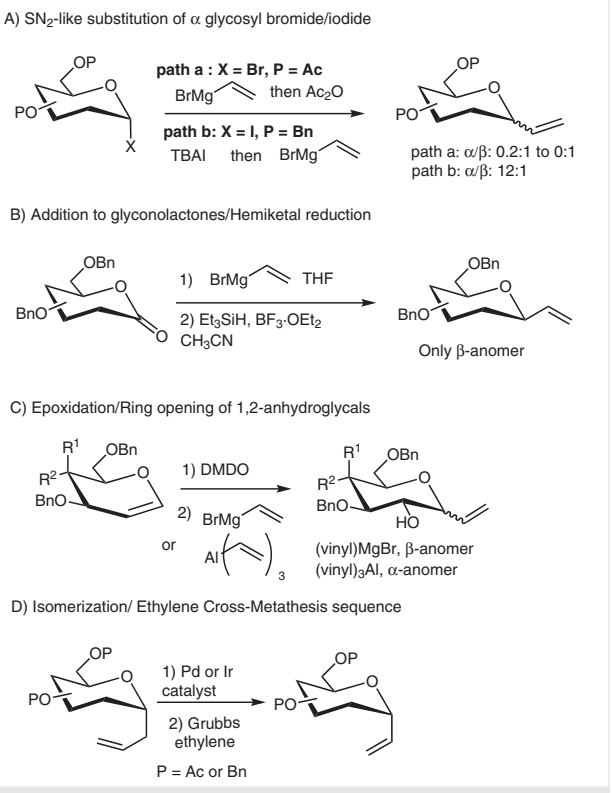
Abstract The synthesis *C*-vinyl glycosides, useful intermediates for the synthesis of *C*-glycoconjugates, was carried out on gram-scale by controlled reduction of the corresponding ethynyl derivatives in good to excellent yields in different carbohydrate series.

Key words *C*-glycosides, controlled reduction, alkynes, gram-scale

C-Glycosidic analogues of natural products have attracted much attention because they can act as stable mimics of their *O*-glycosidic congeners since they are inert towards in vivo enzymatic hydrolysis. Moreover, in some cases, biological activities of *C*-glycosidic analogues can even be improved.[1] In this context, numerous research groups have extensively investigated efficient diastereoselective syntheses of *C*-glycoside building blocks.

One of the most convergent and powerful synthetic strategies to prepare the targeted *C*-glycoconjugates implies metathesis reaction of fully protected *C*-vinyl glycosides as key intermediates.[2] Synthesis of the latter have been implemented through different methods. The first reported one consisting in addition of vinylmagnesium bromide to peracetylated-α-D-glucopyranosyl bromide afforded the expected *C*-vinyl glucoside in only poor yield[3] and often as an inseparable mixture of both anomers[3d] (Scheme 1A, path a). Moreover, following this strategy, a subsequent acetylation step with acetic anhydride was required to offset deprotection due to the excess of Grignard reagent. Later, in the course of the synthesis of *C*-glycoside analogue of Bb-GL2, Gervay-Hague et al. have described the stereoselective preparation of α-*C*-vinyl galactoside by treatment of β-galactosyl iodide (obtained by in situ anomerization of the corresponding α-iodide) with vinylmagnesium bromide in 79% yield on a gram-scale (Scheme 1A, path b).[2b] A two-step strategy from 2,3,4,6-tetra-*O*-benzylglyconolactone has also been described by addition of vinylmagnesium bromide followed by reduction of the hemiketal intermediate (Scheme 1B).[2c,4] By this approach, only β-anomer was formed in moderate yield whatever the series. Synthesis of *C*-vinyl glycoside has also been described from glycal



Scheme 1 Main strategies to access *C*-vinyl glycosides

through epoxidation followed by ring opening of 1,2-anhydro intermediate with vinylaluminum or -magnesium reagents (Scheme 1C).

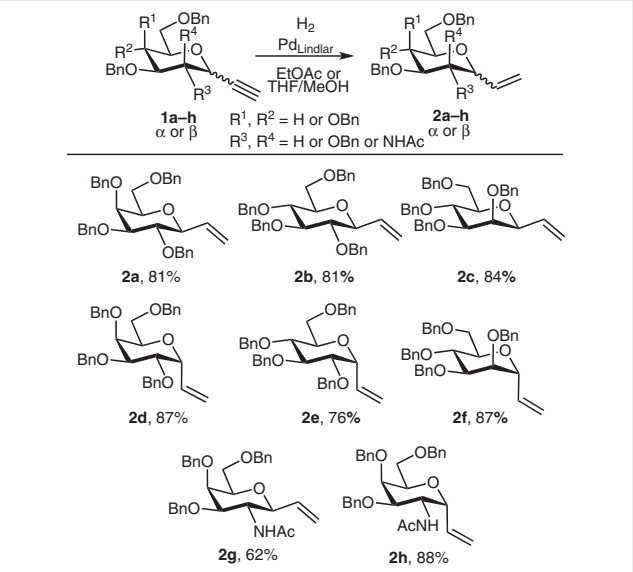
The nature of the organometallic species allowed to isolate selectively either the α-anomer[5] or the β one.[6] Isomerization/ethylene cross-metathesis sequence has been reported from *C*-allyl glycosides to access the corresponding vinylic derivatives (Scheme 1D).[2a,7] Main advantage of the latter methodology is that either the isomerization step[8] or the two-step sequence[7] could be performed on carbohydrates with a great variety of protecting groups. In addition to these main strategies (Scheme 1), the stereoselective palladium-catalyzed π-allyl cycloetherification[9] leading to either α- or β-anomer or the controlled reduction of the α-*C*-alkynyl galactoside[2a] could also be mentioned.

As part of our ongoing program on the preparation of new *C*-galactoside analogues with biological interest, our strategy required the preparation on large scale of either α- or β-anomer of *C*-vinyl galactosides as key intermediates. Herein, we describe a practical gram-scale general synthesis of either α- or β-anomer of *C*-vinyl glycosides in different series.

Initially, we attempted to prepare selectively α- or β-*C*-vinyl glycosides in two steps from glycal as described in Scheme 1C. In our hands, whatever the series, ring opening of 1,2-anhydro sugar intermediates with vinyl organomagnesium reagent afforded only α-anomers in poor yields (23% and 21% in galactose and glucose series, respectively). When the reaction was performed with the vinyl organoalane reagent, α-anomer was also isolated in galactose series in only 40% yield. We then focused our attention on the isomerization/ethylene cross-metathesis sequence in galactose series (Scheme 1D), but the isomerization step remained incomplete whatever the nature of catalyst used resulting in an inseparable mixture of the expected compound and starting material.

The controlled reduction of *C*-glycopyranosyl alkyne appeared to be an interesting pathway since Dondoni have reported the synthesis of either α- or β-anomer of alkynyl derivatives on a large scale.[10] Using Franck's procedure[2a] for the reduction of β-*C*-ethynyl galactoside **1a** in the presence of 66% wt/wt Lindlar palladium charge (Scheme 2), the reaction was complete in 30 minutes but a 1:1 mixture of the expected compound and the over-reduced one was obtained.

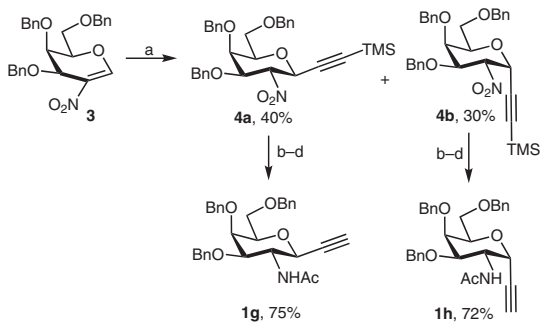
By reducing the catalyst charge to 20% wt/wt and after 45 minutes of reaction, the β-*C*-vinyl galactoside **2a**[4b] was formed as the sole product of the reaction and was isolated in 81% yield. These conditions appeared reproducible in yield up to one gram (Scheme 2). Similarly, our optimized conditions were successfully applied for the controlled reduction of β-*C*-alkynyl derivatives **1b** and **1c** to yield, after purification, the corresponding *C*-vinyl glycoside **2b**[2c] and **2c** in excellent 81 and 84% yield, respectively (Scheme 2). The reduction of the alkynes in α-series was achieved in 1



Scheme 2 Controlled reduction of *C*-ethynyl glycoside **1**

hour reaction time giving rise to the corresponding *C*-vinyl glycoside **2d**[2a,b] to **2f** in a range of 76–87% yield (Scheme 2). It is noteworthy that, with these α-anomers, the TLC monitoring of the reaction remained difficult as the products and the starting materials display the same R_f-value. However, this rugged reaction was successfully implemented on a 4 grams scale on alkyne **1d**.

In view of extending the scope of this reaction, the optimized conditions were applied to *N*-acetylglycosylamine series. The α- or β-anomers of vinyl 2-acetamido-2-deoxy-*C*-galactosides **2g** and **2h** were obtained from the corresponding alkyne, which were prepared in four steps from 3,4,6-tri-*O*-benzyl-2-nitro-D-galactal (**3**) (Scheme 3).



Scheme 3 Preparation of galactosylamine-derived alkynes **1g** and **1h**. *Reagents and conditions*: (a) Lithium TMS-acetylide, THF, –78 °C, 1 h; (b) Zn, concd HCl, AcOH, THF, H_2O, 0 °C, 2 h; (c) Ac_2O, Et_3N, DMAP (5 mol%), CH_2Cl_2, r.t., 1.5 h; (d) aq 1 N NaOH, CH_2Cl_2, MeOH, r.t., 2 h.

In a first attempt, the addition of vinylmagnesium bromide to nitrogalactal **3** was performed leading to an inseparable mixture of the two expected *C*-vinyl-2-nitrogalacto-

sides along with a third product.[11] Then, following a reported procedure in glucose series,[12] the nitrogalactal **3** was treated with lithium trimethylsilylacetylide at –78°C in THF leading to a separable mixture of β-anomer **4a** in 40% yield and α-anomer **4b** in 30% yield. The two anomers were clearly identified from the ^{1}H NMR spectrum of **4a**, which presented a doublet at 4.45 ppm (anomeric proton) with a coupling constant of 10.0 Hz, characteristic of β-anomer configuration. For the compound **4b**, the presence of a doublet at 5.22 ppm with a coupling constant of 5.8 Hz was representative of the anomeric proton of α-anomer. Then, the same three-step sequence (reduction of nitro function, acetylation, and cleavage of silicon–carbon bond) was applied on both anomers leading to the galactosylamine-derived alkynes **1g** and **1h** in 75 and 72% yield, respectively (Scheme 3). Although these two anomers have already been isolated following another strategy,[10] the preparation of these two alkynes **1g** and **1h** from one single starting material, that is, 3,4,6-tri-*O*-benzyl-2-nitro-D-galactal **3**, was highly relevant.

Controlled reduction was then performed on alkyne **1g** under optimized conditions, but the reaction was incomplete even after 6 hours resulting in an inseparable mixture of starting material and expected compound in a 3:7 ratio estimated by ^{1}H NMR analysis. This outcome seemed to be due to the low solubility of alkynes **1g** and **1h** in ethyl acetate. This solvent was then replaced by a methanol/tetrahydrofuran (1:1) mixture allowing a complete reaction after 3 hours. In these conditions, the *C*-vinyl glycosides **2g** and **2h** were isolated in 62 and 88% yield, respectively.

In summary, we have explored the controlled reduction of *C*-ethynyl glycosides to access the corresponding *C*-vinyl glycosides, which are highly valuable building blocks for the synthesis of *C*-glycoconjugates. The *C*-vinyl glycosides were isolated in different series in good to excellent yields on a scale up to 4 grams. In addition, the reaction was also implemented to prepare *C*-vinyl-*N*-acetylgalactosamine derivatives.

All experiments were carried out under argon with anhydrous solvents in dried glassware. THF was dried over activated alumina on a dry station purchased from Innovative Technologies. Commercially available materials were used without further purification. Alkynes **1a–f** were prepared according to reported procedures.[10] The preparation of compounds **1g**,**h** is described in the Supporting Information. Lindlar catalyst was purchased from Sigma-Aldrich. Flash chromatography was performed on silica gel (40–63 μm from Macherey-Nagel) using Reveleris X² Grace apparatus. Analytical TLCs were carried out on pre-coated silica gel 60 F254 from Macherey-Nagel. Optical rotations were measured using a Jasco P2000 at the sodium D line (λ = 589 nm) with a 1 dm path length cell at 25 °C. Melting points were measured using Büchi B-545 apparatus. NMR spectra were recorded on a Bruker Avance 400 spectrometer. Chemical shifts are reported in ppm from TMS as the internal standard for the ^{1}H NMR spectrum and from the residual peaks of the solvent ($CDCl_3$) for ^{13}C NMR spectrum. Structural assignments of the isolated compounds were based on ^{1}H, ^{13}C, COSY and HSQC NMR experiments. High-resolution mass spectroscopy was performed with a Bruker microTOF QIII mass spectrometer using ESI techniques.

C-Vinyl Glycosides 2; General Procedure

To a solution of alkyne **1** in EtOAc (0.03 M, **1a–f**)) or THF/MeOH (1:1, 0.1 M, **1g**, **h**)) was added the Lindlar catalyst (20% wt/wt). The reaction mixture was degassed with argon, saturated with H_2, and stirred at r.t. under a H_2 atmosphere (1 atm). Reaction time was determined by a follow-up performed on TLC indicating the clean reduction of carbohydrate-derived acetylene to a slightly less polar product (only for **1a–c**). Reaction time was also 1 h for derivatives **1d–f** or 3 h for **1g** and **1h**. (***CAUTION***: Reaction time could depend on the quality of the commercial Lindlar catalyst batch). The reaction mixture was filtered through a short pad of Celite and concentrated. The residue was then purified by column chromatography on silica gel to furnish the pure compound.

2,3,4,6-Tetra-*O*-benzyl-1-deoxy-β-D-galactopyranosylethene (2a)[4b]

Yield: 628 mg (81%); white solid; mp 50.9–53.8 °C; R_f = 0.30 (cyclohexane/EtOAc 9:1); $[\alpha]_D^{25}$ +11.4 (*c* 1.0, $CHCl_3$) [Lit.[4b] +19.2 (*c* 1.3, $CHCl_3$)].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.23 (m, 20 H, H-Bn), 6.01–5.93 (m, 1 H, H-1), 5.42 (dd, *J* = 17.2, 1.2 Hz, 1 H, H-2a), 5.26 (dd, *J* = 10.5, 1.5 Hz, 1 H, H-2b), 4.96 and 4.62 (AB syst., *J* = 11.6 Hz, 2 H, CH_2Ph), 4.83 and 4.64 (AB syst., *J* = 10.5 Hz, 2 H, CH_2Ph), 4.75 and 4.71 (AB syst., *J* = 11.8 Hz, 2 H, CH_2Ph), 4.47 and 4.42 (AB syst., *J* = 11.9 Hz, 2 H, CH_2Ph), 3.98 (d, *J* = 2.7 Hz, 1 H, H-4′), 3.74–3.73 (m, 2 H, H-1′, H-3′), 3.62–3.65 (m, 4 H, H-2′, H-5′, H-6′).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.8 (quat-C), 138.4 (quat-C), 138.3 (quat-C), 137.9 (quat-C), 135.4 (C-1), 128.4 (CH), 128.3 (2 × CH), 128.2 (CH), 127.9 (CH), 127.8 (CH), 127.7 (2 × CH), 127.6 (2 × CH), 127.5 (2 × CH), 118.2 (C-2), 84.4 (C-2′), 80.7 (C-3′), 79.0 (C-1′), 76.9 (C-5′), 75.3 (CH_2), 74.6 (CH_2), 74.0 (C-4′), 73.6 (CH_2), 72.6 (CH_2), 68.9 (C-6′).

2,3,4,6-Tetra-*O*-benzyl-1-deoxy-β-D-glucopyranosylethene (2b)[2c]

Yield: 624 mg (81%); white solid; mp 74.0–77.1 °C; R_f = 0.34 (cyclohexane/EtOAc 9:1); $[\alpha]_D^{20}$ +21.9 (*c* 0.24, $CHCl_3$) {Lit.[2c] mp 68–69 °C, $[\alpha]_D^{20}$ +28.0 (*c* 0.2, $CHCl_3$), Lit.[4b] mp 72–73 °C}. Analytical data were in accordance with those reported.

2,3,4,6-Tetra-*O*-benzyl-1-deoxy-β-D-mannopyranosylethene (2c)

Yield: 588 mg (84%); white solid; mp 54.2–55.8 °C; R_f = 0.27 (cyclohexane/EtOAc 9:1); $[\alpha]_D^{25}$ –12.3 (*c* 0.99, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.22 (m, 18 H, H-Bn), 7.19–7.17 (m, 2 H, H-Bn), 5.97–5.88 (m, 1 H, H-1), 5.35–5.31 (m, 1 H, H-2a), 5.19–5.16 (m, 1 H, H-2b), 4.92–4.87 (m, 2 H, CH_2Ph), 4.74–4.64 (m, 4 H, CH_2Ph), 4.59–4.54 (m, 2 H, CH_2Ph), 3.95 (t, *J* = 9.5 Hz, 1 H, H-4′), 3.85–3.83 (m, 1 H, H-1′), 3.82–3.79 (m, 1 H, H-2′), 3.78–3.75 (m, 2 H, H-6′), 3.64 (dd, *J* = 9.4, 2.8 Hz, 1 H, H-3′), 3.52–3.48 (m, 1 H, H-5′).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.6 (quat-C), 138.5 (quat-C), 138.4 (2 quat-C), 135.6 (C-1), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 128.0 (CH), 127.9 (CH), 127.6 (CH), 127.6 (CH), 127.5 (CH), 127.4 (2 × CH), 116.7 (C-2), 84.7 (C-3′), 79.6 (C-5′), 79.4 (C-1′), 76.7 (C-2′), 75.2 (CH_2), 75.1 (C-4′), 74.4 (CH_2), 73.5 (CH_2), 72.2 (CH_2), 69.7 (C-6′).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{36}H_{39}O_5$: 551.2792; found: 551.2799.

2,3,4,6-Tetra-*O*-benzyl-1-deoxy-α-D-galactopyranosylethene (2d)[2a,b]

Yield: 3.4 g (85%); colorless oil; R_f = 0.36 (cyclohexane/EtOAc 9:1); $[\alpha]_D^{25}$ + 60.1 (*c* 1.2, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.24 (m, 20 H, H-Bn), 6.11–6.03 (m, 1 H, H-1), 5.42 (dt, *J* = 17.5, 1.8 Hz, 1 H, H-2a), 5.32 (dt, *J* = 10.8, 1.9 Hz, 1 H, H-2b), 4.84 and 4.58 (AB syst., *J* = 11.6 Hz, 2 H, CH_2Ph), 4.71–4.55 (m, 5 H, H-1′, CH_2Ph), 4.50 and 4.43 (AB syst., *J* = 11.9 Hz, 2 H, CH_2Ph), 4.08–4.04 (m, 1 H, H-2′), 4.03–3.99 (m, 1 H, H-5′), 3.95 (t, *J* = 2.6 Hz, 1 H, H-4′), 3.70–3.56 (m, 3 H, H-3′, H-6′).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.7 (quat C), 138.6 (quat C), 138.4 (quat C), 138.2 (quat C), 132.5 (C-1), 128.3 (3 × CH), 128.2 (CH), 128.1 (CH), 127.8 (CH), 127.7 (CH), 127.6 (CH), 127.6 (CH), 127.5 (CH), 127.5 (CH), 127.4 (CH), 118.1 (C-2), 78.9 (C-3′), 76.8 (C-2′), 75.0 (C-4′), 74.0 (CH_2), 73.3 (C-1′ or CH_2), 73.2 (C-1′ or CH_2), 72.9 (CH_2), 71.8 (C-5′), 68.5 (C-6′).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{36}H_{39}O_5$: 551.2792; found: 551.2792 .

2,3,4,6-Tetra-*O*-benzyl-1-deoxy-α-D-glucopyranosylethene (2e)

Yield: 389 mg (84%); colorless oil; R_f = 0.36 (cyclohexane/EtOAc 9:1); $[\alpha]_D^{25}$ + 58.9 (*c* 0.97, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.24 (m, 18 H, H-Bn), 7.13–7.11 (m, 2 H, H-Bn), 6.19–6.11 (m, 1 H, H-1), 5.49–5.41 (m, 2 H, H-2), 4.94 and 4.78 (AB syst., *J* = 10.9 Hz, 2 H, CH_2Ph), 4.81 and 4.61 (AB syst., *J* = 11.5 Hz, 2 H, CH_2Ph), 4.69 and 4.64 (AB syst., *J* = 11.6 Hz, 2 H, CH_2Ph), 4.63–4.56 (m, 1 H, H-1′), 4.51–4.45 (m, 2 H, CH_2Ph), 3.80–3.60 (m, 6 H, H-2′, H-3′, H-4′, H-5′, H-6′).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.7 (quat-C), 138.2 (quat-C), 138.1 (quat-C), 138.0 (quat-C), 131.9 (C-1), 128.4 (CH), 128.3 (3 × CH), 127.9 (3 × CH), 127.8 (2 × CH), 127.7 (CH), 127.6 (2 × CH), 119.8 (C-2), 82.8 (C-2′ or C-3′ or C-4′), 80.0 (C-2′ or C-3′ or C-4′), 78.3 (C-2′ or C-3′ or C-4′), 75.5 (CH_2), 75.1 (CH_2), 74.1 (C-1′), 73.5 (CH_2), 72.9 (CH_2), 72.0 (C-5′), 69.0 (C-6′).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{36}H_{39}O_5$: 551.2792; found: 551.2790.

2,3,4,6-Tetra-*O*-benzyl-1-deoxy-α-D-mannopyranosylethene (2f)

Yield: 728 mg (87%); colorless oil; R_f = 0.27 (cyclohexane/EtOAc 9:1); $[\alpha]_D^{25}$ + 26.5 (*c* 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.16 (m, 20 H, H-Bn), 5.84–5.76 (m, 1 H, H-1), 5.28–5.18 (m, 2 H, H-2), 4.77 and 4.50 (AB syst., *J* = 11.0 Hz, 2 H, CH_2Ph), 4.71 and 4.64 (AB syst., *J* = 12.4 Hz, 2 H, CH_2Ph), 4.61–4.53 (m, 5 H, 2 × CH_2Ph, H-1′), 3.93 (t, *J* = 7.9 Hz, 1 H, H-4′), 3.85–3.81 (m, 1 H, H-5′), 3.75–3.70 (m, 4 H, H-2′, H-3′, H-6′).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.4 (quat-C), 138.3 (quat-C), 138.2 (2 quat-C), 134.3 (C-1), 128.3 (3 × CH), 128.2 (CH), 127.9 (CH), 127.8 (2 × CH), 127.7 (CH), 127.6 (2 × CH), 127.5 (CH), 127.4 (CH), 117.8 (C-2), 78.5 (C-3′), 76.1 (C-2′), 75.1 (C-4′), 74.4 (CH_2), 74.0 (CH_2), 73.9 (C-5′), 73.3 (CH_2), 72.1 (C-1′), 71.7 (CH_2), 69.4 (C-6′).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{36}H_{38}O_5Na$: 573.2611; found: 573.2628.

2-Acetamido-3,4,6-tri-*O*-benzyl-1,2-dideoxy-β-D-galactopyranosylethene (2g)

Yield: 620 mg (62%); white solid; mp 184.9–186.0 °C; R_f = 0.22 (cyclohexane/EtOAc 5:5); $[\alpha]_D^{25}$ +34.1 (*c* 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ =7.36–7.24 (m, 15 H, H-Bn), 5.88–5.79 (m, 1 H, H-1), 5.31–5.16 (m, 3 H, H-2 and NH), 4.90 and 4.61 (AB syst., *J* = 11.6 Hz, 2 H, CH_2Ph), 4.68 and 4.44 (AB syst., *J* = 11.9 Hz, 2 H, CH_2Ph), 4.47 and 4.43 (AB syst., *J* = 11.8 Hz, 2 H, CH_2Ph), 4.02–3.97 (m, 2 H, H-3′, H-4′), 3.93–3.82 (m, 2 H, H-1′, H-2′), 3.65–3.62 (m, 1 H, H-5′), 3.59–3.58 (m, 2 H, H-6′), 1.85 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ =170.2 (C=O), 138.6 (quat-C), 138.1 (quat-C), 137.9 (quat-C), 135.2 (C-1), 128.5 (CH), 128.4 (CH), 128.2 (2 × CH), 128.0 (2 × CH), 127.9 (CH), 127.8 (CH), 127.5 (CH), 118.7 (C-2), 79.9 (C-4′), 79.4, (C-1′), 76.8 (C-5′), 74.5 (CH_2), 73.5 (CH_2), 72.6 (C-3′), 71.5 (CH_2), 68.7 (C-6′), 52.8 (C-2′), 23.6 (CH_3).

HRMS ESI): *m*/*z* [M + H]$^+$ Calcd for $C_{31}H_{36}NO_5$: 502.2588 ; found: 502.2589.

2-Acetamido-3,4,6-tri-*O*-benzyl-1,2-dideoxy-α-D-galactopyranosylethene (2h)

Yield: 772 mg (88%); white solid; mp 137.5–139.2 °C; R_f = 0.25 (cyclohexane/EtOAc 1:1); $[\alpha]_D^{25}$ +54.1 (*c* 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.27 (m, 15 H, H-Bn), 5.68 (ddd, *J* = 17.3, 10.8, 4.2 Hz, 1 H, H-1), 5.45 (d, *J* = 7.0 Hz, 1 H, NH), 5.35 (ddd, ^3J = 17.3, ^2J = 1.8, ^4J = 1.8 Hz, 1 H, H-2), 5.23 (ddd, ^3J = 10.8, ^2J = 1.8, ^4J = 1.8 Hz, 1 H, H-2), 4.73 and 4.60 (AB syst., *J* = 11.9 Hz, 2 H, CH_2Ph), 4.65–4.61 (m, 1 H, H-1′), 4.58–4.48 (AB syst., *J* = 11.9 Hz, 2 H, CH_2Ph), 4.57 and 4.53 (AB syst., *J* = 12.3 Hz, 2 H, CH_2Ph), 4.29–4.25 (m, 1 H, H-5′), 4.21–4.18 (m, 1 H, H-2′), 4.08–4.04 (m, 1 H, H-6′), 3.90–3.86 (m, 1 H, H-3′), 3.88–3.87 (m, 2 H, H-4′, H-6′), 1.91 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ =169.9 (C=O), 138.4 (quat-C), 138.2 (quat-C), 137.9 (quat-C), 133.6 (C-1), 128.3 (4 × CH), 127.7 (CH), 127.6 (3 × CH), 127.5 (CH), 117.4 (C-2), 74.7 (C-5′), 74.5 (C-3′), 73.1 (CH_2), 72.5 (CH_2), 71.5 (C-4′), 67.6 (C-1′), 65,9 (C-6′), 50.6 (C-2′), 23.2 (CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ Calcd for $C_{31}H_{36}NO_5$: 502.2588 ; found: 502.2594.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611800.

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