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Note

DBU assisted expeditious synthesis of glycosyl dienes via glycosylated β-hydroxy esters☆

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Abstract—DBU catalyzed condensation of 3-*O*-benzyl(methyl)-5,6-dideoxy-1,2-*O*-isopropylidene-β-L-*threo*-hept-4-enofuranuronates with different aldehydes produces the corresponding 3-*O*-benzyl(methyl)-6-carbethoxy-5,6-dideoxy-1,2-*O*-isopropylidene-7-phenyl-β-L-*threo*-hept-4-enofuranoses. The latter on treatment with methanesulfonyl chloride followed by DBU catalyzed E2 reaction of the methanesulfonyloxy intermediates gave the respective 3-*O*-benzyl(methyl)-6-carbethoxy-5,6,7-trideoxy-1,2-*O*-isopropylidene-7-phenyl-β-L-*threo*-hept-4,6-dienofuranose in moderate to good yields.

Keywords: DBU; Aldol type condensation; Glycosyl uronates; Glycosyl dienes

Conjugated butadienes are not only synthetically important intermediates for many cycloaddition reactions but also biologically important structural units in most naturally occurring molecules and synthetic polymers.[1–3] C-Glycosyl compounds as chiral building blocks have been used for the synthesis of many antibiotics and other compounds of great medicinal value.[4] The enantioselective cycloaddition reactions have generally been achieved either by use of chiral catalyst[5] or by chiral dienophile.[6] In addition to the reports for the synthesis of chiral dienes,[7–10] their application in such reactions is noticed rarely primarily due to their difficult synthesis or low yields. Synthesis of glycosyl dienes and their applications in many cycloaddition reactions for the synthesis of a variety of compounds have received much attention recently.[11,12] Encouraged by the above reports we were interested to synthesize glycosyl dienes wherein the diene fragment is at C-4 of the glycofuranose ring. The β,γ-unsaturated glycosyl uronates[13] on aldol type condensation followed by methanesulfonylation of the hydroxyl group and subsequent E2 reaction resulted in the required glycosyl dienes. The method is very simple as it involves the use of inexpensive reagents and very simple workup procedure. All the three reactions in the synthesis viz. isomerisation, condensation and elimination are catalyzed by a single base DBU. To the best of our knowledge this is the first approach to synthesize glycosyl dienes by aldol type condensation followed by elimination.

The synthetic strategy is shown in Scheme 1. The β,γ-unsaturated glycosyl uronates (**2a** and **2b**) were obtained on heating α,β-unsaturated glycosyl uronates (**1a** and **1b**)[14] with DBU (25 mol %), in dry THF at 80 °C for 5 h as reported by us earlier.[13] The uronates (**2a** and **2b**) have the *Z* geometry and were characterized on the basis of their physical data and microanalysis. The disappearance of H-4 signals (at δ 4.20 and 4.15 in **1a** and **1b**, respectively) and appearance of triplets at δ 4.84 ($J = 6.9$ Hz) and 4.81 ($J = 7.0$ Hz) for H-5 in the ^{1}H NMR spectral data of compounds **2a** and **2b**, respectively; and appearance of dd at δ 3.22 ($J = 6.9$, 2.1 Hz) and 3.18 ($J = 7.0$, 2.0 Hz) for H-6 along with other usual signals in the above compounds **2a** and **2b**, respectively, evidenced the migration of double bond from α,β- to β,γ-position. In the ^{13}C NMR spectra of **2a** and **2b**, the signals for C-4 appeared at δ 153.8, 153.6; C-5 at δ

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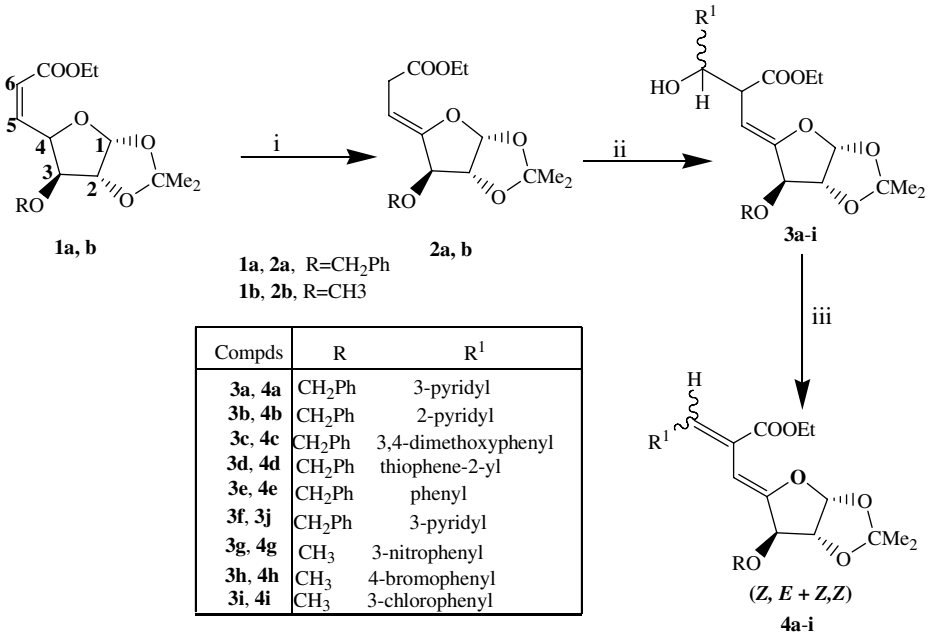

Compds	R	R^1
3a, **4a**	CH_2Ph	3-pyridyl
3b, **4b**	CH_2Ph	2-pyridyl
3c, **4c**	CH_2Ph	3,4-dimethoxyphenyl
3d, **4d**	CH_2Ph	thiophene-2-yl
3e, **4e**	CH_2Ph	phenyl
3f, **3j**	CH_2Ph	3-pyridyl
3g, **4g**	CH_3	3-nitrophenyl
3h, **4h**	CH_3	4-bromophenyl
3i, **4i**	CH_3	3-chlorophenyl

Scheme 1. Reagents and conditions: (i) THF, DBU, 80–90 °C, 5 h; (ii) R^1CHO, DBU; 0–30 °C; (iii) (a) $MeSO_2Cl$, CH_2Cl_2, 0 °C, 0.5–1.0 h; (b) DBU, toluene, reflux, 3–4 h.

97.6, 97.4 while those of C-6 appeared at δ 31.4 and 31.3, respectively. The *Z* geometry of the double bond in compounds **2a** and **2b** was evidenced by NOE experiments. The above glycosyl uronates **2a** and **2b** were reacted with different aldehydes (Scheme 1) separately at 0–30 °C in the presence of DBU (50 mol %) for different interval of time to yield the respective glycosyl β-phenyl-β-hydroxy esters **3a**–**i**. In the above reaction it was observed that aromatic aldehydes with electron-withdrawing substituents gave better yields of β- hydroxy esters than those with electron donating substituents. Heteroaromatic aldehydes viz. 2-pridyl-, 3-pyridyl- and thiophene-2-carboxaldehydes also gave good yields of the respective β-hydroxy esters. Compounds **3a**–**i** were characterized on the basis of their IR, MS, ^1H, ^{13}C NMR spectral data and microanalysis. Due to the diastereoisomeric nature of the compounds (**3a**–**i**), duplicity in many ^{13}C and ^1H NMR signals were observed.

It is interesting to note that the above reaction of α,β-unsaturated glycosyl uronates **1a** and **1b**, with the aldehydes in the presence of DBU did not lead to any Baylis Hilmann adduct, instead we got the isomerized esters **2a** and **2b** along with the respective aldol products in very low yields even after 36 h.

In the next step, the glycosyl β-aryl-β-hydroxy esters **3a**–**i** were converted into their respective *O*-(methanesulfonyl) derivatives by treatment with methanesulfonyl chloride in anhydrous dichloromethane in the presence of triethylamine. The crude intermediate methanesulfonyloxy derivatives were isolated in quantitative yields and used as such (these compounds were not stable even at room temperature for a long time) for further reaction. Finally, these intermediate methanesulfonyloxy derivatives were refluxed in toluene in presence of DBU (100 mol %) to give the respective glycosyl dienes **4a**–**i** (Scheme 1) in moderate to good yields (Table 1) and were characterized on the basis of their spectroscopic data and microanalysis. The glycosyl dienes were a mixture of two geometrical isomers (*ZZ* and *ZE*), which was evidenced on the basis of their ^1H NMR spectral data and NOE experiments. The FABMS of compound **4a** showed a $(M+H)^+$ ion at *m*/*z* 438 while its IR spectrum exhibited absorption band at 1729 cm^{-1} indicating the presence of a conjugated carbethoxy group. In the ^1H NMR spectrum of the above compound, the olefinic proton H-7 appeared as a singlet at δ 6.85 while H-5 was observed as two distinct singlets at δ 5.46 and 5.33, respectively, indicating the presence of the two geometrical isomers (*ZZ* and *ZE*). The anomeric proton (H-1) was also observed as two doublets at δ 6.21 and 6.00 having coupling constant of 3.0 Hz due to the presence of two geometrical isomers *ZZ*

Table 1. Synthesis of glycosyl dienes from β hydroxyl esters

Entry	Diene	Yield (%)	Reaction time (h)	*ZE*/*ZZ* (ratio)
1	**4a**	36	3.0	11/9
2	**4b**	50	1.5	99/1
3	**4c**	40	3.0	50/50
4	**4d**	41	3.0	45/55
5	**4e**	42	3.0	50/50
6	**4f**	40	4.0	80/20
7	**4g**	48	2.5	60/40
8	**4h**	35	3.0	60/40
9	**4i**	45	3.0	80/20

and *ZE*. The ratio of two geometrical isomers was determined on the basis of the integration of H-1 signal in the two isomers and it was found to be 11:9. In the NOE experiments with **4a**, irradiation of H-5 (major isomer) signal resulted in an enhancement of the intensity of H-3 and H-7, indicating a *ZZ* geometry of the double bonds in the major isomer while irradiation of H-5 (minor isomer) signal did not show any NOE with H-7 indicating a *ZE* geometry of the diene. Similarly, all other compounds were characterized. In the ^{13}C NMR spectrum of these glycosyl dienes, duplicity of anomeric carbon (C-1) and some other carbons was observed due to the presence of two geometrical isomers.

In conclusion we have developed a new and simple method for the syntheses of glycosyl dienes involving DBU catalyzed aldol type reaction of β,γ-unsaturated glycosyl uronates with aldehydes and subsequent E2 reaction.

1. Experimental

1.1. General methods

Commercially available reagent grade chemicals were used as received. All reactions were followed by TLC on E. Merck Kieselgel 60 F_{254}, with detection by UV light and/or spraying with 20% H_2SO_4 in EtOH and heating. Column chromatography was performed on Silica Gel (230–400 mesh, E. Merck). IR spectra were recorded as thin films or neat chloroform solution with a Perkin–Elmer Spectrum RX-1 (4000–450 cm^{-1}) spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded on a Brucker DRX-300 in (*D*) chloroform, shift values are in ppm relative to $SiMe_4$ as internal reference, unless otherwise stated; signals are reported as s (singlet), d (doublet), t (triplet), m (multiplet); *J* in hertz. Fast atom bombardment mass spectra (FABMS) were performed by the Mass Spectrometer with a Jeol SX-102 equipment. Elemental analyses were performed on a Perkin–Elmer 2400 II elemental analyzer. The optical rotations were measured in a 1.0 dm tube with a Rudolf Autopol III polarimeter in chloroform. Solvents were dried and stored over activated 4 Å molecular sieve.

1.2. (4*Z*) Ethyl (3-*O*-benzyl-1,2-*O*-isopropylidene-β-L-*threo*)-hept-4-enofuranuronate (2a)

To a magnetically stirred soln of the above compound **1a** (1.2 g, 3.44 mmol) in THF (6.0 mL), DBU (0.13 mL, 25 mol %) was added and the reaction mixture was stirred at 80 °C for 5 h. The reaction mixture was cooled and the solvent evaporated under diminished pressure to give a crude product. The latter was dissolved in EtOAc (2 × 25 mL) and washed with water (2 × 5 mL), the organic layer was dried (Na_2SO_4) and evaporated under diminished pressure to give a crude syrup (1.30 g). The crude product, thus obtained, was chromatographed over silica gel (230–400 mesh) using 9:1 hexane–EtOAc as eluant to give **2a** (1.0 g, 84%) as a colourless oil; $[\alpha]_D$ +35 (*c* 0.10, $CHCl_3$); IR (neat): 1730, 1600 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 7.34–7.28 (m, 5H, Ar*H*), 6.10 (d, *J* 3.2 Hz, H-1), 4.84 (t, *J* 6.9 Hz, 1H, H-5), 4.71, 4.51 (d, *J* 11.8 Hz, 2H, CH_2Ph), 4.45 (d, *J* 3.2 Hz, 1H, H-2), 4.25 (s, 1H, H-3) 4.16 (q, 2H, *J* 7.2 Hz, OCH_2), 3.22 (dd, *J* 6.9, 2.1 Hz, 2H, H-6), 1.45, 1.30 (s, 6H, C*Me*$_2$), 1.23 (t, *J* 7.2 Hz, 3H, Me); ^{13}C NMR (50 MHz, $CDCl_3$): δ 172.1 (C=O), 153.8 (C–4), 137.6, 128.9, 128.3, 128.2, 127.9, 127.4 (Ar*C*), 114.2 (*C*Me$_2$), 107.1 (C-1), 97.6 (C-5), 83.6, 80.7 (C-2, C-3), 70.5 (O*C*H$_2$Ph), 61.0 (O*C*H$_2$), 31.1 (C-6), 28.3, 27.6 (C*Me*$_2$), 14.6 (Me); FABMS: $m/z = 349$ $[M+H]^+$. Anal. Calcd for $C_{19}H_{24}O_6$: C, 65.51; H, 6.89. Found: C, 65.22; H, 6.62.

1.3. (4*Z*) Ethyl (1,2-*O*-isopropylidene-3-*O*-methyl-β-L-*threo*)-hept-4-enofuranuronate (2b)

From **1b** (1.2 g, 4.83 mmol) as a colourless oil; (1.10, 91%) $[\alpha]_D^{27}$ +32 (*c* 0.10, $CHCl_3$); IR (neat): 1728, 1616 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 6.04 (d, *J* 3.2 Hz, H-1), 4.81 (t, *J* 7.0 Hz, 1H, H-5), 4.50 (d, *J* 3.2 Hz, 1H, H-2), 4.05 (s, 1H, H-3), 4.14 (q, *J* 7.2, 2H, OCH_2), 3.34 (s, 3H, OMe), 3.18 (dd, *J* 7.0, 2.0 Hz, 2H, H-6), 1.47, 1.30 (s, 6H, C*Me*$_2$), 1.23 (t, *J* 7.2 Hz, 3H, Me); ^{13}C NMR (50 MHz, $CDCl_3$): δ 172.1 (C=O), 153.6 (C–4), 114.2 (*C*Me$_2$), 107.0 (C-1), 97.4 (C-5), 83.3, 80.1 (C-2, C-3), 61.9 (O*C*H$_2$), 31.3 (C-6), 28.3, 27.6 (C*Me*$_2$), 14.5 (Me); FABMS: $m/z = 273$ $[M+H]^+$. Anal. Calcd for $C_{13}H_{20}O_6$: C, 54.58; H, 7.47. Found: C, 54.23; H, 7.28.

1.4. (4*Z*) 3-*O*-Benzyl-6-carbethoxy-5,6-dideoxy-1,2-*O*-isopropylidene-7-(3-pyridyl)-β-L-*threo*)-hept-4-enofuranose (3a)

To a magnetically stirred soln of compound **2a** (1.0 g, 2.87 mmol) in dry THF (5.0 mL) at 0 °C, 3-pyridylcarboxaldehyde (0.3 mL 3.16 mmol) and DBU (0.21 mL, 50 mol %) were added sequentially. The reaction mixture was stirred for 30 min at 0 °C followed by an additional 9 h at ambient temperature. The solvent evaporated and the residue was partitioned between EtOAc and water. EtOAc layer was separated, dried (Na_2SO_4) and evaporated under diminished pressure to give a crude mass, which was chromatographed over SiO_2 (240–400 mesh) using a gradient of hexane–EtOAc (9:1→4:1) to give compound **3a** as a colourless viscous syrup (1.10 g, 85%); $[\alpha]_D^{27}$ −29 (*c* 0.10, $CHCl_3$); IR (neat): 3397, 1726 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.57 (d, *J* 14.7 Hz, 1H, Py*H*), 8.44 (s, 1H,

PyH), 7.79–7.72 (m, 1H, PyH), 7.41–7.15 (m, 6H, Py*H*, Ar*H*), 6.08, 5.97 (each d, *J* 3.3 and 2.7 Hz, 1H, H-1), 5.01 (m, 1H, H-7), 4.64–4.57 (m, 1H, H-5), 4.47–4.37 (m, 2H, OCH_2Ph), 4.23–4.01 (m, 4H, H-2, OCH_2, H-3), 3.89–3.68 (m, 1H, H-6), 2.05 (br s, 1H, O*H*), 1.39, 1.37 (s, 6H, CMe_2), 1.20 (t, *J* 8.7 Hz, 3H, Me); ^{13}C NMR (50 MHz, $CDCl_3$): δ 173.5, 173.1 (*C*=O), 156.0, 155.0 (C-4), 149.5, 148.9, 137.5, 137.4, 135.0, (Py*C*), 128.9, 128.2, 128.1, 123.7, 123.4 (Ar*C*), 114.4, 114.3 (*C*Me_2), 107.3 (C-1), 98.9, 98.4 (C-5), 83.4, 80.7 (C-2, C-3), 73.7 (C-7), 70.5, 70.1 (O*C*H_2Ph), 61.5 (O*C*H_2), 50.3, 50.1 (C-6), 28.2, 27.9, 27.7, 27.3 (C*Me*$_2$), 14.4 (Me); FABMS: $m/z = 456$ $[M+H]^+$. Anal. Calcd for $C_{25}H_{29}O_7N$: C, 65.93; H, 6.15; N, 3.07. Found: C, 65.80; H, 6.10; N, 3.10.

1.5. (4*Z*) 3-*O*-Benzyl-6-carbethoxy-5,6-dideoxy-7-hydroxy-1,2-*O*-isopropylidene-7-(2-pyridyl)-β-L-*threo*-hept-4-enofuranose (3b)

From **2a** (1.0 g, 2.87 mmol) as a colourless viscous syrup (1.05 g, 82%); $[\alpha]_D^{27}$ −40 (*c* 0.10, $CHCl_3$); IR (neat): 3449, 1722 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.53–8.42 (m, 1H, Py*H*), 7.67–7.17 (m, 8H, Py*H*, Ar*H*), 5.94, 5.84 (each d, *J* 3.0 and 2.8 Hz, 1H, H-1), 5.28–5.00 (m, 1H, H-7), 4.84–4.60 (m, 1H, H-5), 4.50–4.24 (m, 2H, PhCH_2), 4.21–4.04 (m, 4H, H-2, OCH_2, H-3), 3.70–3.65 (m, 1H, H-6), 2.26 (br s, 1H, O*H*), 1.37 and 1.32 (each s, each 3H, CMe_2), 1.13 (t, $J = 6.8$ Hz, 3H, Me); ^{13}C NMR (50 MHz, $CDCl_3$): δ 172.8 (*C*=O), 154.6, 154.1 (C-4), 148.7, 148.1, 137.6, 136.9 (Py*C*), 128.8, 128.2 (ArC), 123.0, 121.8, (Ar*C*, Py*C*), 114.3 (*C*Me_2), 107.3, 107.0 (C-1), 99.7, 98.1 (C-5), 83.5, 80.6 (C-2, C-3), 73.4 (C-7), 70.4 (O*C*H_2Ph), 61.4, 61.1 (O*C*H_2Me), 50.2, 49.3 (C-6), 28.2, 27.6 (C*Me*$_2$), 14.5 (Me); FABMS: $m/z = 456$ $[M+H]^+$. Anal. Calcd for $C_{25}H_{29}O_7N$: C, 65.93; H, 6.15; N, 3.07. Found: C, 65.90; H, 6.12; N, 3.11.

1.6. (4*Z*) 3-*O*-Benzyl-6-carbethoxy-5,6-dideoxy-7-hydroxy-1,2-*O*-isopropylidene-7-(3,4-dimethoxyphenyl)-β-L-*threo*-hept-4-enofuranose (3c)

From **2a** (1.0 g, 2.87 mmol) as a colourless viscous syrup (1.21 g, 83%); $[\alpha]_D^{27}$ −37 (*c* 0.10, $CHCl_3$); IR (neat): 3469, 1725 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.36–7.26 (m, 5H, Ar*H*), 7.11–7.01 (m, 3H, Ar*H*), 6.07, 5.99 (each d, *J* 3.4 Hz, 1H, H-1), 4.96–4.89 (m, 1H, H-7), 4.69–4.50 (m, 1H, H-5), 4.50–4.40 (m, 3H, PhCH_2, H-2), 4.20 (*q*, *J* 7.2 Hz, 2H, OCH_2), 4.09 (s, 1H, H-3), 3.86, 3.71 (s, 3H, OMe), 3.90 (m, 1H, H-6), 2.06 (br s, 1H, –O*H*), 1.41, 1.39 (s, 6H, CMe_2), 1.19 (t, *J* 7.2 Hz, 3H, OCH$_2$*Me*); ^{13}C NMR (50 MHz, $CDCl_3$): δ 173.7, 173.5 (C=O), 154.5, 154.1 (C-4), 137.4, 134.3, 128.8, 128.7, 128.2, 128.1, 120.0, 119.4 (Ar*C*), 114.3 (*C*Me_2), 107.3 (C-1), 98.3 (C-5), 83.5, 80.7 (C-2, C-3), 75.3 (C-7), 70.2 (O*C*H_2Ph), 61.2 (O*C*H_2Me), 56.1, 55.9 (OMe), 50.5, 50.1 (C-6), 28.2, 27.3 (C*Me*$_2$), 14.5 (Me); FABMS: $m/z = 515$ $[M+H]^+$. Anal. Calcd for $C_{28}H_{34}O_9$: C, 65.36; H, 6.61. Found: C, 65.30; H, 6.60.

1.7. (4*Z*) 3-*O*-Benzyl-6-carbethoxy-5,6-dideoxy-7-hydroxy-1,2-*O*-isopropylidene-7-(thiophene-2-yl)-β-L-*threo*-hept-4-enofuranose (3d)

From **2a** (1.0 g, 2.87 mmol) as a colourless viscous syrup (1.03 g, 78%); $[\alpha]_D^{27}$ −25 (*c* 0.10, $CHCl_3$); IR (neat): 3470, 1722 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.36–7.17 (m, 5H, ArH), 7.03 (d, *J* 3.2 Hz, 1H, Thioph*H*), 6.96–6.88 (m, 2H, Thioph*H*), 6.08, 6.06 (each d, *J* 3.0 Hz, 1H, H-1), 5.23–5.16 (m, 1H, H-7), 4.72–4.59 (m, 1H, H-5), 4.40, 4.25 (d, *J* 12.4 Hz, 2H, PhCH_2), 4.16 (d, *J* 3.0 Hz, 1H, H-2), 4.13 (q, *J* 7.2, 2H, OCH_2Me), 4.00 (s, 1H, H-3), 3.69 (m, 1H, H-6), 2.06 (br s, 1H, O*H*), 1.39, 1.35 (s, 6H, CMe_2), 1.22 (t, *J* 7.2 Hz, 3H, Me); ^{13}C NMR (50 MHz, $CDCl_3$): δ 173.2 (C=O), 154.7 (C-4), 137.5, 128.8, 128.7, 128.2, 128.1, 126.9, 125.4, 125.1, 124.9, 124.6 (Ar–*C*, Thioph*C*), 114.3 (*C*Me_2), 107.4 (C-1), 99.4 (C-5), 83.5, 80.6 (C-2, C-3), 71.8 (C-7), 70.3 (O*C*H_2Ph), 61.3 (O*C*H_2Me), 50.3, (C-6), 28.3, 27.6 (C*Me*$_2$), 14.5 (Me); FABMS: $m/z = 461$ $[M+H]^+$. Anal. Calcd for $C_{24}H_{28}O_7S$: C, 62.60; H, 6.08. Found: C, 62.61; H, 6.03.

1.8. (4*Z*) 3-*O*-Benzyl-6-carbethoxy-5,6-dideoxy-7-hydroxy-1,2-*O*-isopropylidene-7-phenyl-β-L-*threo*-hept-4-enofuranose (3e)

From **2a** (1.0 g, 2.87 mmol) as a colourless viscous syrup (1.10 g, 85%); $[\alpha]_D^{27}$ −16 (*c* 0.10, $CHCl_3$); IR (neat): 3470, 1722 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.41–7.11 (m, 10H, Ar*H*), 6.09, 6.00 (each d, *J* 3.2, 2.8 Hz, 1H, H-1), 5.22–5.16 (m, 1H, H-7), 4.99–4.67 (m, 1H, H-5), 4.69 (m, 2H, PhCH_2), 4.40 (d, *J* 3.0 Hz, 1H, H-2), 4.19 (m, 2H, OCH_2Me), 4.00 (s, 1H, H-3), 3.71, 3.69 (m, 1H, H-6), 2.06 (br s, 1H, OH), 1.41, 1.39 and 1.35,1.30 (s, 6H, CMe_2), 1.19 (t, *J* 7.0 Hz, 3H, Me); FABMS: $m/z = 455$ $[M+H]^+$. Anal. Calcd for $C_{26}H_3O_7$: C, 68.72; H, 6.60. Found: C, 68.69; H, 6.78.

1.9. (4*Z*) 6-Carbethoxy-5,6-dideoxy-7-hydroxy-1,2-*O*-isopropylidene-3-*O*-methyl-7-(3-pyridyl)-β-L-*threo*-hept-4-enofuranose (3f)

From **2b** (1.0 g, 2.87 mmol) as a colourless viscous syrup (1.20 g, 87%); $[\alpha]_D^{27}$ −60 (*c* 0.10, $CHCl_3$); IR (neat): 3469, 1729 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.59–8.46 (m, 2H, Py*H*), 7.72 (d, *J* 8.0 Hz, Py*H*), 7.30–7.20 (m, 1H, Py*H*), 6.01, 5.89 (each d, *J* 3.0 and 2.8 Hz, 1H, H-1), 5.30–5.19 (m, 1H, H-7), 4.82–4.60 (m, 1H, H-5), 4.46–4.39 (m, 1H, H-2), 4.16–4.09 (m, 2H, OCH_2Me), 3.94, 3.92 (each s, each 1H, H-3), 3.70–3.65 (m, 1H,

H-6), 3.32, 3.13 (s, 3H, OMe), 2.90 (br s, 1H, OH), 1.40, 1.35 (s, 6H, C*Me*$_2$), 1.16 (m, 3H, Me). ^{13}C NMR (50 MHz, $CDCl_3$): δ 173.8, 173.5 (C=O), 155.5, 154.8 (C-4), 149.3, 148.7, 137.5, 134.7, 123.7 (Py-C), 114.4 (C*Me*$_2$), 107.1 (C-1), 98.5 (C-5), 83.1, 82.8 (C-2, C-3), 73.6, 73.2 (C-7), 61.5 (O*C*H$_2$Me), 56.5 (OMe), 52.4, 50.2 (C-6), 28.2, 27.9, 27.5, 27.3 (C*Me*$_2$), 14.4 (Me); FABMS: $m/z = 380$ $[M+H]^+$. Anal. Calcd for $C_{19}H_{25}O_7N$: C, 60.15; H, 6.59; N, 3.69. Found: C, 60.11; H, 6.60; N, 3.65.

1.10. (4*Z*) 6-Carbethoxy-5,6-dideoxy-7-hydroxy-1,2-*O*-isopropylidene-3-*O*-methyl-7-(3-nitrophenyl)-β-L-*threo*-hept-4-enofuranose (3g)

From **2b** (1.0 g, 3.67 mmol) as a colourless viscous syrup (1.50 g, 97%); $[\alpha]_D^{27}$ −50 (*c* 0.10, $CHCl_3$); IR (neat): 3433, 1720 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.23 (s, 1H, Ar*H*), 8.14 (d, *J* 5.4 Hz, 1H, Ar*H*), 7.84 (t, *J* 8.0 Hz, 1H, Ar*H*), 7.62 (d, *J* 8.0 Hz, Ar*H*), 6.01, 5.87 (each d, *J* 2.8 Hz, 1H, H-1), 5.26–4.94 (m, 1H, H-7), 4.81–4.58 (m, 1H, H-5), 4.39 (d 2.8 Hz, 1H, H-2), 4.04 (*q*, *J* 7.2 Hz, 2H, OCH$_2$), 3.63 (s, 1H, H-3), 3.37 (s, 3H, OCH$_3$), 3.03–2.84 (m, 1H, H-6), 2.90 (br s, 1H, O*H*), 1.28, 1.20 (s, 6H, C*Me*$_2$), 1.16 (t, *J* 7.2 Hz, Me); ^{13}C NMR (50 MHz, $CDCl_3$): δ 172.7, 172.3 (C=O), 148.3 (C-4), 133.8, 133.5, 132.9, 129.2, 129.1, 118.9 (Ar*C*), 114.0 (CMe$_2$), 106.9, 106.8 (C-1), 98.9 (C-5), 83.1, 82.7 (C-2, C-3), 74.6, 74.3 (C-7), 61.0 (O*C*H$_2$), 56.2 (Me), 52.2, 51.3 (C-6), 28.1, 27.9 (C*Me*$_2$), 14.4 (Me); FABMS: *m*/*z* 424 $[M+H]^+$. Anal. Calcd for $C_{20}H_{25}O_9N$: C, 56.73; H, 5.91; N, 3.30. Found: C, 56.68; H, 5.90; N, 3.38.

1.11. (4*Z*) 6-Carbethoxy-5,6-dideoxy-7-hydroxy-1,2-*O*-isopropylidene-3-*O*-methyl-7-(4-bromophenyl)-β-L-*threo*-hept-4-enofuranose (3h)

From **2b** (1.0 g, 3.67 mmol) as a colourless syrup (1.14 g, 86%); $[\alpha]_D^{27}$ −37 (*c* 0.10, $CHCl_3$); IR (neat): 3481, 1731 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44–7.25 (m, 2H, Ar*H*), 7.24–7.20 (m, 2H, Ar*H*), 5.99, 5.92 (each d, *J* 3.6 Hz, 1H, H-1), 5.13–5.09 (m, 1H, H-7), 4.75, 4.54 (each d, *J* 10.6 Hz, 1H, H-5), 4.40 (d, *J* 3.6 Hz, 1H, H-2), 3.99 (s, 1H, H-3), 3.68 (*q*, *J* 7.2 Hz, 2H, OC*H*$_2$), 3.48–3.43 (m, 1H, H-6), 3.31, 3.25 (each s, each 3H, OMe), 2.90 (br s, 1H, O*H*), 1.39, 1.35, (s, 6H, C*Me*$_2$), 1.19 (t, *J* 7.2 Hz, Me). ^{13}C NMR (50 MHz, $CDCl_3$): δ 173.7 (C=O), 155.3, 154.4 (C-4), 140.5, 131.5, 131.3, 128.6, 128.4, 121.5 (Ar*C*), 114.1 (CMe$_2$), 107.0 (C-1), 98.7, 97.1 (C-5), 83.0, 82.2 (C-2, C-3), 75.0, 73.0 (C-7), 66.0 (O*C*H$_2$Me), 56.4 (O*Me*), 50.1, 49.6 (C-6), 27.7, 27.1 CMe$_2$, 15.4 (Me); FABMS: $m/z = 458$ $[M+H]^+$. Anal. Calcd for $C_{20}H_{25}O_7Br$: C, 52.51; H, 5.47. Found: C, 52.50; H, 5.42.

1.12. (4*Z*) 6-Carbethoxy-5,6-dideoxy-7-hydroxy-1,2-*O*-isopropylidene-3-*O*-methyl-7-(3-chlorophenyl)-β-L-*threo*-hept-4-enofuranose (3i)

From **2b** (1.0 g, 3.67 mmol) as a colourless oil (1.36 g, 90%); $[\alpha]_D^{27}$ −15 (*c* 0.10, $CHCl_3$); IR (neat): 3448, 1723 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.36 (s, 1H, Ar*H*), 7.26–7.22 (m, 3H, Ar*H*), 6.01, 5.94 (each d, *J* 3.2 Hz, 1H, H-1), 5.12–4.91 (m, 1H, H-7), 4.74–4.59 (m, 1H, H-5), 4.45–4.40 (m, 1H, H-2), 4.18–4.07 (m, 2H, OCH$_2$Me), 3.98 (s, 1H, H-3), 3.95–3.89 (m, 1H, H-6), 3.35 (s, 3H, OMe), 2.90 (br s, 1H, –OH), 1.40, 1.33 (s, 6H, C*Me*$_2$), 1.16 (t, *J* 7.0 Hz, 3H, Me). ^{13}C NMR (50 MHz, $CDCl_3$): δ 173.2 (C=O), 155.1, 154.2 (C-4), 140.5, 131.5, 131.3, 128.6, 128.4, 121.5 (Ar*C*), 114.0 (*C*Me$_2$), 106.9 (C-1), 98.6, 97.3 (C-5), 83.0, 82.1 (C-2 and C-3), 74.6, 73.0 (C-7), 66.1 (OCH$_2$Me), 56.6 (OMe), 50.3, 49.4 (C-6), 27.7, 27.2 (C*Me*$_2$), 15.2 (Me); FABMS: *m*/*z* 414 $[M+H]^+$. Anal. Calcd for $C_{20}H_{25}O_7Cl$: C, 58.11; H, 6.05. Found: C, 58.10; H, 6.02.

1.13. (4-*Z*,6-*E*/*Z*) 3-*O*-Benzyl-6-carbethoxy-5,6,7-trideoxy-1,2-*O*-isopropylidene-7-(3-pyridyl)-β-L-*threo*-hept-4,6-dienofuranose (4a)

To a magnetically stirred soln of compound **3a** (0.5 g, 1.10 mmol) and triethylamine (1 mL) in CH_2Cl_2 (5 mL) at 0 °C, methanesulfonyl chloride (0.14 mL, 1.21 mmol) was slowly added and the reaction continued for 1 h till the disappearance of the starting material (TLC). The solvent was evaporated and the residue thus obtained was filtered on flash silica gel to give the intermediate methanesulfonyloxy derivative (0.40 g) which was used in the next step. A soln of the above methanesulfonyloxy derivative and DBU (0.17 mL, 100 mol %) in anhydr toluene (5 mL) was refluxed at 130 °C for 3 h. The reaction mixture was cooled, the solvent evaporated and the residue was dissolved in EtOAc (2 × 25 mL) and washed with water (2 × 12.5 mL). The organic layer was dried (Na_2SO_4) and evaporated under diminished pressure to give a residual mass (0.35 g) which was chromatographed over SiO_2 column using a gradient of hexane–EtOAc (19:1→9:1) to give **4a** (0.18 g, 36%) as a colourless foam; $[\alpha]_D^{27}$ −50 (*c* 0.10, $CHCl_3$); IR (neat): 1729 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.63–8.52 (m, 3H, Py*H*), 7.82–7.45 (m, 6H, Py*H*, Ar*H*), 6.85 (s, 1H, H-7), 6.21, 6.00 (d, *J* 3.0 Hz, 1H, H-1), 5.46, 5.33 (s, 1H, H-5), 4.98 (d, *J* 11.2 Hz, 1H, C*H*$_2$Ph), 4.87 (d, *J* 3.0 Hz, 1H, H-2), 4.77 (d, *J* 11.2 Hz, 1H, C*H*$_2$Ph), 4.60 (s, 1H, H-3), 4.35 (q, *J* 7.2 Hz, 2H, OC*H*$_2$), 1.62 and 1.51 (s, 6H, C*Me*$_2$), 1.32 (t, *J* 7.2 Hz, 3H, Me); ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.1 (C=O), 154.4 (C-4), 148.7, 148.4 (C-6), 137.4, 136.8, 132.4, 132.3 (PyC), 130.7, 128.9, 128.9, 128.4, 128.3, 123.4 (Py*C*), 127.6 (ArC), 115.3 (*C*Me$_2$), 108.6 (C-1), 102.8 (C-7), 96.1 (C-

5), 82.8, 82.1 (C-2, C-3), 71.0 (O*C*H$_2$Ph), 61.8 (O*C*H$_2$), 28.2, 27.6 (2 × Me), 14.6 (*Me*); FABMS: $m/z = 438$ [M+H]$^+$. Anal. Calcd for $C_{25}H_{27}O_6N$: C, 68.64; H, 5.94; N, 3.20. Found: C, 68.62; H, 5.90; N, 3.10.

1.14. (4-*Z*,6-*E*/*Z*) 3-*O*-Benzyl-6-carbethoxy-5,6,7-trideoxy-1,2-*O*-isopropylidene-7-(2-pyridyl)-β-L-*threo*-hept-4,6-dienofuranose (4b)

From **3b** (0.5 g, 1.10 mmol) as a colourless foam (0.20 g, 50%); $[\alpha]_D^{27}$ −14 (*c* 0.10, $CHCl_3$); IR (neat): 1728 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.50 (d, *J* 4.0 Hz, 1H, Py*H*), 7.58 (m, 1H, Py*H*), 7.38, 7.08 (m, 7H, ArH, PyH), 6.70 (s, 1H, H-7), 6.22 (d, *J* 3.2 Hz, 1H, H-1), 5.28 (s, 1H, H-5), 4.73–4.48 (m, 4H, OCH$_2$Ph, H-2, H-3), 4.39–4.33 (q, *J* 7.2 Hz, OC*H*$_2$Me), 1.44 and 1.38 (s, 6H, C*Me*$_2$), 1.32 (t, *J* 7.2 Hz, 3H, OCH$_2$Me); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.0 (C=O), 154.4 (C-4), 149.5 (C-6), 142.4 (PyC), 137.4, 136.5, 135.0, 133.6, 128.9, 128.4, 128.2 127.6 (ArC, PyC), 123.9, 122.8 (PyC), 114.9 (*C*Me$_2$), 108.7 (C-1), 103.2 (C-7), 98.3 (C-5), 82.8, 82.2 (C-2, C-3), 70.9 (O*C*H$_2$Ph), 61.4 (O*C*H$_2$Me), 28.2, 27.6 (C*Me*$_2$), 14.6 (Me); FABMS: $m/z = 438$ [M+H]$^+$. Anal. Calcd for $C_{25}H_{27}O_6N$: C, 68.64; H, 5.94; N, 3.20. Found: C, 68.62; H, 6.01; N, 3.16.

1.15. (4-*Z*,6-*E*/*Z*) 3-*O*-Benzyl-6-carbethoxy-5,6,7-trideoxy-1,2-*O*-isopropylidene-7-(3,4-dimethoxyphenyl)-β-L-*threo*-hept-4,6-dienofuranose (4c)

From **3c** (0.5 g, 1.07 mmol) as a colourless foam (0.20 g, 40%) yield; $[\alpha]_D^{27}$ −58 (*c* 0.10, $CHCl_3$); IR (neat): 1724 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.44–6.92 (m, 8H, ArH), 6.68 (s, 1H, H-7), 6.21, 6.04 (each d, *J* 3.0 Hz, 1H, H-1), 5.48, 5.28 (each s, 1H, H-5), 4.98 (d, *J* 11.2 Hz, 1H, PhC*H*$_2$), 4.87 (d, *J* 3.0 Hz, 1H, H-2), 4.77 (d, *J* 11.2 Hz, 1H, PhC*H*$_2$), 4.60 (s, 1H, H-3), 4.35 (*q*, *J* 7.2 Hz, 2H, OC*H*$_2$Me), 1.50 and 1.37 (s, 6H, C*Me*$_2$), 1.28 (t, *J* 7.2 Hz, 3H, OCH$_2$Me); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.1 (C=O), 154.8 (C–4), 152.6 (C-6), 137.6, 135.0, 132.4, 128.9, 128.3, 127.2, 124.6, 121.9 (ArC), 114.7 (*C*Me$_2$), 108.4, 107.7 (C-1), 104.0 (C-7), 99.5 (C-5), 83.2, 82.1 (C-2, C-3), 71.0 (O*C*H$_2$Ph), 61.6 (OCH$_2$), 56.5, 56.2 (O*Me*), 28.3, 28.2, (C*Me*$_2$), 14.7, 14.3 (Me). FABMS: $m/z = 497$ [M+H]$^+$. Anal. Calcd for $C_{28}H_{32}O_8$: C, 67.74; H, 6.45. Found: C, 67.68; H, 6.42.

1.16. (4-*Z*,6-*E*/*Z*) 3-*O*-Benzyl-6-carbethoxy-5,6,7-trideoxy-1,2-*O*-isopropylidene-7-(thiophen-2-carboxaldehyde)-β-L-*threo*-hept-4,6-dienofuranose (4d)

From **3d** (0.5 g, 1.08 mmol) as a colourless foam in (0.20 g, 41%) yield; $[\alpha]_D^{27}$ −54 (*c* 0.10, $CHCl_3$); IR (neat): 1706 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.41 (s, 1H, ThiophH), 7.42–7.26 (m, 7H, ArH, ThiophH), 7.05 (s, 1H, H-7), 6.20, 6.12 (each d, *J* 3.2 Hz, 1H, H-1), 5.48, 5.32 (each s, 1H, H-5), 4.89, 4.68 (d, *J* 11.6 Hz, 2H, PhC*H*$_2$), 4.56 (m, 1H, H-2), 4.60 (s, 1H, H-3), 4.33 (*q*, *J* 6.8 Hz, 2H, OCH$_2$), 1.60, 1.38 (s, 6H, C*Me*$_2$), 1.32 (t, *J* 6.8 Hz, 3H, OCH$_2$Me); ^{13}C NMR (50 MHz, $CDCl_3$): δ 168.9, 167.8 (C=O), 155.9 (C-4), 152.9 (C-6), 139.5, 137.7, 137.5, 137.5 132.5, 128.9, 128.6, 127.4, 125.4, 123.6 (Ar*C*, Thioph*C*), 114.8, 114.6 (*C*Me$_2$), 107.9 (C-1), 103.4 (C-7), 98.8 (C-5), 83.4, 82.1 (C-2, C-3), 70.9 (O*C*H$_2$Ph), 61.8, 51.3 (O*C*H$_2$Me), 30.7, 30.0, 28.3, 28.1 (C*Me*$_2$), 14.7, 14.4 (Me). FABMS: $m/z = 443$ [M+H]$^+$. Anal. Calcd for $C_{24}H_{26}O_6S$: C, 65.16; H, 5.88. Found: C, 65.08; H, 5.75.

1.17. (4-*Z*,6-*E*/*Z*) 3-*O*-Benzyl-6-carbethoxy-5,6,7-trideoxy-1,2-*O*-isopropylidene-7-(phenyl)-β-L-*threo*-hept-4,6-dienofuranose (4e)

From **3e** (0.5 g, 1.08 mmol) as a colourless foam (0.21 g, 42%); $[\alpha]_D^{27}$ −49 (*c* 0.10, $CHCl_3$); IR (neat): 1706 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.34–7.21 (m, 10H, ArH,), 6.70 (s, 1H, H-7), 6.20, 6.12 (each d, *J* 3.4 Hz, 1H, H-1), 5.48 (s, 1H, H-5), 4.89, 4.66 (d, *J* 11.2 Hz, 2H, PhC*H*$_2$), 4.56 (m, 1H, H-2), 4.09 (s,1H, H-3), 4.33 (*q*, *J* 7.0 Hz, 2H, (OCH$_2$), 1.60, 1.38 (s, 3H, C*Me*$_2$), 1.32 (t, *J* 7.0 Hz, 3H, Me); FABMS: $m/z = 437$ [M+H]$^+$. Anal. Calcd for $C_{26}H_{28}O_6$: C, 71.55; H, 6.42. Found: C, 71.52; H, 6.41.

1.18. (4-*Z*,6-*E*/*Z*) 6-Carbethoxy-5,6,7-trideoxy-1,2-*O*-isopropylidene-3-*O*-methyl-7-(3-pyridyl)-β-L-*threo*-hept-4,6-dienofuranose (4f)

From **3f** (0.5 g, 1.31 mmol) as a colourless foam (0.18 g, 40%); $[\alpha]_D^{27}$ −30 (*c* 0.10, $CHCl_3$); IR (neat): 1722 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.71 (s, 1H, Py*H*), 8.50–8.44 (m, 1H, Py*H*), 7.36–7.25 (m, 2H, Py*H*), 6.83 (s, 1H, H-7), 6.17, 5.94 (each d, *J* 3.2 Hz, 1H, H-1), 5.36, 5.30 (s, 1H, H-5), 4.52 (d, *J* 3.2 Hz, 1H, H-2), 4.29–4.16 (m, 2H, OCH$_2$), 3.82 (each s, 1H, H-3), 3.44, 3.40 (s, 3H, OMe), 1.48, 1.45 (s, 6H, C*Me*$_2$), 1.22 (t, *J* 7.2 Hz, Me); FABMS: $m/z = 362$ [M+H]$^+$. Anal. Calcd for $C_{19}H_{23}O_6N$: C, 63.16; H, 6.37; N, 3.88. Found: C, 63.10; H, 6.42. N, 3.80.

1.19. (4-*Z*,6-*E*/*Z*)6-Carbethoxy-5,6,7-trideoxy-1,2-*O*-isopropylidene-3-*O*-methyl-7-(3-nitrophenyl)-β-L-*threo*-hept-4,6-dienofuranose (4g)

From **3g** (0.5 g, 1.18 mmol) as a colourless foam (0.34 g, 48%); $[\alpha]_D^{27}$ −52 (*c* 0.10, $CHCl_3$); IR (neat): 1723 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.17 (t, *J* 3.4 Hz, 1H, ArH), 8.08 (d, *J* 8.4 Hz, 1H, ArH), 7.62–7.42 (m, 2H, ArH), 6.86 (s, 1H, H-7), 6.17 (d, *J* 3.0 Hz, 1H, H-1), 5.35, 5.30 (s, 1H, H-5), 4.51 (d, *J* 3.0 Hz, 1H, H-2), 4.28 (*q*, *J* 7.8 Hz, 2H, OCH$_2$), 3.81 (s, 1H, H-3), 3.40,

(s, 3H, OMe), 1.46, 1.34 (s, 6H, C*Me*$_2$), 1.22 (t, *J* 7.8 Hz, 3H, Me); ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.0, 168.5 (C=O), 156.1 (C-4), 148.3 (C-6), 135.4, 133.7, 130.5, 130.2 (ArC), 113.9 (*C*Me$_2$), 108.2, 107.6 (C-1), 102.3 (C-7), 98.6 (C-5), 83.4, 81.9 (C-3, C-2), 61.4 (OCH_2), 56.4 (OMe), 27.9, 27.7 (C*Me*$_2$), 13.9 (Me); FABMS: $m/z = 406$ $[M+H]^+$. Anal. Calcd for $C_{20}H_{23}O_8N$: C, 59.25; H, 5.68; N, 3.45. Found: C, 59.15; H, 5.61; N, 3.38.

1.20. (4-*Z*,6-*E*/*Z*) 6-Carbethoxy-5,6,7-trideoxy-1,2-*O*-isopropylidene-3-*O*-methyl-7-(4-bromophenyl)-β-L-*threo*-hept-4,6-dienofuranose (4h)

From **3h** (0.5 g, 1.09 mmol) as a colourless foam (0.28 g, 35%); $[\alpha]_D^{27}$ −62 (*c* 0.25, $CHCl_3$); IR (neat): 1726 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.46–7.38 (m, 2H, Ar*H*), 7.33–7.13 (m, 2H, Ar*H*), 6.69 (s, 1H, H-7), 6.14, 5.97 (d, *J* 3.0 Hz, 1H, H-1), 5.41, 5.31 (s, 1H, H-5), 4.52 (d, *J* 3.0 Hz, 1H, H-2), 4.14 (*q*, *J* 7.2 Hz, 2H, OCH_2), 3.80 (s, 1H, H-3), 3.38 (s, 3H, OCH_3), 1.48, 1.36(s, 6H, C*Me*$_2$), 1.25 (t, *J* 7.2 Hz, 3H, Me); ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.9 (C=O), 155.3 (C-4), 153.6 (C-6), 136.5, 135.1, 131.9, 129.9, 123.0, 122.2 (ArC), 114.8 (*C*Me$_2$), 108.4, 107.6 (C-1), 103.2 (C-7), 98.3 (C-5), 84.5, 82.8 (C-3, C-2), 57.1 (OCH_2), 52.6 (OMe), 28.1, 27.6 (C*Me*$_2$), 13.9 (Me); FABMS: $m/z =$ 439 $[M+H]^+$. Anal. Calcd for $C_{20}H_{23}O_6Br$: C, 54.66; H, 5.24. Found: C, 54.62; H, 5.22.

1.21. (4-*Z*,6-*E*/*Z*) 6-Carbethoxy-5,6,7-trideoxy-1,2-*O*-isopropylidene-3-*O*-methyl-7-(3-chlorophenyl)-β-L-*threo*-hept-4,6-dienofuranose (4i)

From **3i** (0.5 g, 1.21 mmol) as a colourless foam(0.21 g, 45%); $[\alpha]_D^{27}$ −48 (*c* 0.10, $CHCl_3$); IR (neat): 1725 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.32–7.19 (m, 4H, Ar*H*), 6.75 (s, 1H, H-7), 6.15 (d, *J* 3.2 Hz, 1H, H-1), 5.43, 5.31 (s, 1H, H-5), 4.51 (d, *J* 3.2 Hz, 1H, H-2), 4.25 (*q*, *J* 6.6 Hz, 2H, O*CH*$_2$), 4.18 (s, 1H, H-3), 3.39 (s, 3H, OMe), 1.45, 1.39 (s, 6H, C*Me*$_2$), 1.23 (t, *J* 6.6 Hz, 3H Me); ^{13}C NMR (50 MHz, $CDCl_3$): δ 174.0 (C=O), 153.8 (C-4), 149.2 (C-6), 138.2, 134.5, 128.8, 128.3, 126.6 (Ar*C*), 114.8 (*C*Me$_2$), 108.5, 107.8 (C-1), 102.9 (C-7), 98.3 (C-5), 84.5, 83.9 (C-3, C-2), 61.7 (OCH_2), 56.9 (OMe), 27.3, 27.6 (C*Me*$_2$), 14.6 (Me); FABMS: $m/z = 395$ $[M+H]^+$. Anal. Calcd for $C_{20}H_{23}O_6Cl$: C, 60.76; H, 5.82. Found: C, 60.66; H, 5.80.

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Supplementary data

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