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A substrate controlled, very highly diastereoselective Morita–Baylis–Hillman reaction: a remote activation of the diastereofacial selectivity in the synthesis of C-3-branched deoxysugars☆

Ram Sagar, Chandra Shekhar Pant, Rashmi Pathak and Arun K. Shaw*

Division of Medicinal and Process Chemistry, Central Drug Research Institute (CDRI), Lucknow 226001, India

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Abstract—The Morita–Baylis–Hillman (MBH) reaction of *p*-nitrobenzaldehyde with C (6) acyl protected enuloside **1** in the presence of $TiCl_4$/TBAI yielded highly diastereoenriched C-3-branched deoxysugar derivative or MBH adduct **1′a** in high yield, while reactions of unprotected enuloside **2a** and C (6) alkyl protected enulosides **2d–e** with *p*-nitrobenzaldehyde under the same conditions afforded the adducts **2′a** and **2′d–e**, respectively, in low yield with moderate selectivity. Several representative aromatic and aliphatic aldehydes were selected to undergo MBH reaction with **1** to give their respective adducts in very good yield with a very high diastereoselectivity. A plausible mechanism based on the assumption of a Zimmerman–Traxler-type transition state was proposed to explain the excellent selectivity observed with adducts derived from **1**. The synthetic application of these adducts were shown by their stereoselective reduction to corresponding *threo* isomers in very good yield.

1. Introduction

Deoxysugars with a branched carbon skeleton occur abundantly in nature and have been found in many antibiotics. The appendage at the branching carbon can be various side chains besides methyl, formyl, hydroxymethyl, 1-hydroxyethyl, acetyl, 2-hydroxyacetyl, 1,3-dimethylpropyl and other side chains.[1,2] There are number of antibiotics that contain C-branched sugars as the glycosidic components[3] and they have been characterized from various natural products.[4] In synthetic organic chemistry C-branched sugars have been identified as useful chiral synthons for the total synthesis of natural products.[2b,3a] Their use has also been explored in the synthesis of non-carbohydrate compounds[5] and carbohydrate mimetics.[3a,c] Some of the most useful methods for the synthesis of C-branched sugars involving the formation of new C–C bond at the branching point take the advantage of the reactivity of carbonyl group of uloses.[6–8] Thus, the literature reports on C-branched sugars for their synthetic importance[6–9] as well as biological significance[1,10] prompted us to develop a convenient strategy for the synthesis of C-3-branched deoxysugars in preparative scale.

The branching of a carbon skeleton by construction of C–C bonds is one of the most challenging tasks in the field of synthetic organic chemistry.[11–13] During the last few years Morita–Baylis–Hillman (MBH) chemistry[14,15] has been recognized as one of the most versatile and more economically feasible C–C bond forming reactions to generate multifunctionalized allylic alcohols generally called MBH or BH adducts. These find various applications as chiral building blocks in organic synthesis.[16] Highly diastereoselective BH reactions have been extensively studied during the past few years.[17] The syntheses of biologically active important molecules involving asymmetric MBH reactions have also been reported.[18] However, the application of the asymmetric MBH reaction in carbohydrate chemistry is very limited.[19,20] Herein, we wish to describe an efficient strategy for an almost completely diastereoselective synthesis of C-3 branched deoxysugars involving the protocols of the asymmetric MBH reaction. To our knowledge, this present study represents an unprecedented substrate controlled/directed, highly diastereoselective MBH reaction, catalyzed by $TiCl_4$/TBAI in carbohydrate chemistry. The various aromatic and aliphatic aldehydes as electrophiles, and sugar-derived chiral-activated alkenes as one of the chiral sources were selected for the present study.

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Keywords: Diastereoselective; Morita–Baylis–Hillman reaction; 2,3-Dideoxy sugar derivatives.

* Corresponding author. Tel.: +91 522 2364145; fax: +91 522 2223405; e-mail: akshaw55@yahoo.com

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2. Results and discussion

The required alkene **1** was prepared from the readily 3,4,6,tri-*O*-acetyl-D-glucal by modification of literature methods.[21] First, we attempted this reaction in CH_2Cl_2 with three-components, *p*-nitrobenzaldehyde (*p*nb), sugar-enone **1** and $TiCl_4$[22] at 0 °C. The adduct was obtained in a very low yield. After several trial experiments using various combinations of substrate and $TiCl_4$ at different temperatures, it was found that stirring a mixture of 2 equiv aldehyde and 1 equiv alkene with 1.5 equiv $TiCl_4$ in CH_2Cl_2 at −78 °C yielded the product (45%) with moderate diastereoselectivity after 10 h, beyond that no appreciable change was noticed in the course of the reaction. However, the yield of the product was increased by 6% when an additive (TBAI or Me_2S) was added. Several research groups have reported the $TiCl_4$ mediated MBH reaction in the presence of additives like TBAI[23,24] or Me_2S.[25–27] Recently, we reported that the $TiCl_4/Me_2S$ mediated BH reaction can be successfully conducted on carbohydrate enals with methyl vinyl ketone, extending the chain of acyclic deoxysugars, where the unsaturation in the enals did not interfere with the electrophilicity of the aldehydic carbon.[28,29] After exploring the combination of $TiCl_4$/TBAI or $TiCl_4/Me_2S$ in different ratios, it was found that 20 mol% of additive with 1.5 equiv $TiCl_4$ turned out to be an effective combination at −78 °C. The loading of 20 mol% of either of the two additives resulted the desired adduct from *p*nb in almost same yield (51%) after 10 h. However, when the temperature of the reaction was gradually increased to −30 °C (−78 °C→−30 °C), remarkable change was observed in the yield of the chromatographically pure adducts (85% with TBAI and 62% with Me_2S). Only one isomer was isolated from each combination. The ^1H NMR and ^{13}C NMR spectra of the crude reaction mixture surprisingly showed a very high degree of diastereoselectivity (>99%). Encouraged by these results, we opted for a representative selection of aromatic and aliphatic aldehydes (Table 1). The reactions were performed at −78 °C→−30 °C. The efficacy of the reactivity of the reagents $TiCl_4$/TBAI and $TiCl_4/Me_2S$ with almost all the aldehydes used in this study showed that $TiCl_4$/TBAI was the superior (Scheme 1).

Table 1. $TiCl_4$/TBAI mediated MBH reaction of enuloside **1** with aldehydes at −78 to −30 °C

Entry	RCHO	Time (h)	Product	dr[a]	Yield (%)[b]
1	*p*-NO_2PhCHO	8	**1′a**	>99/1	85
2	*p*-FPhCHO	48	**1′b**	>99/1	68
3	$CH_3(CH_2)_2CHO$	48	**1′c**	>99/1	82
4	$CH_3(CH_2)_8CHO$	30	**1′d**	>99/1	81
5	*m*-NO_2PhCHO	10	**1′e**	>99/1	64
6	*o*-NO_2PhCHO	6	**1′f**	>99/1	80
7	*p*-CF_3PhCHO	10	**1′g**	>99/1	86
8	PhCHO	92	**1′h**	>99/1	26

[a] Determined by ^1H NMR and ^{13}C NMR of the crude material.
[b] Isolated yield of pure isomer after column chromatography on silica gel.

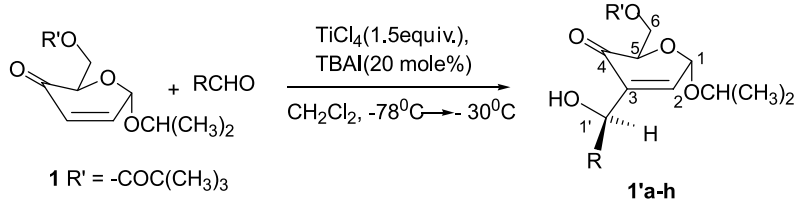
Therefore, herein we wish to highlight our synthetic strategy developed for a very high diastereoselective synthesis of C-3-branched deoxysugar derivatives by taking the advantage of MBH chemistry performed in the presence of $TiCl_4$/TBAI at −78 °C→−30 °C and the plausible mechanism for this reaction. Both aromatic as well as aliphatic aldehydes formed the products in good to very good yield (Table 1) with almost complete diastereoselectivity. As expected the benzaldehyde derived adduct was obtained in low yield (Table 1, entry 8) in 92 h. The MBH reaction of **1** with less reactive aldehyde like *p*-methoxybenzaldehyde did not work under this condition. Once the reaction conditions had been established, its generality with unprotected enuloside **2a** was examined. The free 6-OH in the adduct could be replaced by an amino group, an H atom or a carbon appendage by adopting standard synthetic protocols. This could form novel 2,3,6-trideoxy branched sugar derivatives which exist in important antibiotics.[30] Therefore, when a mixture of enuloside **2a**, *p*nb and $TiCl_4$/TBAI was stirred at −78 °C→−30 °C for 33 h, the expected product formed was in 40% (Table 2, entry 1) with moderate diastereoselectivity.

Table 2. $TiCl_4$/TBAI mediated MBH reaction of enuloside **2a–e**

Entry	R′	Time (h)	Product	dr[a]	Yield (%)[b]
1	H	33	**2′a**	82/18	40
2	CH_3CO	5	**2′b**	>99/1	64
3	*p*-NBz[c]	6	**2′c**	>99/1	88
4	TBDPS	10	**2′d**	83/17	28
5	TBDMS	10	**2′e**	66/34	44

[a] Determined by ^1H NMR and ^{13}C NMR of the crude material.
[b] Isolated yield of pure isomer after column chromatography on silica gel.
[c] *p*-NBz=*p*-nitrobenzoyl group.

The difference in the reactivity of the two enulosides **1** and **2a** with *p*-nitrobenzaldehyde in our MBH reaction can be argued on the basis of the mechanistic aspects of the reaction, as well as the geometry of the proposed transition states (Scheme 4). Both the active alkenes follow the same multiple mechanistic pathways taking place successively. It can be presumed that the reaction starts with nucleophilic attack of iodide from the TBAI to enuloside (Michael acceptor), with concomitant shifting of the 2,3-double bond to 3,4. This generates the oxyanion from the C-4 carbonyl which in turn attacks the carbonyl carbon of the titanium-coordinated pivaloyl group. By virtue of this conjugative



1 R' = -COC(CH3)3

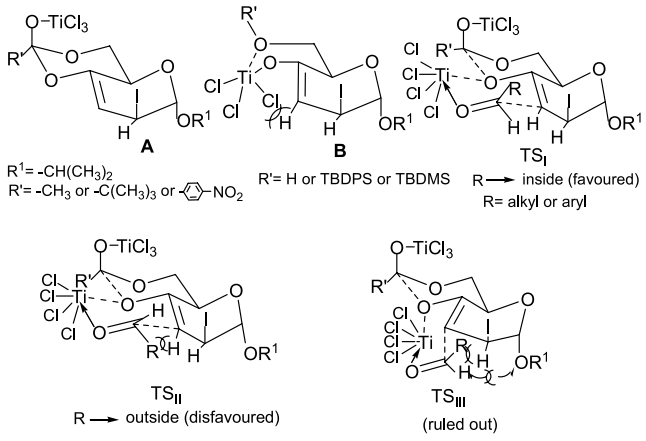
1'a-h

Scheme 1.

effect the formation of an orthoester intermediate[31] 'A' could therefore be predicted. This resembles a *trans* decalin (pseudo) conformation that can activate the site of reaction (C-3) of the enolate. The conjugate addition of iodide to the unprotected enuloside **2a** in the presence of the lewis acid could generate an unfavorable intermediate 'B', where conformation of one of the rings is in a twist-boat form that brings steric crowding near the site of the reaction. This mechanism can justify the low yield of adduct and its moderate selectivity from enuloside **2a**. The reaction of **2a** with *p*nb in presence of $TiCl_4/Me_2S$ did not form any adduct.

In order to justify the above mechanistic argument, the MBH reactions between other acyl (acetate and benzoyl, **2b–c**) and alkyl protected *tert*-butyldiphenyllsilyl and *tert*-butyldimethylsilyl (TBDPS and TBDMS, **2d–e**) enulosides, and *p*nb in the presence of $TiCl_4$/TBAI at $-78\,^{\circ}C \rightarrow -30\,^{\circ}C$ were carried out. The acetyl and *p*-nitrobenzoyl protected enulosides furnished the respective adducts in good to very good yield with same selectivity. The alkyl protected enulosides (**2d–e**) formed their respective adducts in low to moderate yield with moderate selectivity (Scheme 2) (Table 2).

A very high diastereoselective MBH chemistry described herein may be explained on the basis of the assumption that Zimmermann–Traxler-type transition-state[32] TS-I, involving A and the titanium coordinated aldehyde, was formed. Among the other possible chelated transition-states TS-II or TS-III, the latter can be completely ruled out by considering severe steric repulsion arising due to 1,3-diaxial type interactions between the α-faced *O*-isopropyl group at C-1, and the approaching aldehyde from the same face during the reaction as depicted in Scheme 4. The transition-state TS-II is also unfavorable due to steric repulsion between the R-group of the approaching aldehyde, and the hydrogen at C-3 of the enuloside, therefore, giving preference to TS-I over TS-II. Thus, consideration of the



Scheme 4.

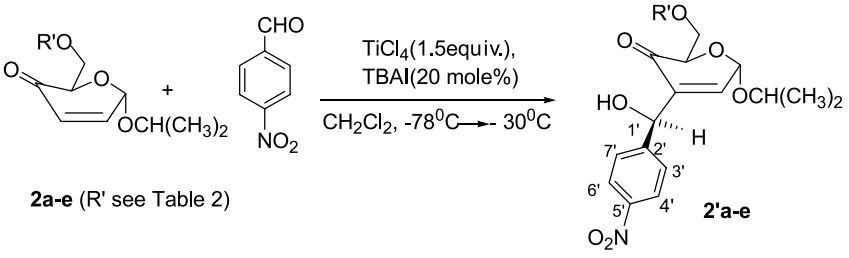
stereochemical model TS-I revealed that one of the enantiotopic faces of the aldehyde, playing a key role in the diastereoface selectivity, was well disposed to C-3 of the enuloside, resulting in its intermolecular diastereoselective *re*-face attack at the electrophilic carbonyl carbon of the approaching aldehyde.

In order to show the synthetic utility of these adducts, the C-4 keto groups of **1′a**, **1′d** and **1′f** were subjected to stereoselective reduction with $NaBH_4$ in the presence of $CeCl_3 \cdot 7H_2O$ (Scheme 3) to obtain their *threo* derivatives **3′a**, **3′d** and **3′f** in 78, 68 and 74%, respectively (Table 3).

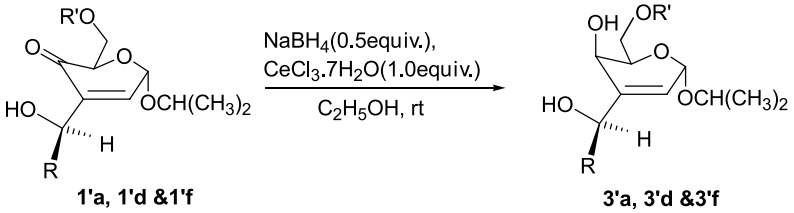
Table 3. Diastereoselective reduction of Baylis–Hillman adducts (**1′a**, **1′d** and **1′f**) with $NaBH_4$ and $CeCl_3 \cdot 7H_2O$

Entry	B–H adducts	Time (h)	Product	dr[a]	Yield (%)[b]
1	**1′a**	2	**3′a**	>99/1	78
2	**1′d**	5	**3′d**	>99/1	68
3	**1′f**	5	**3′f**	>99/1	74

[a] Determined by ^1H NMR and ^{13}C NMR of the crude material.
[b] Isolated yield of pure isomer after column chromatography on silica gel.



Scheme 2.



Scheme 3.

3. Conclusion

In summary, we have developed and disclosed herein a new and convenient strategy for the almost complete diastereoselective synthesis of new multifunctionalized unsaturated C-3-alkylated 2,3-dideoxy sugars[1] or derivatives of pyran-3-ones in a good to very good yield. This involves $TiCl_4$/TBAI-mediated asymmetric Morita–Baylis–Hillman reaction performed at $-78\,^{\circ}C \rightarrow -30\,^{\circ}C$ involving a readily available sugar-derived enuloside and various aldehydes.[33] On the basis of the experimental results, it was postulated that a plausible chelated transition-state TS-I played a key role in the formation of a very high diastereoenriched MBH adduct involving multiple mechanistic pathways. The energetically favored orthoester intermediate A governed the remote activation[34] of reaction site C-3 of the enuloside, resulting the most favorable approach for the incoming titanium-coordinated aldehyde to be from *re*-face, making the whole reaction a substrate controlled diastereoselective MBH reaction.[35] The low yield of adducts **2a′**, **2d′**, **2e′** from enulosides **2a**, **2d**, **2e** is attributed to an energetically unfavored twist-boat intermediate B. The resulting unprecedented C-3 branched deoxy sugar derivatives (or pyran-3-ones) may be as useful as other versatile key intermediates like Corey's lactone, the Wieland–Miescher ketone, and the Prelog–Djerassi lactone which will find numerous applications as chiral building blocks for the construction of medicinally important molecules. These may exhibit activities[9,36] such as anti-microbial anti-viral, anti-fungal, anti-coccidial, anti-inflammatory, anti-cancer, etc. through skeleton rearrangement and functional group transformation/manipulation or structural diversification (Fig. 1). Our efforts to make this synthetic strategy more versatile to obtain novel highly functionalized MBH adducts as chiral building blocks from other active sugar-enones are underway.

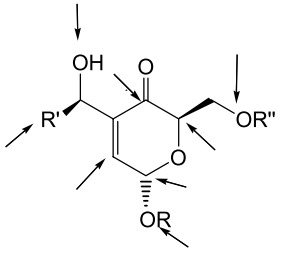


Figure 1. Arrow shows the site for diversification.

4. Experimental

4.1. General

All the reactions were monitored by warming the $CeSO_4$ (1% in 1 M H_2SO_4) sprayed precoated silica gel TLC plates at 100 °C. NMR spectra were recorded on Bruker Avance DPX 200 FT, Bruker Robotics and Bruker DRX 300 Spectrometers at 200, 300 MHz (^1H) and 50, 75 MHz (^{13}C). For ^{13}C NMR reference $CDCl_3$ appeared at 77.4 ppm, unless otherwise stated. Mass spectra were recorded on a JEOL SX 102/DA 6000 mass spectrometer using argon/xenon (6 kV, 100 mA) as the FAB gas. Organic solvents were dried by standard methods. Aldehydes were purchased from Aldrich and Fluka chemical co. Enones **1** and **2a–e** were synthesized in the lab. IR spectra were recorded on Perkin–Elmer 881 and FTIR-8210 PC Shimadzu Spectrophotometers. Optical rotations were determined on an Autopol III polarimeter using a 1 dm cell at 28 °C in methanol or chloroform as the solvent; concentrations mentioned are in g/100 mL. Elemental analyses were carried out on Carlo-Erba-1108 and Vario EL III instruments.

4.2. Typical reaction procedure for the preparation of MBH adducts

To a stirred solution of tetrabutylammonium iodide, TBAI, (0.2 mmol) in dry CH_2Cl_2 (5 mL) at $-78\,^{\circ}C$ was added $TiCl_4$ (1.5 mmol) dropwise. After stirring for two minutes, a mixture containing, **1** (1 mmol) and *p*-nitrobenzaldehyde (2 mmol) in dry CH_2Cl_2 (5 mL) was added. The reaction mixture was slowly warmed to $-30\,^{\circ}C$ and stirred for the specified time depending on the enulosides and aldehydes used. A saturated aqueous solution of sodium bicarbonate was added, followed by filtration through a celite pad. The organic layer from the filtrate was separated, and the aqueous layer was again extracted with ethyl acetate. The organic layers were then combined, washed with brine solution, and dried over sodium sulfate. The crude product obtained after evaporation of the solvent was chromatographed to yield pure compounds.

4.2.1. Isopropyl-6-*O*-trimethylacetyl-3-[hydroxy (4-nitrophenyl) methyl]-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranoside-4-ulose (1′a). Oil. Eluent for column chromatography (20% ethyl acetate/hexane); [Found: C, 59.32; H, 6.72; N, 3.09. $C_{21}H_{27}NO_8$ requires C, 59.85; H, 6.46; N, 3.32%]; R_f (25% ethyl acetate/hexane) 0.39; $[\alpha]_D = -1.33$ (*c* 0.30, CH_3OH); ν_{max} (neat) 3483, 1724, 1684 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.22 (2H, d, $J_{4',3' \text{ or } 6',7'} = 8.7$ Hz, H-4′ and H-6′), 7.57 (2H, d, $J_{3',4' \text{ or } 7',6'} = 8.7$ Hz, H-3′ and H-7′), 6.60 (1H, d, $J_{2,1} = 3.6$ Hz, H-2), 5.68 (1H, d, $J_{1',OH} = 4.2$ Hz, H-1′), 5.40 (1H, d, $J_{1,2} = 3.6$ Hz, H-1), 4.67 (1H, dd, $J_{5,6a} = 2.4$ Hz, $J_{5,6b} = 5.6$ Hz, H-5), 4.52 (1H, dd, $J_{6a,5} = 2.4$ Hz, $J_{6a,6b} = 11.9$ Hz, H-6a), 4.40 (1H, dd, $J_{6b,5} = 5.7$ Hz, $J_{6b,6a} = 12.0$ Hz, H-6b), 4.05 (1H, sept., $J = 6.3$ Hz, –OC*H* $(CH_3)_2$), 3.13 (1H, d, $J_{OH,1'} = 4.8$ Hz, –O*H*), 1.24 (3H, d, $J = 6.0$ Hz, $-OCH(CH_3)_2$), 1.19 (3H, d, $J = 6.0$ Hz, $-OCH(CH_3)_2$),1.14 (9H, s, $-OCOC(CH_3)_3$); δ_C (50 MHz, $CDCl_3$) 194.9 (C-4), 178.5 ($-OCOC(CH_3)_3$), 148.0 (C-3 and C-5′), 141.2 (C-2), 138.9 (C-2′), 128.0 (C-4′ and C-6′), 124.1 (C-3′ and C-7′), 92.1 (C-1), 72.9 (C-5), 71.8 ($-OCH(CH_3)_2$), 70.6 (C-1′), 63.0 (C-6), 39.1 ($-OCOC(CH_3)_3$), 27.4 ($-OCH(CH_3)_2$), 23.5, 22.1 ($-OCH(CH_3)_2$); *m/z* (FABMS) 422 $[M+H]^+$, 362 $[M-OCH(CH_3)_2]^+$, 260, 243, 232, 217, 154, 136.

4.2.2. Isopropyl-6-*O*-trimethylacetyl-3-[hydroxy (4-fluorophenyl) methyl]-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranoside-4-ulose (1′b). Oil. Eluent for column chromatography (12% ethyl acetate/hexane); [Found: C, 63.50; H, 7.52. $C_{21}H_{27}O_6F$ requires C, 63.94; H, 6.89%]; R_f (25% ethyl acetate/hexane) 0.45; $[\alpha]_D = -8.48$ (*c* 0.33, CH_3OH); ν_{max} (neat) 3481, 1726, 1686 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.34–7.04 (4H, m, Ph *H*), 6.56 (1H, d, $J_{2,1} = 3.6$ Hz, H-2), 5.57 (1H, s, H-1′), 5.38 (1H, d, $J_{1,2} =$

3.6 Hz, H-1), 4.66 (1H, dd, $J_{5,6a}$=2.6 Hz, $J_{5,6b}$=5.6 Hz, H-5), 4.53 (1H, dd, $J_{6a,5}$=2.6 Hz, $J_{6a,6b}$=11.9 Hz, H-6a), 4.39 (1H, dd, $J_{6b,5}$=5.7 Hz, $J_{6b,6a}$=11.9 Hz, H-6b), 4.02 (1H, sept., J=6.2 Hz, –OC*H*$(CH_3)_2$), 3.00 (1H, br s, –OH), 1.24 (3H, d, J=6.1 Hz, –OCH(C*H*$_3)_2$), 1.19 (3H, d, J=6.3 Hz, –OCH(C*H*$_3)_2$), 1.16 (9H, s, –OCOC(C*H*$_3)_3$); δ_C (50 MHz, $CDCl_3$) 195.2 (C-4), 178.5 (–OCOC$(CH_3)_3$), 160.4 (C-5′), 140.6 (C-2), 139.6 (C-3), 136.4 (C-2′), 129.0 (C-4′ and C-6′), 128.9 (C-3′ and C-7′), 92.2 (C-1), 72.9 (C-5), 71.6 (–O*C*H$(CH_3)_2$), 70.9 (C-1′), 63.1 (C-6), 39.1 (–OCO*C*$(CH_3)_3$), 27.5 (–OCOC(*C*H$_3)_3$), 23.6, 22.1 (–OCH(*C*H$_3)_2$); *m/z* (FAB MS) 394 $[M]^+$, 376 $[M-H_2O]^+$, 335 $[M-OCH(CH_3)_2]^+$.

4.2.3. Isopropyl-6-*O*-trimethylacetyl-3-(1-hydroxybutyl)-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranoside-4-ulose (1′c). Oil. Eluent for column chromatography (12% ethyl acetate/hexane); [Found: C, 62.79; H, 8.07. $C_{18}H_{30}O_6$ requires C, 63.13; H, 8.83%]; R_f (30% ethyl acetate/hexane) 0.55; $[\alpha]_D$=+44 (*c* 0.20, CH_3OH); ν_{max} (neat) 3424, 1726, 1686 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 6.73 (1H, d, $J_{2,1}$=3.7 Hz, H-2), 5.39 (1H, d, $J_{1,2}$=3.7 Hz, H-1), 4.68 (1H, dd, $J_{5,6a}$=2.6 Hz, $J_{5,6b}$=5.7 Hz, H-5), 4.54 (1H, dd, $J_{6a,5}$=2.6 Hz, $J_{6a,6b}$=11.9 Hz, H-6a), 4.41 (2H, dd, $J_{6b,5}$=5.7 Hz, $J_{6b,6a}$=11.9 Hz, H-6b and H-1′), 4.04 (1H, sept., J=6.2 Hz, –OC*H*$(CH_3)_2$), 1.66–1.33 (4H, m, C-2′ and C-3′), 1.26 (3H, d, J=6.2 Hz, –OCH(C*H*$_3)_2$), 1.21 (3H, d, J=6.3 Hz, –OCH(C*H*$_3)_2$), 1.18 (9H, s, –OCOC(C*H*$_3)_3$), 0.93 (3H, t, J=7.2 Hz, H-4′); δ_C (50 MHz, $CDCl_3$) 195.4 (C-4), 178.5 (–O*C*OC$(CH_3)_3$, 140.0 (C-2), 139.4 (C-3), 92.2 (C-1), 72.9 (C-5), 71.5 (–O*C*H$(CH_3)_2$), 69.7 (C-1′), 63.2 (C-6), 39.2 (–OCO*C*$(CH_3)_3$), 38.3 (C-2′), 27.5 (–OCOC(*C*H$_3)_3$), 23.6, 22.2 (–OCH(*C*H$_3)_2$), 19.3 (C-3′), 14.2 (C-4′); *m/z* (FABMS) 343 $[M+H]^+$, 324 $[M-H_2O]^+$, 283 $[M-OCH(CH_3)_2]^+$, 265, 223, 181.

4.2.4. Isopropyl-6-*O*-trimethylacetyl-3-(1-hydroxydecyl)-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranoside-4-ulose (1′d). Oil. Eluent for column chromatography (10% ethyl acetate/hexane); [Found: C, 67.51; H, 9.24. $C_{24}H_{42}O_6$ requires C, 67.57; H, 9.92%]; R_f (15% ethyl acetate/hexane) 0.33; $[\alpha]_D$=+32.5 (*c* 0.24, CH_3OH); ν_{max} (neat) 3449, 1726, 1687 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 6.66 (1H, d, $J_{2,1}$=3.6 Hz, H-2), 5.32 (1H, d, $J_{1,2}$=3.6 Hz, H-1), 4.60 (1H, dd, $J_{5,6a}$=2.6 Hz, $J_{5,6b}$=5.7 Hz, H-5), 4.48 (1H, dd, $J_{6a,5}$=2.6 Hz, $J_{6a,6b}$=11.9 Hz, H-6a), 4.33 (1H, dd, $J_{6b,5}$=5.7 Hz, $J_{6b,6a}$=11.9 Hz, H-6b), 4.30 (1H, t, J=3.1 Hz, H-1′), 4.05 (1H, sept., J=6.2 Hz, –OC*H*$(CH_3)_2$), 1.55 (2H, m, H-2′), 1.16 (20H, m, –OCH(C*H*$_3)_2$ and H-3′ to H-9′), 1.11 (9H, s, (–OCOC(C*H*$_3)_3$), 0.80 (3H, t, J=6.6 Hz, H-10′); δ_C (50 MHz, $CDCl_3$) 195.4 (C-4); 178.5 (–OCOC$(CH_3)_3$), 140.0 (C-2), 139.4 (C-3), 92.2 (C-1), 72.9 (C-5), 71.5 (–O*C*H$(CH_3)_2$), 70.0 (C-1′), 63.2 (C-6), 39.2 (–OCO*C*$(CH_3)_3$), 36.2, 32.3, 30.1, 30.0, 29.8, 29.7 (C-2′ to C-7′), 27.5 (–OCOC(*C*H$_3)_3$), 26.2 (C-8′), 23.6 (C-9′), 23.0, 22.2 (–OCH(*C*H$_3)_2$), 14.5 (C-10′); *m/z* (FABMS) 426 $[M]^+$, 408 $[M-H_2O]^+$, 367 $[M-OCH(CH_3)_2]^+$, 265.

4.2.5. Isopropyl-6-*O*-trimethylacetyl-3-[hydroxy (3-nitrophenyl) methyl]-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranoside-4-ulose (1′e). Oil. Eluent for column chromatography (14% ethyl acetate/hexane); [Found: C, 59.57; H, 5.92; N, 3.25. $C_{21}H_{27}NO_8$ requires C, 59.85; H, 6.46; N, 3.32%] R_f (25% ethyl acetate/hexane) 0.42; $[\alpha]_D$=+4.95 (*c* 0.20, $CHCl_3$); ν_{max} (neat) 3483, 1728, 1689 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.26 (1H, s, H-3′), 8.14 (1H, d, $J_{5',6'}$=7.2 Hz, H-5′), 7.73 (1H, d, $J_{7',6'}$=7.3 Hz, H-7′), 7.53 (1H, t, $J_{6',5' \text{ or } 7'}$=7.8 Hz, H-6′), 6.71 (1H, d, $J_{2,1}$=3.5 Hz, H-2), 5.42 (1H, d, $J_{1,2}$=3.6 Hz, H-1), 5.68 (1H, s, H-1′), 4.66 (1H, dd, $J_{5,6a}$=2.6 Hz, $J_{5,6b}$=5.4 Hz, H-5), 4.50 (1H, dd, $J_{6a,5}$=2.4 Hz, $J_{6a,6b}$=11.8 Hz, H-6a), 4.37 (1H, dd, $J_{6b,5}$=5.6 Hz, $J_{6b,6a}$=11.9 Hz, H-6b), 4.06 (1H, sept., J=6.2 Hz, –OC*H*$(CH_3)_2$), 1.24 (3H, d, J=6.2 Hz, –OCH(C*H*$_3)_2$), 1.20 (3H, d, J=6.2 Hz, –OCH(C*H*$_3)_2$), 1.13 (9H, s, (–OCOC(C*H*$_3)_3$); δ_C (50 MHz, $CDCl_3$) 195.0 (C-4), 178.0 (–OCOC$(CH_3)_3$), 148.8 (C-3), 143.1 (C–4′), 141.2 (C-2), 138.8 (C-2′), 133.1 (C-3′), 129.8 (C-5′), 123.3 (C-7′), 122.1 (C-6′), 92.0 (C-1), 72.9 (C-5), 71.8 (–O*C*H$(CH_3)_2$), 70.6 (C-1′), 63.0 (C-6), 39.1 (–OCO*C*$(CH_3)_3$), 27.4 (–OCOC(*C*H$_3)_3$), 23.5, 22.1 (–OCH(*C*H$_3)_2$); *m/z* (FABMS) 421 $[M]^+$, 404 $[M-OH]^+$, 362 $[M-OCH(CH_3)_2]^+$, 278, 260, 243, 218, 154.

4.2.6. Isopropyl-6-*O*-trimethylacetyl-3-[hydroxy (2-nitrophenyl) methyl]-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranoside-4-ulose (1′f). Oil. Eluent for column chromatography (15% ethyl acetate/hexane); [Found: C, 59.70; H, 6.71; N, 3.71. $C_{21}H_{27}NO_8$ requires C, 59.85; H, 6.46; N, 3.32%]; R_f (25% ethyl acetate/hexane) 0.40; $[\alpha]_D$=−6.13 (*c* 0.23, $CHCl_3$); ν_{max} (neat) 3478, 1727, 1687 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.97 (1H, d, J=8.0 Hz, H-4′), 7.68 (2H, m, H-5′ and H-6′), 7.46 (1H, t, J=7.3 Hz, H-7′), 6.66 (1H, d, $J_{2,1}$=3.6 Hz, H-2), 6.17 (1H, d, $J_{1',OH}$=4.0 Hz, H-1′), 5.39 (1H, d, $J_{1,2}$=3.6 Hz, H-1), 4.69 (1H, dd, $J_{5,6a}$=2.4 Hz, $J_{5,6b}$=5.8 Hz, H-5), 4.52 (1H, dd, $J_{6a,5}$=2.4 Hz, $J_{6a,6b}$=11.9 Hz, H-6a), 4.36 (1H, dd, $J_{6b,5}$=5.8 Hz, $J_{6b,6a}$=11.9 Hz, H-6b), 4.06 (1H, sept., J=6.1 Hz, –OC*H*$(CH_3)_2$), 3.41 (1H, d, $J_{OH,1'}$=4.9 Hz, O*H*), 1.25 (3H, d, J=6.1 Hz, –OCH(C*H*$_3)_2$), 1.19 (3H, d, J=6.1 Hz, –OCH(C*H*$_3)_2$), 1.14 (9H, s, –OCOC(C*H*$_3)_3$); δ_C (50 MHz, $CDCl_3$) 194.4 (C-4), 178.4 (–OCOC$(CH_3)_3$), 148.6 (C-3), 141.2 (C-2), 138.0 (C-3′), 136.0 (C-2′), 133.9 (C-4′), 129.2 (C-5′ and C-6′), 125.0 (C-7′), 92.1 (C-1), 72.7 (C-5), 71.6 (–O*C*H$(CH_3)_2$), 66.4 (C-1′), 63.0 (C-6), 39.1 (–OCO*C*$(CH_3)_3$), 27.4 (–OCOC(*C*H$_3)_3$), 23.5, 22.1 (–OCH(*C*H$_3)_2$); *m/z* (FABMS) 420 $[M-1]^+$, 404 $[M-OH]^+$, 362 $[M-OCH(CH_3)_2]^+$, 278, 260, 218, 154.

4.2.7. Isopropyl-6-*O*-trimethylacetyl-3-[hydroxy (4-trifluoromethylphenyl) methyl]-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranoside-4-ulose (1′g). Oil. Eluent for column chromatography (14% ethyl acetate/hexane); [Found: C, 58.45; H, 5.93. $C_{22}H_{27}F_3O_6 \cdot 1/4H_2O$ requires C, 58.85; H, 6.17%]; R_f (20% ethyl acetate/hexane) 0.40; $[\alpha]_D$=+3.87 (*c* 0.28, $CHCl_3$); ν_{max} (neat) 3467, 1728, 1690 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.62 (2H, d, $J_{4',3' \text{ or } 6',7'}$=8.2 Hz, H-4′ and H-6′), 7.50 (2H, d, $J_{3',4' \text{ or } 7',6'}$=8.2 Hz, H-3′ and H-7′), 6.59 (1H, d, $J_{2,1}$=3.7 Hz, H-2), 5.62 (1H, s, H-1′), 5.39 (1H, d, $J_{1,2}$=3.6 Hz, H-1), 4.66 (1H, dd, $J_{5,6a}$=2.6 Hz, $J_{5,6b}$=5.4 Hz, H-5), 4.51 (1H, dd, $J_{6a,5}$=2.6 Hz, $J_{6a,6b}$=11.9 Hz, H-6a),), 4.40 (1H, dd, $J_{6b,5}$=5.4 Hz, $J_{6b,6a}$=11.9 Hz, H-6b), 4.03 (1H, sept., J=6.1 Hz, –OC*H*$(CH_3)_2$ 1.24 (3H, d, J=6.1 Hz, –OCH(C*H*$_3)_2$), 1.19 (3H, d, J=6.1 Hz, –OCH(C*H*$_3)_2$), 1.13 (9H, s, –OCOC(C*H*$_3)_3$); δ_C (75 MHz, $CDCl_3$) 194.6 (C-4); 177.9 (–OCOC$(CH_3)_3$), 144.1 (C-3), 140.4 (C-2), 138.6 (C-2′ and C-5′), 127.0 (*C*F_3), 126.9 (C-4′ and

C-6′), 125.3 (C-3′ and C-7′), 91.5 (C-1), 72.3 (C-5), 71.2 (–O*C*H(CH$_3$)$_2$), 70.5 (C-1′), 62.4 (C-6), 38.5 (–OCO*C*(CH$_3$)$_3$), 26.8 (–OCOC(*C*H$_3$)$_3$), 23.0, 21.5 (–OCH(*C*H$_3$)$_2$); *m/z* (FAB MS) 443 [M−1]$^+$, 427 [M−OH]$^+$, 385 [M−OCH(CH$_3$)$_2$]$^+$, 368, 301, 283, 266, 240.

4.2.8. Isopropyl-6-*O*-trimethylacetyl-3-[hydroxy (phenyl) methyl]-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranoside-4-ulose (1′h). Oil. Eluent for column chromatography (12% ethyl acetate/hexane); [Found: C, 64.94; H, 7.19. C$_{21}$H$_{28}$O$_6$·1/2H$_2$O requires C, 65.43; H, 7.58%]; R_f (20% ethyl acetate/hexane) 0.49; $[\alpha]_D=-10.0$ (*c* 0.08, CHCl$_3$); ν_{max} (neat) 3430, 1727, 1687 cm^{-1}; δ_H (200 MHz, CDCl$_3$) 7.38–7.33 (5H, m, Ph*H*), 6.56 (1H, dd, $J_{2,1}=3.7$ Hz, and $J_{2,1'}=1.2$ Hz, H-2), 5.38 (1H, d, $J_{1,2}=3.6$ Hz, H-1), 5.58 (1H, s, H-1′), 4.66 (1H, dd, $J_{5,6a}=2.6$ Hz, $J_{5,6b}=5.7$ Hz, H-5), 4.53 (1H, dd, $J_{6a,5}=2.6$ Hz, $J_{6a,6b}=11.9$ Hz, H-6a), 4.40 (1H, dd, $J_{6b,5}=5.7$ Hz, $J_{6b,6a}=11.9$ Hz, H-6b), 4.02 (1H, sept., $J=6.2$ Hz, –OC*H*(CH$_3$)$_2$), 1.24 (3H, d, $J=6.2$ Hz, –OCH(C*H*$_3$)$_2$), 1.18 (3H, d, $J=6.2$ Hz, –OCH(C*H*$_3$)$_2$), 1.15 (9H, s, –OCOC(C*H*$_3$)$_3$); δ_C (50 MHz, CDCl$_3$) 195.2 (C-4), 178.4 (–OCOC(CH$_3$)$_3$), 140.6 (C-2 and C-2′), 139.7 (C-3), 128.9 (C-3′ and C-7′), 128.4 (C-5′), 127.2 (C-4′ and C-6′), 92.2 (C-1), 72.9 (C-5), 71.5 (C-1′ and –O*C*H(CH$_3$)$_2$), 63.1 (C-6), 39.1 (–OCO*C*(CH$_3$)$_3$), 27.4 (–OCOC(*C*H$_3$)$_3$), 23.5, 22.1 (–OCH(*C*H$_3$)$_2$); *m/z* (FABMS) 375 [M−1]$^+$, 359 [M−OH]$^+$, 317 [M−OCH(CH$_3$)$_2$]$^+$, 233, 215, 198, 173, 154.

4.2.9. Isopropyl-6-hydroxy-3-[hydroxy (4-nitrophenyl) methyl]-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranoside-4-ulose (2′a). Oil. Eluent for column chromatography (30% ethyl acetate/hexane); [Found: C, 54.29; H, 6.07; N, 3.87. C$_{16}$H$_{19}$NO$_7$·H$_2$O requires C, 54.01; H, 5.95; N, 3.94%]; R_f (50% ethyl acetate/hexane) 0.39; $[\alpha]_D=-10.86$ (*c* 0.09, CHCl$_3$); ν_{max} (neat) 3405, 1686 cm^{-1}; δ_H (200 MHz, CDCl$_3$) 8.21 (2H, d, $J_{4',3' \text{ or } 6',7'}=8.6$ Hz, H-4′ and H-6′), 7.57 (2H, d, $J_{3',4' \text{ or } 7',6'}=8.7$ Hz, H-3′ and H-7′), 6.63 (1H, d, $J_{2,1}=3.4$ Hz, H-2), 5.71 (1H, s, H-1′), 5.42 (1H, d, $J_{1,2}=3.7$ Hz, H-1), 4.46 (1H, t, $J=3.9$ Hz, H-5), 4.13–3.96 (2H, m, H-6a and OC*H*(CH$_3$)$_2$), 3.89 (1H, dd, $J_{6b,5}=3.9$ Hz, $J_{6b,6a}=11.9$ Hz, H-6b), 1.23 (3H, d, $J=6.3$ Hz, –OCH(C*H*$_3$)$_2$), 1.19 (3H, d, $J=6.2$ Hz, –OCH(C*H*$_3$)$_2$); δ_C (50 MHz, CDCl$_3$) 196.7 (C-4) 148.0 (C-3 and C-5′), 141.3 (C-2), 139.3 (C-2′), 128.0 (C-4′ and C-6′), 124.1 (C-3′ and C-7′), 92.2 (C-1), 74.5 (C-5), 71.9 (–O*C*H(CH$_3$)$_2$), 70.0 (C-1′), 62.0 (C-6), 23.5, 22.1 (–OCH(*C*H$_3$)$_2$); *m/z* (FABMS) 338 [M+1]$^+$, 320 [M−OH]$^+$, 307 [M−32]$^+$, 278 [M−OCH (CH$_3$)$_2$]$^+$, 218, 154, 136.

4.2.10. Isopropyl-6-*O*-acetyl-3-[hydroxy (4-nitrophenyl) methyl]-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranoside-4-ulose (2′b). Oil. Eluent for column chromatography (18% ethyl acetate/hexane); [Found: C, 57.01; H, 5.36; N, 3.83. C$_{18}$H$_{21}$NO$_8$ requires C, 56.98; H, 5.58; N, 3.69%]; R_f (30% ethyl acetate/hexane) 0.39; $[\alpha]_D=-7.93$ (*c* 0.12, CHCl$_3$). ν_{max} (neat) 3483, 1740, 1692 cm^{-1}; δ_H (200 MHz, CDCl$_3$) 8.22 (2H, d, $J_{4',3' \text{ or } 6',7'}=8.7$ Hz, H-4′ and H-6′) 7.58 (2H, d, $J_{3',4' \text{ or } 7',6'}=8.7$ Hz, H-3′and H-7′), 5.69 (1H, s, H-1′), 6.65 (1H, d, $J_{2,1}=3.7$ Hz, H-2), 5.42 (1H, d, $J_{1,2}=3.6$ Hz, H-1), 4.65 (1H, t, $J_{5,6a\&6b}=4.5$ Hz, H-5), 4.46 (2H, d, $J_{6a\&6b,\ 5}=4.5$ Hz, H-6), 4.02 (1H, sept., $J=6.1$ Hz, –OCH (CH$_3$)$_2$), 3.13 (1H, br s, –OH), 2.03 (3H, s, OCOCH$_3$), 1.24 (3H, d, $J=6.1$ Hz, –OCH(C*H*$_3$)$_2$), 1.19 (3H, d, $J=6.1$ Hz, –OCH(C*H*$_3$)$_2$); δ_C (50 MHz, CDCl$_3$) 194.7 (C-4), 171.0 (–O*C*OCH$_3$), 148.0 (C-3 and C-5′), 141.1 (C-2), 138.9 (C-2′), 128.0 (C-4′ and C-6′), 124.0 (C-3′ and C-7′), 92.4 (C-1), 72.5 (C-5), 72.2 (–O*C*H(CH$_3$)$_2$), 70.3 (C-1′), 62.8 (C-6), 23.4, 22.3 (–OCH(*C*H$_3$)$_2$), 21.0 (CO*C*H$_3$); *m/z* (FABMS) 380 [M+1]$^+$, 362 [M−OH]$^+$, 320 [M−OCH (CH$_3$)$_2$]$^+$, 307, 289, 260, 232, 154.

4.2.11. Isopropyl-6-*O*-4-nitrobenzoyl-3-[hydroxy (4-nitrophenyl) methyl]-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranoside-4-ulose (2′c). Amorphous solid. Eluent for column chromatography (16% ethyl acetate/hexane); [Found: C, 56.27; H, 4.98; N, 5.79. C$_{23}$H$_{22}$N$_2$O$_{10}$ requires C, 56.79; H, 4.55; N, 5.75%]; R_f (25% ethyl acetate/hexane) 0.50; $[\alpha]_D=-39.13$ (*c* 0.05, CHCl$_3$); ν_{max} (neat) 3453, 1727, 1688 cm^{-1}; δ_H NMR (300 MHz, CDCl$_3$) 8.27 (2H, d, $J_{4'',3'' \text{ or } 6'',7''}=9.0$ Hz, H-4″ and H-6″), 8.19 (2H, d, $J_{4',3' \text{ or } 6',7'}=9.0$ Hz, H-4′ and H-6′), 8.13 (2H, d, $J_{3'',4'' \text{ or } 7'',6''}=9.0$ Hz, H-3″ and H-7″), 7.59 (2H, d, $J_{3',4' \text{ or } 7',6'}=9.0$ Hz, H-3′ and H-7′), 6.68 (1H, d, $J_{2,1}=3.7$ Hz, H-2), 5.44 (1H, d, $J_{1,2}=3.9$ Hz, H-1), 5.74 (1H, s, H-1′), 4.83–4.78 (2H, m, H-5 and H-6a), 4.73 (1H, dd, $J_{6b,5}=5.7$ Hz, $J_{6b,6a}=12.0$ Hz, H-6b), 4.02 (1H, sept., $J=6.3$ Hz, –OC*H*(CH$_3$)$_2$), 1.24 (3H, d, $J=6.0$ Hz, –OCH(C*H*$_3$)$_2$), 1.20 (3H, d, $J=6.0$ Hz, –OCH(C*H*$_3$)$_2$); δ_C (50 MHz, CDCl$_3$) 194.4 (C-4) 164.6 (C-1″), 151.0 (C-5″), 148.0 (C-5′), 147.8 (C-3), 141.3 (C-2), 138.9 (C-2′), 135.4 (C-2″), 131.1 (C-4″ and C-6″), 128.0 (C-4′ andC-6′), 124.1 (C-3′ and C-7′), 123.9 (C-3″ and C-7″), 92.5 (C-1), 72.5 (C-5), 72.4 (–O*C*H(CH$_3$)$_2$), 70.2 (C-1′), 64.1 (C-6), 23.5, 22.3 (–OCH(*C*H$_3$)$_2$); *m/z* (FABMS) 487 [M+1]$^+$, 469 [M−OH]$^+$, 427 [M−OCH(CH$_3$)$_2$]$^+$, 410, 392, 307, 289, 278, 154.

4.2.12. Isopropyl-6-*O*-trimethyldiphenylsilyl-3-[hydroxy (4-nitrophenyl)methyl]-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranoside-4-ulose (2′d). Oil. Eluent for column chromatography (10% ethyl acetate/hexane); [Found: C, 65.82; H, 6.26; N, 2.12. C$_{32}$H$_{37}$NO$_7$Si·1/2H$_2$O requires C, 65.73; H, 6.55; N, 2.39%]; R_f (20% ethyl acetate/hexane) 0.50; $[\alpha]_D=+9.0$ (*c* 0.20, CHCl$_3$); ν_{max} (neat) 3464, 1688 cm^{-1}; δ_H (200 MHz, CDCl$_3$) 8.17 (2H, d, $J_{4',3' \text{ or } 6',7'}=8.7$ Hz, H-4′ and H-6′), 7.66–7.63 (4H, m, Ph*H*), 7.56 (2H, d, $J_{3',4' \text{ or } 7',6'}=8.7$ Hz, H-3′ and H-7′), 7.42–7.36 (6H, m, PhH), 6.58 (1H, dd, $J_{2,1}=3.6$ Hz, $J_{2,1'}=1.0$ Hz, H-2), 5.62 (1H, s, H-1′), 5.47 (1H, d, $J_{1,2}=3.5$ Hz, H-1), 4.50 (1H, dd, $J_{5,6a}=2.8$ Hz, $J_{5,6b}=4.6$ Hz, H-5), 4.09–3.99 (3H, m, H-6a, H-6b and OC*H*(CH$_3$)$_2$), 1.23 (3H, d, $J=6.3$ Hz, –OCH(C*H*$_3$)$_2$), 1.19 (3H, d, $J=6.3$ Hz, –OCH(C*H*$_3$)$_2$), 0.98 (9H, s, –C(C*H*$_3$)$_3$); δ_C (50 MHz, CDCl$_3$) 196.1 (C-4), 148.1 (C-5′), 148.0 (C-3), 141.6 (C-2), 139.3 (C-2′), 136.0 (Ph*C*), 133.0 (Ph*C*), 130.1 (C-4′ and C-6′), 128.0 (Ph*C*), 124.1 (C-3′ and C-7′), 92.1 (C-1), 76.1 (C-5), 71.6 (–O*C*H(CH$_3$)$_2$), 71.2 (C-1′), 63.7 (C-6), 27.0 (–C(*C*H$_3$)$_3$), 23.6, 22.1 (–OCH(*C*H$_3$)$_2$), 19.6 (–*C*(CH$_3$)$_3$); *m/z* (FABMS) 574 [M−1]$^+$, 558 [M−OH]$^+$, 518 [M−(CH$_3$)$_3$C]$^+$, 498, 458, 438, 365, 335, 307, 241.

4.2.13. Isopropyl-6-*O*-trimethyldimethylsilyl-3-[hydroxy (4-nitrophenyl)methyl]-2,3-dideoxy-α-D-*glycero*-hex-2-enopyranoside-4-ulose (2′e). Oil. Eluent for column chromatography (12% ethyl acetate/hexane); [Found: C, 58.42; H, 7.26; N, 2.81. C$_{22}$H$_{33}$NO$_7$Si requires C, 58.52; H,

7.36; N, 3.10%]; R_f (30% ethyl acetate/hexane) 0.30; $[\alpha]_D = +8.33$ (*c* 0.24, $CHCl_3$); ν_{max} (neat) 3467, 1687 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 8.20 (2H, d, $J_{4',3' \text{ or } 6',7'} = 8.7$ Hz, H-4′ and H-6′), 7.56 (2H, d, $J_{3',4' \text{ or } 7',6'} = 8.4$ Hz, H-3′ and H-7′), 6.57 (1H, d, $J_{2,1} = 3.6$ Hz, H-2), 5.63 (1H, s, H-1′), 5.45 (1H, d, $J_{1,2} = 3.6$ Hz, H-1), 4.44 (1H, t, $J = 3.6$ Hz, H-5), 4.08–4.01 (3H, m, H-6a, H-6b and –OC*H*$(CH_3)_2$), 1.24 (3H, d, $J = 6.0$ Hz, –OCH(C*H*$_3)_2$), 1.19 (3H, d, $J = 6.0$ Hz, –OCH(C*H*$_3)_2$), 0.84 (9H, s, –C(C*H*$_3)_3$), 0.03 (6H, s, –Si(C*H*$_3)_2$); δ_C (50 MHz, $CDCl_3$) 196.1 (C-4), 147.7 (C-3 and C-5′), 141.1 (C-2), 138.6 (C-2′), 127.5 (C-4′ and C-6′), 123.6 (C-3′ and C-7′), 91.7 (C-1), 75.7 (C-5), 71.2 (–O*C*H$(CH_3)_2$), 70.6 (C-1′), 62.5 (C-6), 25.7 (–C(*C*H$_3)_3$) 23.1, 21.7 (–OCH(*C*H$_3)_2$), 18.2 (–*C*$(CH_3)_3$), −5.46 (–Si(*C*H$_3)_2$; *m/z* (FABMS) 452 $[M+1]^+$, 434 $[M-OH]^+$, 392 $[M-OCH(CH_3)_2]^+$, 334, 318, 289, 266.

4.2.14. Isopropyl-6-*O*-(trimethylacetyl)-3-[hydroxy (4-nitrophenyl) methyl]-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (3′a). Solid, mp 122–24 °C. Eluent for column chromatography (30% ethyl acetate/hexane); [Found: C, 59.62; H, 6.41; N, 3.34. $C_{21}H_{29}NO_8$ requires C, 59.56; H, 6.90; N, 3.30%]; R_f (40% ethyl acetate/hexane) 0.47; $[\alpha]_D = +36.84$ (*c* 0.03, $CHCl_3$); ν_{max} (KBr) 3425, 3027, 2978, 1728 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 8.19 (2H, d, $J_{4',3' \text{ or } 6',7'} = 8.7$ Hz, H-4′ and H-6′), 7.57 (2H, d, $J_{3',4' \text{ or } 7',6'} = 8.5$ Hz, H-3′ and H-7′), 5.66 (1H, d, $J_{2,1} = 2.8$ Hz, H-2), 5.44 (1H, d, $J_{1',OH} = 6.5$ Hz, H-1′) 5.12, (1H, d, $J_{1,2} = 2.8$ Hz, H-1), 4.39 (1H, dd, $J_{6b,5} = 4.9$ Hz, $J_{6b,6a} = 12.2$ Hz, H-6b), 4.27 (1H, d, $J = 7.2$ Hz, H-4), 4.17 (1H, dd, $J_{6a,5} = 2.1$ Hz, $J_{6a,6b} = 12.2$ Hz, H-6a), 4.01 (1H, sept., $J = 6.0$ Hz, –OC*H*$(CH_3)_2$), 3.87 (1H, m, H-5), 1.23 (3H, d, $J = 6.1$ Hz, –OCH(C*H*$_3)_2$), 1.16 (3H, d, $J = 6.1$ Hz, –OCH(C*H*$_3)_2$), 1.11 (9H, s, –OCOC(C*H*$_3)_3$); δ_C (50 MHz, $CDCl_3$) 180.4 (–OCOC$(CH_3)_3$), 149.4 (C-5′), 147.7 (C-3), 141.6 (C-2′), 127.3 (C-4′ and C-6′), 126.8 (C-2), 123.9 (C-3′ and C-7′), 93.0 (C-1), 76.4 (C-5), 70.7 (–O*C*H$(CH_3)_2$), 70.4 (C-1′), 65.2 (C-4), 64.3 (C-6), 39.2 (–OCO*C*$(CH_3)_3$), 27.4 (–OCOC(*C*H$_3)_3$), 24.0, 22.1 (–OCH(*C*H$_3)_2$); *m/z* (FABMS) 422 $[M-1]^+$, 406 $[M-OH]^+$, 364 $[M-OCH(CH_3)_2]^+$, 346 $[M-18-OCH(CH_3)_2]^+$, 262, 244, 154.

4.2.15. Isopropyl-6-*O*-(trimethylacetyl)-3-(1-hydroxy decyl)-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (3′d). Solid, mp 55–56 °C. Eluent for column chromatography (18% ethyl acetate/hexane); [Found: C, 65.31; H, 10.55. $C_{24}H_{44}O_6 \cdot 1/2H_2O$ requires C, 65.86; H, 10.36%]; R_f (20% ethyl acetate/hexane) 0.37; $[\alpha]_D = +33.50$ (*c* 0.14, $CHCl_3$); ν_{max} (KBr) 3440, 2934, 1724, 1460, 1373 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 5.60 (1H, d, $J_{2,1} = 2.3$ Hz, H-2), 5.08 (1H, d, $J_{1,2} = 2.8$ Hz, H-1), 4.35–4.33 (2H, m, H-1′ and H-5), 4.21 (1H, d, $J = 6.3$ Hz, H-4), 4.20 (1H, m, H-6a), 4.01 (1H, dd, $J_{6b,5} = 6.0$ Hz, $J_{6b,6a} = 12.1$ Hz, H-6b), 3.99 (1H, m, –OC*H*$(CH_3)_2$), 1.71 (2H, m, H-2′), 1.26–1.22 (26H, m, –OCH(C*H*$_3)_2$, –OCOC(C*H*$_3)_3$ and H-3′ to H-9′), 1.17 (3H, d, $J = 6.0$ Hz, –OCH(C*H*$_3)_2$), 0.88 (3H, t, $J = 6.7$ Hz, H-10′); δ_C (50 MHz, $CDCl_3$) 179.6 (–OCOC$(CH_3)_3$), 142.4 (C-3), 124.5 (C-2), 92.8 (C-1), 76.7 (C-5), 71.0 (–O*C*H$(CH_3)_2$), 70.1 (C-1′), 65.7 (C-4), 64.5 (C-6), 39.3 (–OCO*C*$(CH_3)_3$), 35.1, 32.3, 30.0, 29.8, 29.7 (C-2′ to C-7′), 27.6 (–OCOC(*C*H$_3)_3$), 26.2 (C-8′), 24.1 (C-9′), 23.0, 22.1 (–OCH(*C*H$_3)_2$), 14.5 (C-10′); *m/z* (FABMS) 427 $[M-H]^+$, 411 $[M-H_2O+1]^+$, 369 $[M-OCH(CH_3)_2]^+$, 351, 267, 249.

4.2.16. Isopropyl-6-*O*-(trimethylacetyl)-3-[hydroxy (2-nitrophenyl) methyl]-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (3′f). Sticky oil. Eluent for column chromatography (25% ethyl acetate/hexane); [Found: C, 59.70; H, 6.88; N, 2.90. $C_{21}H_{29}NO_8$ requires C, 59.56; H, 6.90; N, 3.30%]; R_f (40% ethyl acetate/hexane) 0.49; $[\alpha]_D = -38.89$ (*c* 0.09, $CHCl_3$); ν_{max} (neat) 3428, 2925, 1721, 1349 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.88 (1H, d, $J_{4',5'} = 7.5$ Hz, H-4′), 7.87 (1H, d, $J_{7',6'} = 7.3$ Hz, H-7′), 7.67 (1H, t, $J_{6',7' \text{ or } 5'} = 7.3$ Hz, H-6′), 7.45 (1H, t, $J_{5',4' \text{ or } 6'} = 7.5$ Hz, H-4′), 6.03 (1H, brd, $J_{1',OH} = 5.8$ Hz, H-1′), 5.52 (1H, br s, H-2), 5.05 (1H, d, $J_{1,2} = 2.8$ Hz, H-1), 4.43 (1H, dd, $J_{6a,5} = 4.7$ Hz, $J_{6a,6b} = 12.1$ Hz, H-6a), 4.19 (1H, dd, $J_{6b,5} = 2.0$ Hz, $J_{6b,6a} = 12.2$ Hz, H-6b), 4.12 (1H, d, $J = 7.1$ Hz, H-4), 4.06–3.89 (2H, m, H-5 and –OC*H*$(CH_3)_2$), 1.24 (3H, d, $J = 6.4$ Hz, –OCH(C*H*$_3)_2$), 1.20 (3H, d, $J = 6.3$ Hz, –OCH(C*H*$_3)_2$), 1.14 (9H, s, –OCOC(C*H*$_3)_3$); δ_C (50 MHz, $CDCl_3$) 180.2 (–O*C*OC$(CH_3)_3$), 148.7 (C-3), 140.5 (C-3′), 136.5 (C-2′), 133.5 (C-4′), 129.6 (C-6′), 129.0 (C-5′), 126.3 (C-2), 125.0 (C-7′), 92.9 (C-1), 72.2 (C-5), 70.4 (C-1′ and –O*C*H$(CH_3)_2$), 65.1 (C-4), 64.3 (C-6), 39.3 (–OCO*C*$(CH_3)_3$), 27.5 (–OCOC(*C*H$_3)_3$), 24.0, 22.1 (–OCH(*C*H$_3)_2$); *m/z* (FABMS) 424 $[M+1]^+$, 364 $[M-OCH(CH_3)_2]^+$, 346 $[M-H_2O-OCH(CH_3)_2]^+$, 265, 244, 202.

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