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Radical reactions on enol-esters: facile synthesis of 3-ulosonic acid derivatives and chiral spiroacetals☆

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Abstract—A two-step approach to 3-ulosonic acid derivatives and chiral spiroacetals from enol-esters is presented. The strategy involves 1,4-addition of a variety of alcohols onto enol-esters in the presence of NBS to give α-bromoacetals, which undergo a regio- and stereoselective radical cyclisation to give the highly functionalised chiral spiroacetals, while debromination gives 3-ulosonic acid derivatives.

1. Introduction

Ulosonic acids[1] are very important carbohydrate constituents of cellular and bacterial membranes and are implicated in several biological functions. Amongst the most essential members of this class of natural products are KDO (3-deoxy-D-manno-2-octulosonic acid) and sialic acid (*N*-acetyl neuraminic acid—NANA). Studies on the biological activity of analogues of KDO and NANA have shown the potential inhibitory activity of such compounds in the biosynthesis of membrane lipopolysaccharides of bacteria and against viruses. NANA, KDO and their alkyl, acyl, deoxy derivatives, aza-, carbocyclic analogues and size or chain modified derivatives are considered[2–12] to play an important role at the cell surface as glycocongugates. Similarly, spiroacetals enjoy widespread occurrence as part of many naturally[13] occurring substances, amongst which, Papulachandrins A–D,[14] having antibiotic activity, represent a pyranoside based spiroacetal. Amongst the several methodologies[15–17] for the synthesis of this substructural unit, the most common route[15] is acid catalysed acetalisation of dihydroxyketone. In continuation of our efforts on the use of radical reactions,[18,19] herein, we report a two step protocol, haloetherification of enol esters and debromination of α-bromoacetals for the synthesis of 3-ulosonic acid derivatives and chiral spiro acetals[18] (Fig. 1). Even though enol esters are well known to undergo halo etherification with a halogen source in the presence of alcohols, their utilisation in

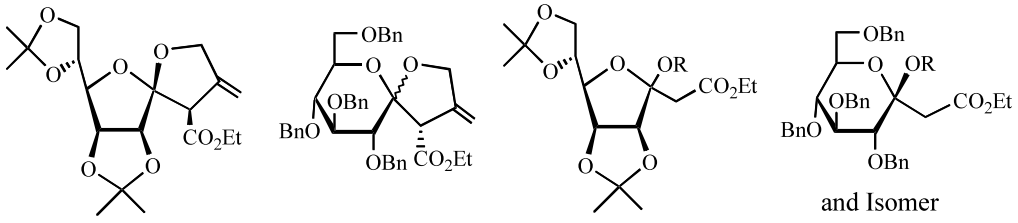

Figure 1.

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0957-4166/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
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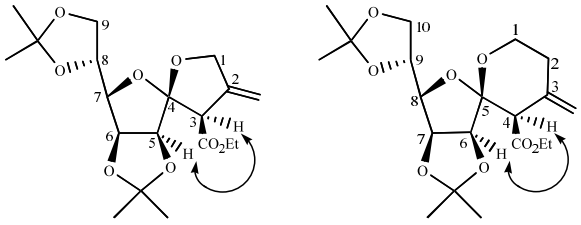
organic synthesis is not well exploited. Since the 3-ulosonic acids and spiroacetals are anomeric systems, it was envisaged that the enol esters could be converted in two steps into the targets by bromination-etherification and debromination.

2. Results and discussion

2.1. Synthesis of spiro acetal saccharides

The enol ester **1**,[20] derived from D-manno lactone on reaction with NBS (Scheme 1) in the presence of propargyl alcohol gave α-bromo acetals **4**/**4a**[21–25] through a bromo-etherification reaction (Table 1). The epimers **4** and **4a** were separated by chromatography and independently subjected to regio- and stereoselective radical cyclisation[26] of the 5-hexynyl system using n-Bu_3SnCl[27,28]–$NaCNBH_3$[29] in the presence of AIBN in t-BuOH at reflux to afford the functionalised spiroacetal **5**.[18] The stereochemistry at the spirocentre in **5** (Fig. 2) was defined by extensive ^1H NMR studies (DQFCOSY, NOESY), difference NOE and indirect couplings. Of special significance is the characteristic cross peak in the NOESY spectrum of **5** between H-3 and H-5. Both the epimeric bromo acetals gave the same product **5** on radical cyclisation. Further, **1** was then subjected to addition with several alcohols to give acetals **6**/**6a**, **7**/**7a**, **10**/**10a** and **11**/**11a** (Table 1). The epimeric mixture of bromo acetals **6**/**6a**, **7**/**7a**, **10**/**10a** and **11**/**11a** on exposure to n-Bu_3SnCl–$NaCNBH_3$ gave the spiro acetals **8**, **9**, **12** and **13**, respectively, whose structures were unambiguously characterised from ^1H NMR spectral studies. Characteristic indirect couplings (^3J) in the six-membered ring, as well as the cross peak in the NOESY spectrum between protons H-4 and H-6 were utilised to fix the structure and stereochemistry of **9** (Fig. 2). The indirect couplings $J_{1,2}$, $J_{1',2}$ and $J_{2,3}$ of 7.8, 7.8 and 4.7 Hz are consistent with the expected stereochemistry at C-2 in **12**.

Spiroacetals containing hydroxyl groups have been the subject of recent interest. After successful radical cyclisation of 5- and 6-hexynyl systems, the study was extended to the 5-oxo[30] radical systems to furnish spiroacetals bearing hydroxyl groups. Accordingly, **10**/**10a** was subjected to ozonolysis to afford aldehydes **14**/**14a**, which successfully underwent regio- and stereoselective cyclisation onto the carbonyl to afford the spiroacetal **15** in 84% yield. Compound **15** with $J_{2,3}$ 4.2 Hz, similar to **12**, confirms the stereochemistry at the C-2 centre.

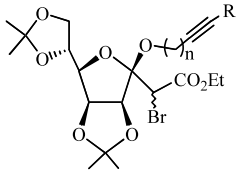
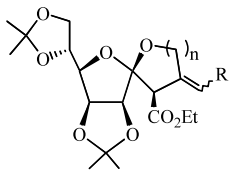
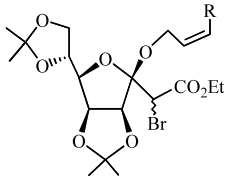
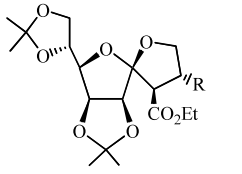
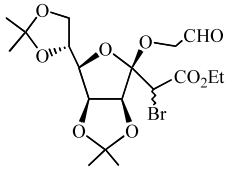
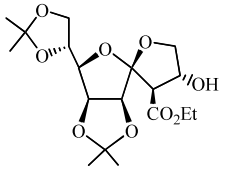


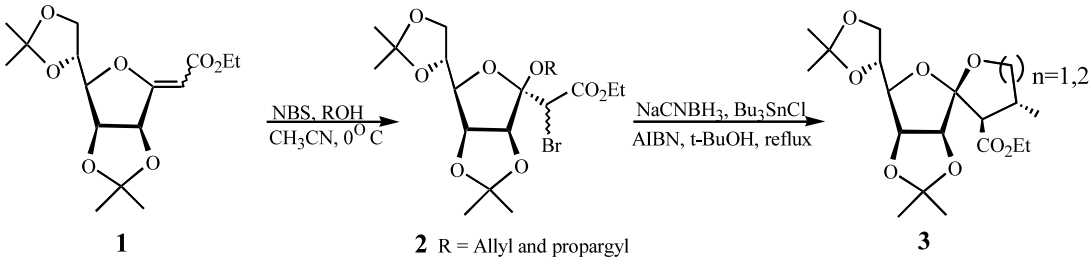
5 **9**

Figure 2. NOE structures of **5** and **9**.

After the successful conversion of **1** into α-anomeric spiro acetals by the regio- and stereoselective radical cyclisation[26] protocol, the same study was extended to the pyranosidic enol ester **16**. Accordingly **16**,[31] on

Table 1. Synthesis of chiral spiro acetals from **1**

bromo acetal	spiro acetal
 **4/4a** n = 1, R = H **6/6a** n = 1, R = CH_2OH **7/7a** n = 2, R = H	 **5** n = 1, R = H **8** n = 1, R = CH_2OH (79%) **9** n = 2, R = H (78%)
 **10/10a** R = H **11/11a** R = CH_2OH	 **12** R = CH_3 (85%) **13** R = CH_2CH_2OH (67%)
 **14/14a**	 **15** (84%)



1 **2** R = Allyl and propargyl **3**

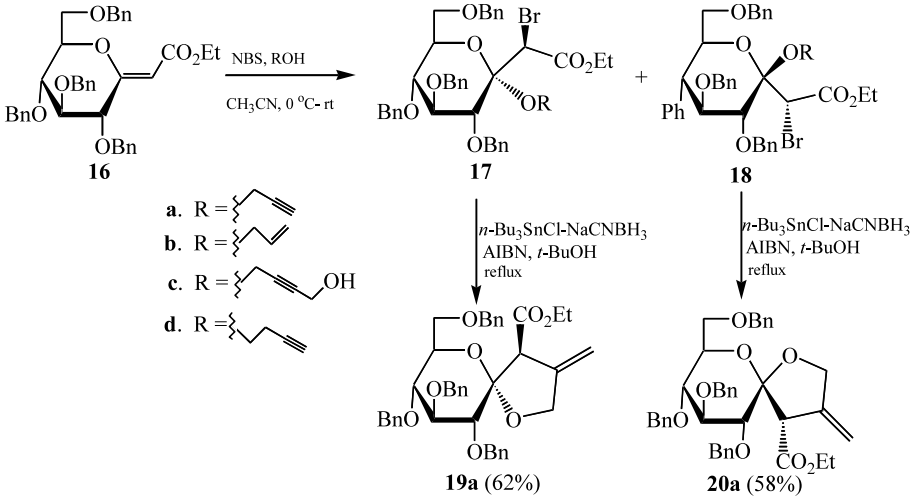
Scheme 1.

reaction with NBS (Scheme 2) in the presence of propargyl alcohol gave a separable mixture of bromo acetals **17a** (56%) and **18a** (13%) through a 1,4-addition reaction. The epimers were separated by chromatography and independently subjected to regio- and stereoselective radical cyclisation with n-Bu_3SnCl–$NaCNBH_3$ and AIBN in t-BuOH at reflux to afford the functionalised spiroacetals **19a** and **20a**, respectively.

The stereochemistry at the spirocentre in **19a** and **20a** was defined by extensive ^1H NMR studies.[32] Characteristic NOE between H3–H5 supports the structure **19a** (Fig. 3) whereas those between H3–H6 and H3–H8, the structure **20a**. All substituents in the six-membered ring are in energetically favored equatorial positions. The structure for **19a** and **20a** is further supported by the large value of about 9.0 Hz for $J_{5,6}$, $J_{6,7}$ and $J_{7,8}$. Unlike in the earlier study on the conversion of **1** to spiro acetals, the pyranosidic enol-ester **16**, gave anomeric isomers of bromo acetals, which gave the α- and β-anomeric spiro acetals **19a** and **20a**, respectively.

In a further study, **16** was subjected to addition with a variety of alcohols such as allyl and homopropargyl alcohols to give a separable mixture of isomers **17b** and **18b**; **17d** and **18d** respectively, while butyn-1,4-diol gave inseparable mixture of isomers **17c**/**18c**. Acetals **17b** and **18b** underwent radical cyclisation to afford the 1,6-dioxaspiro[4,5]decane systems **19b** and **20b** (Table 2), while the mixture of **17c**/**18c** gave **19c**/**20c** as an inseparable mixture of isomers. Attempted radical cyclisation on 6-heptynyl systems **17d** and **18d** did not give the expected cyclised products; instead they underwent radical debromination to furnish the important class of 3-non-ulosonic acid derivatives **21** and **22**, respectively. The stereochemistry at the anomeric centre in **19b** and **20b** was defined based on the earlier NMR studies on spiroacetals and was further confirmed from indirect couplings $J_{1,2}$, $J_{1',2}$, $J_{2,3}$ of 6.5, 11.1, 7.9 respectively, and characteristic strong NOEs between H1–H2 and weak NOEs like H1′–H2, H2–H3.

The successful radical debromination of **17d** and **18d** to give ulosonic acid derivatives **21** and **22** prompted us to undertake the study on the debromination of systems such as **2** (Scheme 1). Accordingly, enol ester **1** on reaction with NBS (Scheme 3) in the presence of water resulted in the stereoselective formation of bromoacetal **23** as a separable mixture of epimers at C-2 centre. The reductive debromination of the bromoacetal **23** was



Scheme 2.

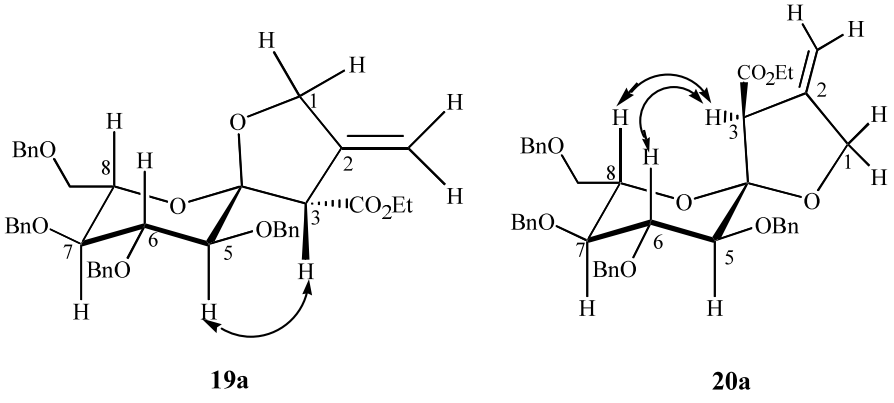
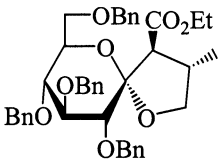
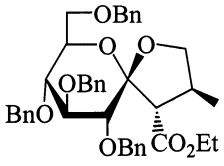
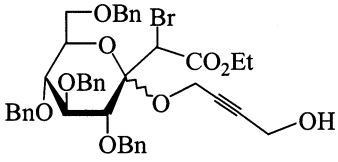
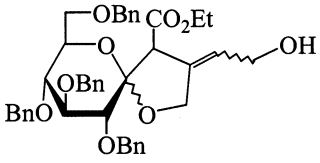
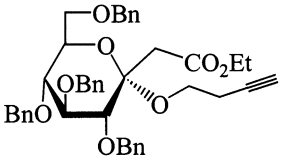
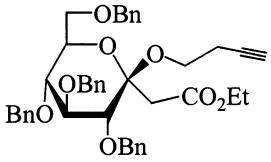
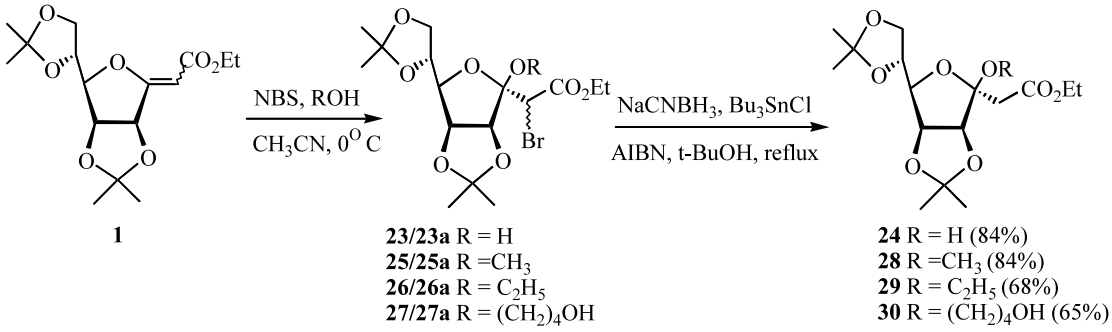


Figure 3. NOE structures of **19a** and **20a**.

Table 2. Synthesis of pyranosidic chiral spiro acetals

α-Bromoacetal	Spiroacetal/ 3-Ulosonic acid	
17b and **18b**	 **19b** (67%)	 **20b** (67%)
 **17c / 18c**	 **19c / 20c** (73 %)	
17d and **18d**	 **21** (74%)	 **22** (67%)



1

23/23a R = H
25/25a R =CH_3
26/26a R = C_2H_5
27/27a R = $(CH_2)_4OH$

24 R = H (84%)
28 R =CH_3 (84%)
29 R = C_2H_5 (68%)
30 R = $(CH_2)_4OH$ (65%)

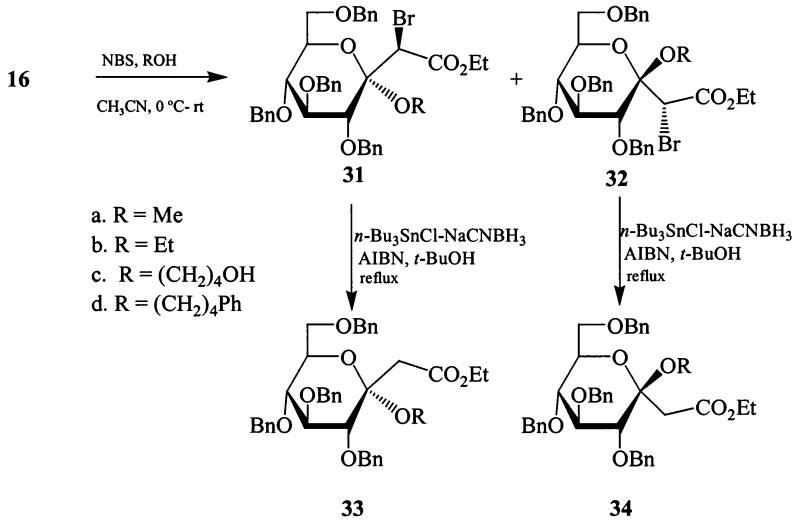
Scheme 3.

efficiently achieved by treatment with a catalytic amount of Bu_3SnCl and AIBN in the presence of $NaCNBH_3$ in *t*-BuOH at reflux to give the 2-deoxy-3-octulosonic acid **24**.

The bromoacetalisation reaction on **1** was then extended to various aliphatic alcohols, such as methanol, ethanol and butane-1,4-diol under the above reaction conditions to afford the bromoacetals **25**–**27**, respectively. The reductive debromination of bromoacetals **25**–**27** with Bu_3SnCl–$NaCNBH_3$ gave the 2-deoxy-3-octulosonic acid derivatives **28**–**30**, respectively.

The study was further extended on **16** with methanol and ethanol (Scheme 4) to afforded separable acetals **31a** (62%) and **32a** (11%); **31b** (56%) and **32b** (15%), respectively, while butane-1,4-diol and 4-phenyl-butan-1-ol gave an inseparable mixture of isomers **31c**/**32c** (63%) and **31d**/**32d** (59%), respectively.

Acetals **31a**–**d** and **32a**–**d** on reductive debromination (*n*-Bu_3SnCl–$NaCNBH_3$, AIBN) in *t*-BuOH at reflux afforded the corresponding 2-deoxy-3-nonulosonic acid derivatives **33a** (62%) and **34a** (67%), **33b** (56%) and **34b** (58%), respectively, while **31c**/**32c** and **31d**/**32d** afforded **33c**/**34c** (89%) and **33d**/**34d** (59%) as an inseparable mixture of isomers. The stereochemistry at the anomeric carbon was confirmed from the extensive NMR studies. The three bond carbon-proton coupling constants ($^3J_{C\text{-}1,H\text{-}3}$) which is related to the C_1–C_2–C_3–H dihedral angle has been used for the conformational analysis of sugar molecules.[33] In **33a** $^3J_{C\text{-}2,H\text{-}4}$ was found to be 1.5 Hz at 36.96 ppm (δ C2) indicating the H4 and C2 are *cis* and in **34a** the coupling constant is 2.7 Hz at 37.05 ppm (δ C2) indicating *trans* conformation (Fig. 4).[6,12,34]



Scheme 4.

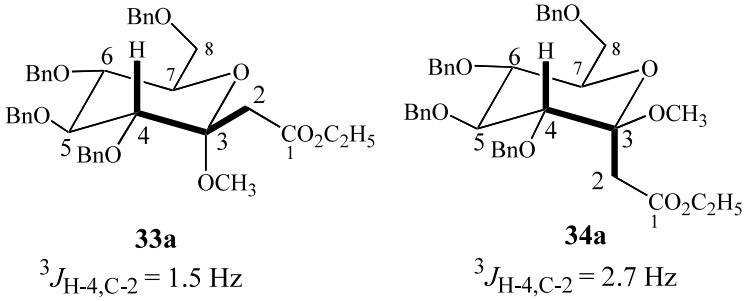


Figure 4. Structure of **33a** and **34a**.

Thus, in the present protocol, enol esters **1** and **16** were successfully converted into chiral spiro acetals, wherein **16** gave both the α- and β-anomeric spiro acetals. Similarly, **1** and **16** having the requisite acetic acid moiety in the carbon framework, for the first time were efficiently exploited for the synthesis of 3-ulosonic acid derivatives. Thus, the mild and stereoselective methodology presents a novel and versatile route to different classes of chiral compounds such as 3-ulosonic acid derivatives and spiroacetals.

3. Experimental

Solvents were dried over standard drying agents and freshly distilled prior to use. ^{1}H NMR (200 MHz, 500 MHz) spectra were recorded in deuteriochloroform. solution with tetramethylsilane as an internal reference on Varian Gemini-200 MHz and INOVA-500 MHz spectrometers J values are given in Hz. Optical rotations were measured with a JASCO DIP-370 instrument, and $[\alpha]_D$ values are in units of 10^{-1} deg cm^2 g^{-1}. Organic solutions were dried over anhydrous Na_2SO_4 and concentrated below 40°C in vacuo.

3.1. Ethyl 2-bromo-2-[6-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-2,2-dimethyl-4-(2-ropynyloxy)-(3a*S*,4*S*,6*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxol-4-yl]acetate 4 and 4a

To a stirred solution of **1** (1.3 g, 3.96 mmol) and propargyl alcohol (0.47 mL, 7.92 mmol) in dry acetonitrile (5 mL), *N*-bromo succinimide (0.7 g, 3.93 mmol) was added in portions at 0°C. The reaction mixture was brought to room temperature and stirred for 2 h. Solvent was removed under reduced pressure, diluted with water (50 mL) and extracted into ether (2×50 mL). The combined ether layers were washed with brine (25 mL) and dried (Na_2SO_4). Evaporation of solvent and purification of residue by column chromatography (finer than 200 mesh Si-gel, ethyl acetate:pet. ether, 1:9) gave **4** and **4a** (1.43 g) in 78% yield as a separable mixture of isomers in 3:1 ratio, respectively. First eluted was **4** (1.07 g) in 59% yield as a light yellow syrup; $[\alpha]_D = -5.4$ (*c* 2.26, $CHCl_3$); IR (Neat): 1072, 1152, 1744, 2984 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.24–1.38 (m, 9H, CH_3), 1.42, 1.53 (2s, 6H, CH_3), 2.40 (t, 1H, ≡CH), 3.96–4.05 (m, 2H, H-7,8), 4.14 (dd, 1H, $J_{7,8} = 4.0$, $J_{8,8'} = 7.3$ Hz, H-8′), 4.22 (q, 2H, -OCH_2CH$_3$), 4.31–4.41 (m, 1H, H-6), 4.41 (d, 1H, $J_{9,9'} = 2.4$ Hz, H-9), 4.43 (d, 1H, $J_{9,9'} = 2.4$ Hz, H-9′), 4.56 (d, 1H, $J_{4,5} = 4.8$

Hz, H-4), 4.81 (s, 1H, H-2), 4.83 (dd, 1H, $J_{4,5}=4.8$, $J_{5,6}=6.1$ Hz, H-5); EIMS (m/z, %): 449 (6), 139 (59), 137 (58), 101 (79), 43 (100). Anal. calcd for $C_{19}H_{27}BrO_8$: C, 49.26; H, 5.87. Found: C, 49.21; H, 5.77. Second eluted was **4a** (0.35 g) in 19% yield as a light yellow syrup; $[\alpha]_D=+5.4$ (c 1.50, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.22–1.40 (m, 9H, CH_3), 1.44, 1.48 (2s, 6H, CH_3), 2.35 (t, 1H, ≡CH), 4.00–4.12 (m, 3H, H-7,8,8′), 4.20–4.32 (m, 2H, -OCH_2CH$_3$), 4.33–4.43 (m, 1H, H-6), 4.48 (d, 1H, $J_{9,9'}=2.6$ Hz, H-9), 4.55 (d, 1H, $J_{9,9'}=2.6$ Hz, H-9′), 4.60 (d, 1H, $J_{4,5}=5.6$ Hz, H-4), 4.85 (s, 1H, H-2), 4.90 (dd, 1H, $J_{4,5}=5.6$, $J_{5,6}=3.9$ Hz, H-5); EIMS (m/z,%): 451 (47), 449 (46), 409 (14), 315 (21), 218 (44), 216 (82), 20 (100). Anal. found: C, 49.18; H, 5.81.

3.2. Ethyl 2-bromo-2-[6-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-4-(4-hydroxy-2-butynyloxy)-2,2-dimethyl-(3a*S*,4*S*,6*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxol-4-yl]acetate 6 and 6a

To a stirred solution of **1** (0.25 g, 0.76 mmol) and 2-butyne-1,4-diol (0.13 g, 1.52 mmol) in dry acetonitrile (3 mL), *N*-bromo succinimide (0.14 g, 0.76 mmol) was added, worked up and purified as described for **4**, to give **6** and **6a** (0.24 g) in 64% yield as a separable mixture of isomers in 3:1 ratio, respectively. First eluted was **6** (0.18 g) in 48% as a light yellow syrup; $[\alpha]_D=-29.1$ (c 3.76, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.30 (t, 3H, -OCH$_2CH_3$), 1.35 (s, 6H, CH_3), 1.46, 1.52 (2s, 6H, CH_3), 3.15 (br. s, 1H, -OH), 3.95–4.06 (m, 1H, H-8), 4.10–4.30 (m, 7H, H-6,7,8′,12,12′,-OCH_2CH$_3$), 4.30–4.43 (m, 2H, H-9,9′), 4.48 (d, 1H, $J_{4,5}=5.5$ Hz, H-4), 4.78–4.92 (m, 2H, H-2,5); FABMS (m/z, %): 479 (28), 477 (30), 351 (51), 349 (50), 55 (100), 41 (96). Anal. calcd for $C_{20}H_{29}BrO_9$: C, 48.69; H, 5.92. Found: C, 48.62; H, 5.84. Second eluted was **6a** (0.06 g) in 16% as a syrup; $[\alpha]_D=-5.4$ (c 0.92, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.20–1.40 (m, 9H, CH_3), 1.45–1.52 (m, 6H, CH_3), 3.15 (br. s, 1H, -OH), 4.05–4.39 (m, 9H, H-7,8,8′,9,9′,12,12′,-OCH_2CH$_3$), 4.40–4.46 (m, 1H, H-6), 4.55 (d, 1H, $J_{4,5}=5.5$ Hz, H-4), 4.85–4.96 (m, 2H, H-2,5).

3.3. Ethyl 2-bromo-2-[4-(3-butynyloxy)-6-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-2,2-dimethyl-(3a*S*,4*S*,6*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxol-4-yl]acetate 7 and 7a

To a stirred solution of **1** (0.57 g, 1.73 mmol) and homo propargyl alcohol (0.24 g, 3.42 mmol) in dry acetonitrile (5 mL), *N*-bromo succinimide (0.31 g, 1.73 mmol) was added, worked up and purified as described for **4**, to give **7** and **7a** (0.64 g) in 78% yield as a separable mixture of isomers in 3.5:1 ratio, respectively. First eluted was **7** (0.49 g) in 61% yield as a light yellow syrup; $[\alpha]_D=+3.4$ (c 2.02, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.21–1.45 (m, 12H, CH_3), 1.51 (s, 3H, CH_3), 1.90 (t, 1H, ≡CH), 2.35–2.50 (m, 2H, H-10,10′), 3.50–3.66 (m, 1H, H-9), 3.88–4.02 (m, 3H, H-8,8′,9′), 4.02–4.22 (m, 3H, H-7, -OCH_2CH$_3$), 4.24–4.39 (m, 1H, H-6), 4.50 (d, 1H, $J_{4,5}=5.0$ Hz, H-4), 4.72–4.83 (m, 2H, H-2,5); FABMS (m/z, %): 477 (M-1, 9), 463 (100), 461 (100). Anal. calcd for $C_{20}H_{29}BrO_8$: C, 50.32; H, 6.12. Found: C, 50.24; H, 6.07. Second eluted was **7a** (0.14 g) in 17% yield as a light yellow syrup; $[\alpha]_D=+28.4$ (c 1.05, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.26–1.38 (m, 9H, CH_3), 1.42, 1.49 (2s, 6H, CH_3), 1.90 (t, 1H, ≡CH), 2.30–2.40 (m, 2H, H-10,10′), 3.69–3.80 (m, 1H, H-9), 3.92–4.16 (m, 4H, H-7,8,8′,9′), 4.16–4.30 (m, 3H, H-6, -OCH_2CH$_3$), 4.58 (d, 1H, $J_{4,5}=5.0$ Hz, H-4), 4.82–4.90 (m, 2H, H-2,5).

3.4. Ethyl 2-[4-allyloxy-6-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-2,2-dimethyl-(3a*S*,4*S*,6*R*,6a*S*)-perhydrofuro-[3,4-*d*][1,3]dioxol-4-yl]-2-bromoacetate 10 and 10a

To a stirred solution of **1** (1.0 g, 3.04 mmol) and allyl alcohol (0.35 g, 6.09 mmol) in dry acetonitrile (5 mL), *N*-bromo succinimide (0.54 g, 3.04 mmol) was added, worked up and purified as described for **4**, to give **10** and **10a** (1.12 g) in 79% yield as a separable mixture of isomers in 2.7:1 ratio, respectively. First eluted was **10** (0.81 g) in 57% yield as a light yellow syrup; $[\alpha]_D=+4.2$ (c 2.20, $CHCl_3$); IR (Neat): 1032, 1152, 1200, 1744, 2976 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.25–1.42 (m, 12H, CH_3), 1.52 (s, 3H, CH_3), 3.87–4.08 (m, 4H, H-6,7,8,8′), 4.24 (q, 2H, -OCH_2CH$_3$), 4.32–4.45 (m, 2H, H-9,9′), 4.58 (d, 1H, $J_{4,5}=4.8$ Hz, H-4), 4.78–4.86 (m, 2H, H-2,5), 5.15 (dd, 1H, $J_{10,11}=10.2$, $J_{11,11'}=2.0$ Hz, H-11), 5.28 (dd, 1H, $J_{10,11'}=17.1$, $J_{11,11'}=2.0$ Hz, H-11′), 5.80–6.00 (m, 1H, H-10); FABMS (m/z, %): 448 (3), 101 (56), 59 (47), 43 (100), 41 (100). Anal. calcd for $C_{19}H_{29}BrO_8$: C, 49.04; H, 6.28. Found: C, 48.99, H, 6.22. Second eluted was **10a** (0.30 g) in 22% yield as a light yellow syrup; $[\alpha]_D=+26.4$ (c 1.72, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.23–1.38 (m, 6H, CH_3), 1.40, 1.45, 1.50 (3s, 9H, CH_3), 3.84 (dd, 1H, $J_{7,8}=3.6$, $J_{8,8'}=7.0$ Hz, H-8), 3.98–4.15 (m, 2H, H-7,8′), 4.15–4.32 (m, 3H, H-6, -OCH_2CH$_3$), 4.32–4.49 (m, 2H, H-9,9′), 4.62 (d, 1H, $J_{4,5}=4.8$ Hz, H-4), 4.87 (dd, 1H, $J_{4,5}=4.8$, $J_{5,6}=6.0$ Hz, H-5), 4.94 (s, 1H, H-2), 5.14 (dd, 1H, $J_{10,11}=11.4$, $J_{11,11'}=2.0$ Hz, H-11), 5.25 (dd, 1H, $J_{10,11'}=17.1$, $J_{11,11'}=2.0$ Hz, H-11′), 5.72–5.94 (m, 1H, H-10).

3.5. Ethyl 2-bromo-2-[6-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-4-[4-hydroxy-(*Z*)-2-butenyloxy]-2,2-dimethyl-(3a*S*,4*S*,6*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxol-4-yl]acetate 11 and 11a

To a stirred solution of **1** (2.0 g, 6.09 mmol) and *cis*-2-butene-1,4-diol (1.07 g, 12.19 mmol) in dry acetonitrile (10 mL), *N*-bromo succinimide (1.08 g, 6.09 mmol) was added, worked up and purified as described for **4**, to give a non-separable mixture of isomers (2.6:1) of **11** and **11a** (2.32 g) in 77% yield as a light yellow syrup; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.22–1.44 (m, 12H, CH_3), 1.50 (s, 3H, CH_3), 3.90–4.14 (m, 5H, H-6,8,8′, -OCH_2CH$_3$), 4.15–4.46 (m, 5H, H-7,9,9′,12,12′), 4.50, 4.56 (2d, 1H, $J_{4,5}=4.8$ Hz, H-4), 4.70–4.88 (m, 2H, H-2,5), 5.40–5.60 (m, 1H, H-10), 5.66–5.80 (m, 1H, H-11); FABMS (m/z, %): 497 (M$^+$+2, 13), 495 (14), 481 (53), 479 (47), 409 (47), 407 (47), 351 (100), 349 (99). Anal. calcd for $C_{20}H_{31}BrO_9$: C, 48.49; H, 6.31; Found: C, 48.40; H, 6.25.

3.6. Ethyl 2-bromo-2-[3,4,5-tri(benzyloxy)-6-benzyloxymethyl-2-(2-propynyloxy)-(2*R*,3*R*,4*S*,5*R*,6*R*)-tetrahydro-2*H*-2-pyranyl]acetate 17a and ethyl 2-bromo-2-[3,4,5-tri(benzyloxy)-6-benzyloxymethyl-2-(2-propynyloxy)-(2*S*,3*R*,4*S*,5*R*,6*R*)-tetrahydro-2*H*-2-pyranyl]-acetate 18a

To a stirred solution of **16** (0.5 g, 0.82 mmol) and propargyl alcohol (0.1 g, 1.64 mmol) in dry acetonitrile (5 mL), *N*-bromo succinimide (0.14 g, 0.82 mmol) was added, worked up and purified as described for **4**, to give **17a** and **18a** as a separable mixture of isomers in 4:1 ratio respectively. First eluted was **18a** (0.08 g) in 13% as a light yellow syrup; $[\alpha]_D = +34.6$ (*c* 0.8, $CHCl_3$); IR (neat): 680, 1120, 1640, 2880 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.20 (t, 3H, $J_{1,2} = 8.0$, $J_{1,3} = 16.0$ Hz, CH_3), 2.35 (br.s, 1H), 3.66–3.74 (m, 2H), 3.78–3.85 (m, 1H), 3.92 (d, 1H, $J = 8.0$ Hz), 4.05–4.20 (m, 5H), 4.45–4.80 (m, 10H), 7.10–7.38 (m, 20H). Second eluted was **17a** (0.34 g) in 56% as a light yellow syrup; $[\alpha]_D = +26.0$ (*c* 1, $CHCl_3$); IR (neat): 720, 1200, 1650, 2900 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.20 (t, 3H, $J_{1,2} = 7.1$, $J_{1,2} = 14.2$ Hz, CH_3), 2.40 (br.s, 1H, ≡CH), 3.60–3.95 (m, 4H), 4.00–4.20 (m, 3H), 4.38–4.52 (m, 3H), 4.54–4.70 (m, 4H), 4.87–4.94 (m, 5H), 7.10–7.40 (m, 20H).

3.7. Ethyl 2-[2-allyloxy-3,4,5-tri(benzyloxy)-6-benzyloxymethyl-(2*R*,3*R*,4*S*,5*R*,6*R*)-tetrahydro-2*H*-2-pyranyl]-acetate 17b and ethyl 2-[2-allyloxy-3,4,5-tri(benzyloxy)-6-benzyloxymethyl-(2*S*,3*R*,4*S*,5*R*,6*R*)-tetrahydro-2*H*-2-pyranyl]acetate 18b

To a stirred solution of **16** (0.5 g, 0.82 mmol) and allyl alcohol (0.8 mL, 1.64 mmol) in dry acetonitrile (5 mL), *N*-bromo succinimide (0.14 g, 0.82 mmol) was added, worked up and purified as described for **4**, to give **17b** and **18b** as a separable mixture of isomers in 4.5:1 ratio respectively. First eluted was **18b** (0.07 g) in 12% as a light yellow syrup; $[\alpha]_D = +14.9$ (*c* 0.4, $CHCl_3$); IR (neat): 740, 1180, 1240, 1660, 2880 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.24 (t, 3H, $J_{1,2} = 6.8$, $J_{1,3} = 13.6$ Hz, CH_3), 3.55–3.90 (m, 5H), 3.94–4.30 (m, 5H), 4.45–4.70 (m, 4H), 4.82–4.90 (m, 3H), 4.95–5.15 (m, 2H), 5.20–5.40 (m, 2H), 5.85–6.10 (m, 1H), 7.10–7.45 (m, 20H). Second eluted was **17b** (0.32 g) in 52% as a light yellow syrup; $[\alpha]_D = +26.0$ (*c* 0.25, $CHCl_3$); IR (neat): 720, 1160, 1260, 1650, 3280 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.22 (t, 3H, $J_{1,2} = 6.8$, $J_{1,3} = 13.6$ Hz, CH_3), 3.60–3.90 (m, 5H), 4.00–4.30 (m, 5H), 4.50–4.70 (m, 4H), 4.74–4.88 (m, 3H), 4.90–5.10 (m, 2H), 5.15–5.40 (m, 2H), 5.85–6.10 (m, 1H), 7.10–7.40 (m, 20H).

3.8. Ethyl 2-bromo-2-[3,4,5-tri(benzyloxy)-6-benzyloxymethyl-2-(4-hydroxy-2-butynyloxy)-(3*R*,4*S*,5*R*,6*R*)-tetrahydro-2*H*-2-pyranyl]acetate 17c/18c

To a stirred solution of **16** (0.5 g, 0.82 mmol) and butyn-1,4-diol (0.14 g, 1.64 mmol) in dry acetonitrile (5 mL), *N*-bromo succinimide (0.14 g, 0.82 mmol) was added, worked up and purified as described for **4**, to give **17c** and **18c** as an inseparable mixture of isomers (0.36 g) in 64% as a light yellow syrup; $[\alpha]_D = +58.0$ (*c* 0.6, $CHCl_3$); IR (neat): 780, 1100, 1240, 1660, 2950 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.22 (t, 3H, $J_{1,2} = 5.4$, $J_{1,3} = 10.8$ Hz, CH_3), 3.60–3.75 (m, 3H), 3.80–3.92 (m, 2H), 4.00–4.18 (m, 3H), 4.22 (d, 2H, $J = 5.4$ Hz), 4.38–4.50 (m, 3H), 4.54–4.70 (m, 3H), 4.80–5.98 (m, 5H), 7.10–7.38 (m, 20H).

3.9. Ethyl 2-bromo-2-[3,4,5-tri(benzyloxy)-6-benzyloxymethyl-2-(3-buntynyloxy)-(2*R*,3*R*,4*S*,5*R*,6*R*)-tetrahydro-2*H*-2-pyranyl]acetate 17d and ethyl 2-bromo-2-[3,4,5-tri(benzyloxy)-6-benzyloxymethyl-2-(3-buntynyloxy)-(2*S*,3*R*,4*S*,5*R*,6*R*)-tetrahydro-2*H*-2-pyranyl]acetate 18d

To a stirred solution of **16** (0.6 g, 1.00 mmol) and 3-butyn-1-ol (0.03 mL, 2.00 mmol) in dry acetonitrile (5 mL), *N*-bromo succinimide (0.17 g, 1.00 mmol) was added, worked up and purified as described for **4**, to give **17d** and **18d** as a separable mixture of isomers in 2.8:1 ratio respectively. First eluted was **18d** (0.11 g) in 15% as a light yellow syrup; $[\alpha]_D = +33.2$ (*c* 0.5, $CHCl_3$); IR (neat): 720, 1120, 1660, 2900 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.20 (t, 3H, $J_{1,2} = 5.0$, $J_{1,3} = 7.5$ Hz, CH_3), 1.82 (br.s, 1H, ≡CH), 2.42 (t, 2H, $J_{1,2} = 5.0$, $J_{1,3} = 7.5$ Hz, ≡CCH_2), 3.60–3.75 (m, 3H), 3.78–3.88 (m, 3H), 3.90–4.00 (m, 1H), 4.08–4.18 (m, 3H), 4.45–4.65 (m, 5H), 4.68–4.80 (m, 4H), 7.08–7.36 (m, 20H). Second eluted was **17d** (0.33 g) in 44% as a light yellow syrup; $[\alpha]_D = +18.2$ (*c* 1, $CHCl_3$); IR (neat): 745, 1110, 1260, 1710, 2900 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.22 (t, 3H, $J_{1,2} = 10.2$, $J_{1,3} = 17.9$ Hz, CH_3), 1.98 (br.s, 1H, ≡CH), 2.60 (t, 2H, $J_{1,2} = 5.1$, $J_{1,3} = 7.69$ Hz, ≡CCH_2), 3.60–3.94 (m, 6H), 3.98–4.20 (m, 4H), 4.45–4.70 (m, 4H), 4.72–5.00 (m, 5H), 7.05–7.45 (m, 20H).

3.10. Ethyl 6′-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-2′,2′-dimethyl-4-methylene-(2′*R*,3*R*,3a′*S*,6′*R*,6a′*S*)-spiro[3*H*,4*H*,5*H*-furan-2,4′-perhydrofuro[3,4-*d*][1,3]-dioxole]-3-carboxylate 5

A solution of **4** (0.2 g, 0.43 mmol), sodium cyanoborohydride (0.05 g, 0.86 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated to reflux under a nitrogen atmosphere AIBN (catalytic) was added and stirred for further 2 h. The reaction mixture was brought to room temperature, solvent evaporated and residue purified by column chromatography (60–120 mesh Si-gel, ethyl acetate:pet. ether, 1:9) to give **5** (0.1 g) in 60% yield as a colourless syrup; $[\alpha]_D = +78.7$ (*c* 1.80, $CHCl_3$); IR (Neat): 1072, 1744, 2944 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.26 (t, 3H, -OCH_2CH_3), 1.30, 1.37, 1.43, 1.44 (4s, 12H, CH_3), 3.58 (s, 1H, H-3), 3.87 (dd, 1H, $J_{8,9'} = 4.1$, $J_{9,9'} = 8.7$ Hz, H-9′), 3.97 (dd, 1H, $J_{6,7} = 2.8$, $J_{7,8} = 8.2$ Hz, H-7), 4.07 (dd, 1H, $J_{8,9} = 6.2$, $J_{9,9'} = 8.7$ Hz, H-9), 4.16–4.22 (m, 2H, -OCH_2CH_3), 4.34–4.39 (m, 1H, H-8), 4.44 (br.d, 1H, $J_{1,1'} = 12.8$ Hz,

H-1′), 4.57 (br. d, 1H, $J_{1,1'}=12.8$ Hz, H-1), 4.80–4.84 (m, 2H, H-5,6), 5.07 (d, 1H, $J=4.3$ Hz, $=CH_2$), 5.26 (d, 1H, $J=4.3$ Hz, $=CH_2$); EIMS (m/z, %): 369 (42), 141 (35), 101 (92), 81 (36), 43 (100). Anal. calcd for $C_{19}H_{28}O_8$: C, 59.36; H, 7.34. Found: 59.27; H, 7.25. A solution of **4a** (0.2 g, 0.43 mmol), sodium cyanoborohydride (0.05 g, 0.86 mmol) and trybutyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux, after workup and purification gave **5** (0.11 g, 66%), which was identical in all respects with the product prepared from **4**.

3.11. Ethyl 6′-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-4-[2-hydroxy-(*Z*)-ethylidene]-2′,2′-dimethyl-(2′*R*,3*R*,3a′*S*,6′*R*,6a′*S*)-spiro[3*H*,4*H*,5*H*-furan-2,4′-perhydrofuro-[3,4-*d*][1,3]dioxole]-3-carboxylate 8

A solution of **6** and **6a** (0.045 g, 0.09 mmol), sodium cyanoborohydride (0.01 g, 0.18 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux, worked up and purified as described for **5**, to give **8** (0.03 g) in 79% yield as a colourless syrup; $[\alpha]_D=+41.6$ (*c* 0.64, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.20–1.38 (m, 9H, CH_3), 1.38–1.47 (m, 6H, CH_3), 2.10 (br. s, 1H, -OH), 3.50, 3.75 (2s, 1H, H-3), 3.77–3.85 (m, 1H, H-8), 3.88 (dd, 1H, $J_{8,9}=4.5$, $J_{9,9'}=8.6$ Hz, H-9), 4.05 (dd, 1H, $J_{8,9'}=5.4$, $J_{9,9'}=8.6$ Hz, H-9′), 4.10–4.46 (m, 5H, H-7,11,11′, -OCH_2CH$_3$), 4.46–4.61 (m, 2H, H-5,6), 4.74–4.82 (m, 2H, H-1,1′), 5.56–5.77 (m, 1H, H-10); FABMS (m/z, %): 415 (M^++1, 24), 399 (38), 137 (46), 133 (100), 111 (57). Anal. calcd for $C_{20}H_{30}O_9$: C, 57.96; H, 7.30. Found: C, 57.90; H, 7.23.

3.12. Ethyl 6-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-2,2-dimethyl-4′-methylene-(3′*R*,3a*S*,4′*R*,6*R*,6a*S*)-spiro[perhydrofuro[3,4-*d*][1,3]dioxole-4,2′-(3′*H*,4′*H*,5′*H*,6′*H*-pyran)]-3′-carboxylate 9

A solution of **7** and **7a** (0.08 g, 0.16 mmol), sodium cyanoborohydride (0.02 g, 0.33 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was refluxed for 2 h, worked up and purified as described for **5**, to give **9** (0.05 g) in 78% yield as a colourless syrup; $[\alpha]_D=-19.4$ (*c* 1.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (t, 3H, -OCH$_2$$CH_3$), 1.29, 1.37, 1.43, 1.45 (4s, 12H, CH_3), 2.09 (dd, 1H, $J_{1,2'}=2.6$, $J_{2,2'}=14.0$ Hz, H-2′), 2.51 (ddd, 1H, $J_{1,2}=12.5$, $J_{1',2}=5.8$ Hz, H-2), 3.36 (s, 1H, H-4), 3.68 (ddd, 1H, $J_{1,1'}=10.8$ Hz, H-1), 3.78 (br. dd, 1H, H-1′), 3.79 (m, 1H, $J_{7,8}=3.4$, $J_{8,9}=8.1$ Hz, H-8), 3.96 (dd, 1H, $J_{9,10}=4.3$, $J_{10,10'}=8.9$ Hz, H-10), 4.09 (dd, 1H, $J_{9,10'}=6.3$ Hz, H-10′), 4.10–4.25 (m, 2H, -OCH_2CH$_3$), 4.37 (ddd, 1H, H-9), 4.67 (d, 1H, $J_{6,7}=5.9$ Hz, H-6), 4.78 (dd, 1H, H-7), 4.97 (t, 1H, $J=1.7$ Hz, $=CH_2$), 5.03 (t, 1H, $=CH_2$); FABMS (m/z, %): 399 (M^++1, 17), 383 (100), 295 (29), 165 (31), 141 (46), 109 (29). Anal. calcd for $C_{20}H_{30}O_8$: C, 60.29; H, 7.59. Found: C, 60.18; H, 7.47.

3.13. Ethyl 6′-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-2′,2′,4-trimethyl-(2′*R*,3*R*,3a′*S*,4*R*,6′*R*,6a′*S*)-spiro[3*H*,4*H*,5*H*-furan-2,4′-perhydrofuro[3,4-*d*][1,3]-dioxole]-3-carboxylate 12

A solution of **10** and **10a** (0.05 g, 0.10 mmol), sodium cyanoborohydride (0.01 g, 0.20 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux for 2 h, worked up and purified as described for **5**, to give **12** (0.035 g) in 85% yield as a colourless syrup; $[\alpha]_D=+70.1$ (*c* 1.40, $CHCl_3$); IR (Neat): 1072, 1200, 1736, 2960 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.16 (t, 3H, -OCH$_2$$CH_3$), 1.22 (s, 6H, CH_3), 1.34, 1.40 (2s, 6H, CH_3), 1.70 (d, 2H, CH_3), 2.35–2.52 (m, 1H, H-2), 2.68 (d, 1H, $J_{2,3}=5.0$ Hz, H-3), 3.46 (t, 1H, $J_{1,1'}=8.5$, $J_{1,2}=8.0$ Hz, H-1), 3.77 (dd, 1H, $J_{8,9}=7.6$, $J_{9,9'}=4.2$ Hz, H-9), 3.90 (dd, 1H, $J_{8,9'}=8.5$, $J_{9,9'}=4.2$ Hz, H-9′), 3.96–4.21 (m, 4H, H-1′,7, -OCH_2CH$_3$), 4.21–4.36 (m, 1H, H-8), 4.62 (d, 1H, $J_{5,6}=6.0$ Hz, H-5), 4.72 (dd, 1H, $J_{5,6}=6.0$, $J_{6,7}=3.4$ Hz, H-6); EIMS (m/z, %): 371 (32), 101 (79), 83 (95), 43 (100), 41 (97); FABMS (m/z, %): 387 (10), 371 (47), 101 (79), 83 (90), 43 (100), 41 (82). Anal. calcd for $C_{19}H_{30}O_8$: C, 59.05; H, 7.82. Found: C, 59.00; H, 7.76.

3.14. Ethyl 6′-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-4-(2-hydroxyethyl)-2′,2′-dimethyl-(2′*R*,3*R*,3a′*S*,4*R*,6′*R*,6a′*S*)-spiro[3*H*,4*H*,5*H*-furan-2,4′-perhydrofuro[3,4][1,3]dioxole]-3-carboxylate 13

A solution of **11** and **11a** (0.25 g, 0.50 mmol), sodium cyanoborohydride (0.06 g, 1.00 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux 2 h, worked up and purified as described for **5**, to give **13** (0.14 g) in 67% yield as a syrup; $[\alpha]_D=+74.5$ (*c* 1.50, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.24–1.40 (m, 12H, CH_3), 1.45 (s, 3H, CH_3), 1.52–1.68 (m, 1H, H-10), 1.70–1.84 (m, 1H, H-10′), 2.45–2.60 (m, 1H, H-2), 2.86 (d, 1H, $J_{2,3}=4.8$ Hz, H-3), 3.58 (t, 1H, $J_{1,1'}=8.0$, $J_{1,2}=7.8$ Hz, H-1), 3.64–3.90 (m, 3H, H-7,9,9′), 3.90–4.26 (m, 5H, H-1′,11,11′, -OCH_2CH$_3$), 4.26–4.38 (m, 1H, H-8), 4.70 (d, 1H, $J_{5,6}=4.8$ Hz, H-5), 4.75 (dd, 1H, $J_{5,6}=4.8$, $J_{6,7}=4.0$ Hz, H-6).

3.15. Ethyl 6′-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-4-hydroxy-2′,2′-dimethyl-(2′*R*,3*R*,3a′*S*,4*R*,6′*R*,6a′*S*)-spiro-[3*H*,4*H*,5*H*-furan-2,4′-perhydrofuro[3,4-*d*][1,3]dioxole]-3-carboxylate 15

A solution of **10** (0.25 g, 0.54 mmol) in dry CH_2Cl_2 (3 mL) was treated with ozone gas at −78°C (acetone+solid CO_2), until the colour of the solution changes to light blue (10 min). Triphenylphosphine (0.14 g, 0.54 mmol) was added to the reaction mixture at the same temperature and brought it to room temperature over 30 min. Evaporation of CH_2Cl_2 and purification of residue by column chromatography (60–120 mesh Si-gel, ethyl acetate:pet. ether, 1:9) gave ethyl 2-bromo-2-[6-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-4-formylmethoxy-2,2-dimethyl-(3a*S*,4*S*,6*R*,6a*S*)-per-

hydrofuro[3,4-*d*][1,3]dioxol-4-yl]acetate **14** (0.23 g) in 92% yield as a colourless syrup; $[\alpha]_D = +13.4$ (*c* 1.80, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 1.22–1.45 (m, 12H, CH_3), 1.54 (s, 3H, CH_3), 3.82–4.05 (m, 4H, H-8,8′,9,9′), 4.15–4.40 (m, 4H, H-6,7, -OCH_2CH_3), 4.64 (d, 1H, $J_{4,5} = 6.0$ Hz, H-4), 4.79 (s, 1H, H-2), 4.86 (dd, 1H, $J_{4,5} = 6.0$, $J_{5,6} = 3.6$ Hz, H-5), 9.70 (s, 1H, -CHO).

A solution of **14** (0.15 g, 0.32 mmol), sodium cyanoborohydride (0.04 g, 0.64 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux for 2 h, worked up and purified as described for **5**, to give **15** (0.1 g) in 84% yield as a colourless syrup; $[\alpha]_D = +31.2$ (*c* 1.00, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 1.21–1.40 (m, 9H, CH_3), 1.43, 1.48 (2s, 6H, CH_3), 2.04 (d, 1H, -OH), 2.88 (d, 1H, $J_{2,3} = 4.2$ Hz, H-3), 3.44–3.73 (m, 3H, H-1,1′,2), 3.81 (dd, 1H, $J_{8,9} = 5.9$, $J_{9,9'} = 4.0$ Hz, H-9), 3.90 (dd, 1H, $J_{8,9'} = 8.5$, $J_{9,9'} = 4.0$ Hz, H-9′), 4.00–4.23 (m, 3H, H-8, -OCH_2CH_3), 4.26–4.40 (m, 1H, H-7), 4.65 (d, 1H, $J_{5,6} = 5.0$ Hz, H-5), 4.80 (dd, 1H, $J_{5,6} = 5.0$, $J_{6,7} = 3.8$ Hz, H-6); EIMS (*m*/*z*, %): 375 (6), 115 (36), 101 (60), 81 (54), 70 (53), 60 (100). Anal. calcd for $C_{18}H_{28}O_9$: C, 55.66; H, 7.27. Found: C, 55.61; H, 7.22.

3.16. Ethyl 8,9,10-tri(benzyloxy)-7-benzyloxymethyl-3-methylene-(4*S*,5*S*,7*R*,8*R*,9*S*,10*R*)-1,6-dioxaspiro[4.5]-decane-4-carboxylate 19a

A solution of **17a** (0.2 g, 0.26 mmol), sodium cyanoborohydride (0.03 g, 0.53 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux for 2 h, worked up and purified as described for **5**, to give **19a** (0.11 g) in 62% yield as a colourless syrup; $[\alpha]_D = +37.25$ (*c* 0.75, $CHCl_3$), IR (neat): 760, 1150, 1660, 2950, 3490 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.16 (t, 3H), 3.63 (dd, 1H, $J_{1,2} = 1.7$, $J_{1,3} = 11.3$ Hz), 3.73–3.83 (m, 4H), 3.94 (d, 1H, $J = 9.6$ Hz), 3.99–4.16 (m, 2H), 4.09 (t, 1H, $J = 9.6$ Hz), 4.45 (d, 1H, $J = 11.96$ Hz), 4.47–4.53 (m, 3H), 4.66–4.78 (m, 2H), 4.82–5.02 (m, 4H), 5.21–5.26 (m, 2H, =CH_2), 7.22–7.44 (m, 20H); FABMS (*m*/*z*,%): 664 (M^+, 4), 181 (13), 154 (6), 121 (18), 91 (100). Anal. calcd for $C_{41}H_{44}O_8$: C, 74.08; H, 6.67. Found: C, 74.05; H, 6.64.

3.17. Ethyl 8,9,10-tri(benzyloxy)-7-benzyloxymethyl-3-methylene-(4*R*,5*R*,7*R*,8*R*,9*S*,10*R*)-1,6-dioxaspiro[4.5]-decane-4-carboxylate 20a

A solution of **18a** (0.1 g, 0.13 mmol), sodium cyanoborohydride (0.01 g, 0.26 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux for 2 h, worked up and purified as described for **5**, to give **20a** (0.026 g) in 58% yield as a colourless syrup; $[\alpha]_D = +21.7$ (*c* 0.5, $CHCl_3$); IR (neat): 760, 1100, 1680, 2950, 3480 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.20 (t, 3H, CH_3), 3.59–3.69 (m, 2H), 3.65 (d, 1H, $J = 9.1$ Hz), 3.75 (t, 1H, $J = 8.1$, 9.1 Hz), 3.81 (t, 1H, $J = 9.1$ Hz), 4.13 (m, 2H, H1, 1′), 4.41 (dt, 1H, $J = 2.0$, 2.0, 11.9 Hz), 4.49–4.56 (m, 5H), 4.73 (ABq, 2H), 4.81 (ABq, 2H), 4.84 (d, 1H, $J = 11.9$ Hz), 5.02 (dd, 2H, $J = 2.0$, 4.5 Hz, =CH_2), 5.08 (dd, 1H, $J = 2.0$, 4.0 Hz, =CH_2), 7.14–7.34 (m, 20H); FABMS (*m*/*z*, %): 687 (M^++23, 10), 181 (15), 154 (10), 121 (25), 91 (100). Anal. calcd for $C_{41}H_{44}O_8$: C, 74.08; H, 6.67. Found: C, 74.04; H, 6.62.

3.18. Ethyl 8,9,10-tri(benzyloxy)-7-benzyloxymethyl-3-methyl-(3*S*,4*S*,5*S*,7*R*,8*R*,9*S*,10*R*)-1,6-dioxaspiro[4.5]-decane-4-carboxylate 19b

A solution of **17b** (0.2 g, 0.26 mmol), sodium cyanoborohydride (0.03 g, 0.53 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux for 2 h, worked up and purified as described for **5**, to give **19b** (0.12 g) in 67% yield as a colourless syrup; $[\alpha]_D = +28.65$ (*c* 1, $CHCl_3$); IR (neat): 700, 1050, 1280, 1660, 2940 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.22 (t, 3H, $J_{1,2} = 6.8$, $J_{1,3} = 13.6$ Hz, OCH_2CH_3), 1.64 (d, 3H, $J = 6.8$ Hz, CH_3), 2.35–2.50 (m, 1H), 2.66 (d, 1H, $J = 6.8$ Hz), 3.55–3.90 (m, 5H), 3.94–4.30 (m, 3H), 4.46–4.72 (m, 4H), 4.74–4.86 (m, 3H), 4.90–5.02 (m, 3H), 7.12–7.44 (m, 20H); FABMS (*m*/*z*,%): 689 (M^++23, 14), 552 (8), 289 (28), 181 (72), 105 (100). Anal. calcd for $C_{41}H_{46}O_8$: C, 73.85; H, 6.95. Found: C, 73.82; H, 6.94.

3.19. Ethyl 8,9,10-tri(benzyloxy)-7-benzyloxymethyl-3-methyl-(3*S*,4*S*,5*R*,7*R*,8*R*,9*S*,10*R*)-1,6-dioxaspiro[4.5]-decane-4-carboxylate 20b

A solution of **18b** (0.1 g, 0.13 mmol), sodium cyanoborohydride (0.016 g, 0.26 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux for 2 h, worked up and purified as described for **5**, to give **20b** (0.06 g) in 67% yield as a colourless syrup; $[\alpha]_D = +16.3$ (*c* 1, $CHCl_3$); IR (neat): 750, 1040, 1280, 1640, 2950 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.20 (t, 3H, $J = 6.8$, 13.6 Hz, OCH_2CH_3), 1.66 (d, 3H, $J = 13.6$ Hz, CH_3), 2.30–2.45 (m, 1H, H-2), 2.70 (d, 1H, $J = 13.6$ Hz, H-3), 3.54–3.88 (m, 5H), 3.96–4.30 (m, 3H), 4.46–4.70 (m, 4H), 4.82–4.86 (m, 3H), 5.02 (ABq, 3H, $J = 13.6$ Hz), 7.15–7.45 (m, 20H); FABMS (*m*/*z*, %): 689 (M^++23, 10), 289 (30), 235 (26), 123 (70), 105 (100). Anal. calcd for $C_{41}H_{46}O_8$: C, 73.85; H, 6.95. Found: C, 73.84; H, 6.93.

3.20. Ethyl 8,9,10-tri(benzyloxy)-7-benzyloxymethyl-3-[2-hydroxy-ethylidene]-(7*R*,8*R*,9*S*,10*R*)-1,6-dioxaspiro-[4.5]decane-4-carboxylate 19c/20c

A solution of **17c**/**18c** (0.15 g, 0.216 mmol), sodium cyanoborohydride (0.02 g, 0.43 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux for 2 h, worked up and purified as described for **5**, to give **19c**/**20c** (0.11 g) in 73% yield as a colourless syrup; $[\alpha]_D = +46.05$ (*c* 0.25, $CHCl_3$); IR (neat): 840, 1100, 1380, 2850, 3440 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.20 (t, 3H OCH_2CH_3), 3.63 (dd, 1H, $J = 1.7$, 11.3 Hz), 3.73–3.83 (m, 4H), 3.94 (d, 1H, $J = 9.6$ Hz), 3.99–4.16 (m, 2H), 4.09–4.45 (m, 3H), 4.51–4.56 (m, 2H), 4.66–4.87 (m, 4H), 4.91–5.26 (m, 4H), 5.85–6.10 (m, 1H, =CH), 7.22–7.45 (m, 20H); FABMS (*m*/*z*,%):

717 (M^++23, 32), 391 (36), 271 (42), 240 (78), 91 (100). Anal. calcd for $C_{42}H_{46}O_9$: C, 72.60; H, 6.67; Found: C, 72.55; H, 6.64.

3.21. Ethyl 2-bromo-2-[6-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-4-hydroxy-2,2-dimethyl-(3a*S*,4*S*,6*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxol-4-yl]acetate 23 and 23a

To a stirred solution of enol ester **1** (1.0 g, 3.04 mmol) and water (0.5 mL) in dry acetonitrile (5 mL), *N*-bromo succinimide (0.54 g, 3.04 mmol) was added, worked up and purified as described for **4**, to give **23** and **23a** (0.98 g) in 76% yield as a separable mixture of isomers (2.9:1). First eluted was **23** (0.74 g) in 57% yield as a light yellow syrup; $[\alpha]_D = +28.8$ (*c* 2.05, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.20–1.45 (m, 12H, CH_3), 1.50 (s, 3H, CH_3), 3.92–4.02 (m, 3H, H-7,8,8′), 4.05–4.18 (m, 1H, H-6), 4.30 (q, 2H, -O*CH*$_2$CH$_3$), 4.55 (d, 1H, $J_{4,5} = 4.5$ Hz, H-4), 4.80–4.90 (m, 2H, H-2,5); FABMS (*m*/*z*, %): 411 (17), 383 (25), 352 (45), 350 (100), 43 (67). Anal. calcd for $C_{16}H_{25}BrO_8$: C, 45.19; H, 5.93; Found: C, 45.11; H, 5.86. Second eluted was **23a** (0.25 g) in 19% yield as a light yellow syrup; $[\alpha]_D = +39.2$ (*c* 0.55, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.20–1.40 (m, 9H, CH_3), 1.42, 1.46 (2s, 6H, CH_3), 3.60–3.95 (m, 3H, H-7,8,8′), 4.05–4.10 (m, 1H, H-6), 4.12 (q, 2H, -O*CH*$_2$CH$_3$), 4.32 (d, 1H, $J_{4,5} = 4.2$ Hz, H-4), 4.80–4.95 (m, 2H, H-2,5).

3.22. Ethyl 2-bromo-2-[6-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-4-methoxy-2,2-dimethyl-(3a*S*,4*S*,6*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxol-4-yl]acetate 25 and 25a

To a stirred solution of **1** (1.0 g, 3.04 mmol) and methanol (2 mL) in dry acetonitrile (5 mL), *N*-bromo succinimide (0.54 g, 3.04 mmol) was added, worked up and purified as described for **4**, to give **25** and **25a** (1.08 g) in 81% yield as a separable mixture of isomers (3.2:1). First eluted was **25** (0.82 g) in 61% yield as a light yellow syrup; ^1H NMR (200 MHz, $CDCl_3$): δ 1.25–1.38 (m, 9H, CH_3), 1.40, 1.52 (2s, 6H, CH_3), 3.36 (s, 3H, -OMe), 3.83 (dd, 1H, $J_{7,8} = 4.0$, $J_{8,8'} = 5.4$ Hz, H-8), 3.90–4.08 (m, 2H, H-6,8′), 4.21 (q, 2H, -O*CH*$_2$CH$_3$), 4.35 (dd, 1H, $J_{5,6} = 5.4$, $J_{6,7} = 11.8$ Hz, H-7), 4.48 (d, 1H, $J_{4,5} = 5.4$ Hz, H-4), 4.74–4.80 (m, 2H, H-2,5); FABMS (*m*/*z*, %): 425 (24), 409 (31), 360 (56), 265 (100), 74 (67). Anal. calcd for $C_{17}H_{27}BrO_8$: C, 46.48; H, 6.19. Found: C, 46.41; H, 6.13. Second eluted was **25a** (0.25 g) in 20% yield as a light yellow syrup; IR (neat): 1096, 1750, 2980 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.24–1.40 (m, 9H, CH_3), 1.44, 1.49 (2s, 6H, CH_3), 3.46 (s, 3H, -OMe), 3.78 (dd, 1H, $J_{7,8} = 4.0$, $J_{8,8'} = 8.0$ Hz, H-8), 3.98–4.15 (m, 2H, H-6,8), 4.20–4.40 (m, 3H, H-7, -O*CH*$_2$CH$_3$), 4.52 (d, 1H, $J_{4,5} = 6.0$ Hz, H-4), 4.83 (dd, 1H, $J_{4,5} = 6.0$, $J_{5,6} = 4.0$ Hz, H-5), 4.85 (s, 1H, H-2).

3.23. Ethyl 2-bromo-2-[6-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-4-ethoxy-2,2-dimethyl-(3a*S*,4*S*,6*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxol-4-yl]acetate 26 and 26a

To a stirred solution of **1** (0.5 g, 1.52 mmol) and ethanol (2 mL) in dry acetonitrile (5 mL), *N*-bromo succinimide (0.27 g, 1.52 mmol) was added, worked up and purified as described for **4**, to give **26** and **26a** (0.5 g) in 73% yield as a separable mixture of isomers in 3.2:1 ratio, respectively. First eluted was **26** (0.38 g) in 56% yield as a light yellow syrup; ^1H NMR (200 MHz, $CDCl_3$): δ 1.16 (t, 3H, -OCH$_2$*CH*$_3$), 1.28 (t, 3H, -OCH$_2$*CH*$_3$), 1.32 (s, 6H, CH_3), 1.36, 1.50 (2s, 6H, CH_3), 3.37–3.54 (m, 1H, H-8), 3.80–4.05 (m, 4H, H-6,8′, -O*CH*$_2$CH$_3$), 4.17 (q, 2H, -O*CH*$_2$CH$_3$), 4.26–4.38 (m, 1H, H-7), 4.46 (d, 1H, $J_{4,5} = 5.7$ Hz, H-4), 4.73–4.80 (m, 2H, H-2,5); FABMS (*m*/*z*, %): 439 (13), 425 (31), 380 (56), 182 (100), 35 (54). Anal. calcd for $C_{18}H_{29}BrO_8$: C, 47.69; H, 6.45. Found: C, 47.62; H, 6.38. Second eluted was **26a** (0.119 g) in 17% yield as a light yellow syrup; ^1H NMR (200 MHz, $CDCl_3$): δ 1.24–1.52 (m, 18H, CH_3), 3.60–3.72 (m, 1H, H-8), 3.80 (dd, 1H, $J_{5,6} = 4.0$, $J_{6,7} = 8.0$ Hz, H-6), 3.85–4.12 (m, 3H, H-6, -O*CH*$_2$CH$_3$), 4.19–4.40 (m, 3H, H-7, -O*CH*$_2$CH$_3$), 4.56 (d, 1H, $J_{4,5} = 5.5$ Hz, H-4), 4.80–4.91 (m, 2H, H-2,5).

3.24. Ethyl 2-bromo-2-[6-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-4-(4-hydroxybutoxy)-2,2-dimethyl-(3a*S*,4*S*,6*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxol-4-yl]acetate 27 and 27a

To a stirred solution of **1** (1.0 g, 3.04 mmol) and butane-1,4-diol (0.54 mL, 6.09 mmol) in dry acetonitrile (10 mL), *N*-bromo succinimide (0.54 g, 3.04 mmol) was added, worked up and purified as described for **4**, to give **27** and **27a** (0.98 g) in 65% yield as a separable mixture of isomers in 2.6:1 ratio, respectively. First eluted was **27** (0.7 g) in 47% yield as a light yellow syrup; ^1H NMR (200 MHz, $CDCl_3$): δ 1.20–1.50 (m, 19H, CH_3, -OCH$_2$*CH*$_3$, H-10,10′,11,11′), 3.82–4.05 (m, 3H, H-7,8,8′), 4.08–4.34 (m, 6H, H-9,9′,12,12′, -O*CH*$_2$CH$_3$), 4.44–4.52 (m, 1H, H-6), 4.55 (d, 1H, $J_{4,5} = 4.0$ Hz, H-4), 4.75 (s, 1H, H-2), 4.80 (dd, 1H, $J_{4,5} = 4.0$, $J_{5,6} = 5.6$ Hz, H-5); FABMS (*m*/*z*, %): 498 (M^++1, 7), 483 (24), 278 (45), 178 (100), 81 (56). Anal. calcd for $C_{20}H_{33}BrO_9$: C, 48.30; H, 6.69. Found: C, 48.21; H, 6.61. Second eluted was **27a** (0.27 g) in 18% yield as a light yellow syrup; ^1H NMR (200 MHz, $CDCl_3$): δ 1.20–1.50 (m, 19H, CH_3, -OCH$_2$*CH*$_3$, H-10,10′,11,11′), 3.62–3.76 (m, 2H, H-9,9′), 3.94–4.04 (m, 2H, H-8,8′), 4.05–4.45 (m, 7H, H-4,6,7,12,12′, -O*CH*$_2$CH$_3$), 4.70 (s, 1H, H-2), 4.90–5.00 (m, 1H, H-5).

3.25. Ethyl 2-bromo-2-[3,4,5-tri(benzyloxy)-6-benzyloxymethyl-2-methoxy-(2*R*,3*R*,4*S*,5*R*,6*R*)-tetrahydro-2*H*-2-pyranyl]acetate (31a) and ethyl 2-bromo-2-[3,4,5-tri(benzyloxy)-6-benzyloxymethyl-2-methoxy-(2*S*,3*R*,4*S*,5*R*,6*R*)-tetrahydro-2*H*-2-pyranyl]acetate 32a

To a stirred solution of **16** (0.2 g, 0.32 mmol) and methanol (0.5 mL) in dry acetonitrile (2 mL), *N*-bromo succinimide (0.05 g, 0.32 mmol) was added, worked up and purified as described for **4**, to give **31a** and **32a** as a separable mixture of isomers in 5.8:1 ratio, respectively. First eluted was **32a** (0.02 g) in 11% as a light yellow syrup; $[\alpha]_D = -12.3$ (*c* 0.5, $CHCl_3$); IR (neat):

700, 1120, 1660, 2880 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.24 (t, 3H, $J=5.4$, 8.1 Hz, OCH_2CH_3), 3.44 (s, 3H, OCH_3), 3.60–4.00 (m, 5H), 4.16–4.20 (m, 3H), 4.44–4.58 (m, 9H), 7.10–7.40 (m, 20H). Second eluted was **31a** (0.145 g) in 62% as a light yellow syrup; $[\alpha]_D = -26.0$ (c 1, $CHCl_3$); IR (neat): 780, 1100, 1650, 2910 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.25 (t, 3H, $J=4.3$, 8.6 Hz, OCH_2CH_3), 3.40 (s, 3H, OCH_3), 3.50–3.76 (m, 4H), 4.00–4.06 (m, 2H), 4.10–4.22 (m, 3H), 4.44–4.64 (m, 4H), 4.70–4.90 (m, 4H), 7.14–7.36 (m, 20H).

3.26. Ethyl 2-bromo-2-[3,4,5-tri(benzyloxy)-6-benzyloxymethyl-2-ethoxy-(2*R*,3*R*,4*S*,5*R*,6*R*)-tetrahydro-2*H*-2-pyranyl]acetate (31b) and ethyl 2-bromo-2-[3,4,5-tri(benzyloxy)-6-benzyloxymethyl-2-ethoxy-(2*S*,3*R*,4*S*,5*R*,6*R*)-tetrahydro-2*H*-2-pyranyl]acetate 32b

To a stirred solution of **16** (0.2 g, 0.32 mmol) and ethanol (0.5 mL) in dry acetonitrile (2 mL), *N*-bromo succinimide (0.05 g, 0.32 mmol) was added, worked up and purified as described for **4**, to give **31b** and **32b** as a separable mixture of isomers in 4:1 ratio, respectively. First eluted was **32b** (0.02 g) in 15% as a light yellow syrup; $[\alpha]_D = +8.8$ (c 0.6, $CHCl_3$); IR (neat): 780, 1120, 1240, 1670, 2900 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.22 (t, 6H, $J_{1,2}=4.76$, $J_{1,3}=9.52$ Hz, OCH_2CH_3), 3.50–3.78 (m, 5H), 3.95–4.24 (m, 4H, OCH_2), 4.45–4.70 (m, 4H), 4.72–4.92 (m, 4H), 5.05 (ABq, 2H, $J=14.2$ Hz), 7.10–7.40 (m, 20H). Second eluted was 31b (0.135 g) in 56% as a syrup; $[\alpha]_D = +12.0$ (c 1.5, $CHCl_3$); IR (neat): 740, 1130, 1265, 1680, 3280 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.22 (t, 6H, $J_{1,2}=4.78$, $J_{1,3}=9.54$ Hz, OCH_2CH_3), 3.52–3.78 (m, 5H), 3.95–4.25 (m, 4H, OCH_2), 4.47–4.72 (m, 4H), 4.73–4.90 (m, 4H), 4.95–5.10 (m, 2H), 7.15–7.40 (m, 20H).

3.27. Ethyl 2-bromo-2-[3,4,5-tri(benzyloxy)-6-benzyloxymethyl-2-(4-hydroxybutoxy)-(3*R*,4*S*,5*R*,6*R*)-tetrahydro-2*H*-2-pyranyl]acetate 31c/32c

To a stirred solution of **16** (0.2 g, 0.32 mmol) and butane-1,4-diol (0.06 mL, 0.65 mmol) in dry acetonitrile (2 mL), *N*-bromo succinimide (0.05 g, 0.32 mmol) was added, worked up and purified as described for **4**, to give **31c**/**32c** as an inseparable mixture of isomers (0.135 g) in 63% yield as a colourless syrup; $[\alpha]_D = -32.15$ (c 0.25, $CHCl_3$); IR (neat): 720, 1080, 1240, 1720, 2910 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.20 (t, 3H, $J_{1,2}=5.55$, $J_{1,3}=8.33$ Hz, OCH_2CH_3), 1.60–1.78 (m, 4H), 3.60–3.70 (m, 4H), 3.78–3.90 (m, 3H), 4.05–4.20 (m, 2H), 4.42–4.62 (m, 5H), 4.64–4.90 (m, 5H), 7.04–7.38 (m, 20H).

3.28. Ethyl 2-bromo-2-[3,4,5-tri(benzyloxy)-6-benzyloxymethyl-2-(4-phenylbutoxy)-(3*R*,4*S*,5*R*,6*R*)-tetrahydro-2*H*-2-pyranyl]acetate 31d/32d

To a stirred solution of **16** (0.2 g, 0.32 mmol) and 4-phenyl-butane-1-ol (0.09 g, 0.65 mmol) in dry acetonitrile (2 mL), *N*-bromo succinimide (0.05 g, 0.32 mmol) was added, worked up and purified as described for **4**, to give **31d**/**32d** as an inseparable mixture of isomers (0.162 g) in 59% yield as a light yellow syrup; $[\alpha]_D = +28.8$ (c 0.5, $CHCl_3$); IR (neat): 710, 1160, 1660, 2890 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.20 (t, 3H, $J_{1,2}=5.55$, $J_{1,3}=8.33$ Hz, OCH_2CH_3), 1.60–1.78 (m, 4H), 2.68 (t, 2H, $J_{1,2}=5.55$, $J_{1,3}=8.33$ Hz, CH_2CH_2Ph), 3.56–3.70 (m, 4H), 3.80–3.90 (m, 1H), 4.06–4.20 (m, 2H), 4.42–4.60 (m, 5H), 4.62–4.90 (m, 5H), 7.04–7.18 (m, 25H).

3.29. Ethyl 2-[6-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-4-hydroxy-2,2-dimethyl-(3a*S*,4*R*,6*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxol-4-yl]acetate 24

A solution of **23** and **23a** (0.2 g, 0.46 mmol), sodium cyanoborohydride (0.05 g, 0.93 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux for 1 h, worked up and purified as described for **5**, to give **24** (0.13 g) in 84% yield as a colourless syrup; $[\alpha]_D = +5.25$ (c 0.60, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 1.24–1.35 (m, 6H, CH_3), 1.36, 1.43, 1.48 (3s, 9H, CH_3), 2.75 (d, 2H, $J_{2,2'}=7.7$ Hz, $-CH_2CO_2Et$), 3.92–4.10 (m, 3H, H-6,8,8′), 4.20 (q, 2H, $-OCH_2CH_3$), 4.28–4.40 (m, 1H, H-7), 4.48 (d, 1H, $J_{4,5}=5.7$ Hz, H-4), 4.84 (dd, 1H, $J_{4,5}=5.7$, $J_{5,6}=4.0$ Hz, H-5); FABMS (m/z, %): 346 (M^+, 5), 331 (32), 272 (100), 74 (56). Anal. calcd for $C_{16}H_{26}O_8$: C, 55.48; H, 7.57. Found: C, 55.41; H, 7.52.

3.30. Ethyl 2-[6-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-4-methoxy-2,2-dimethyl-(3a*S*,4*R*,6*R*,6a*S*)–perhydrofuro-[3,4-*d*][1,3]dioxol-4-yl]acetate 28

A solution of **25** and **25a** (0.15 g, 0.34 mmol), sodium cyanoborohydride (0.04 g, 0.68 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux, worked up and purified as described for **5**, to give **28** (0.1 g) in 84% yield as a colourless syrup; $[\alpha]_D = +46.0$ (c 1.05, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 1.24–1.40 (m, 9H, CH_3), 1.44, 1.48 (2s, 6H, CH_3), 2.86 (s, 2H, $-CH_2CO_2Et$), 3.22 (s, 3H, -OMe), 3.70 (dd, 1H, $J_{7,8}=4.3$, $J_{8,8'}=8.2$ Hz, H-8), 3.92 (dd, 1H, $J_{5,6}=4.3$, $J_{6,7}=8.6$ Hz, H-6), 4.05 (dd, 1H, $J_{7,8'}=4.3$, $J_{8,8'}=6.5$ Hz, H-8′), 4.15 (q, 2H, $-OCH_2CH_3$), 4.26–4.38 (m, 1H, H-7), 4.60 (d, 1H, $J_{4,5}=6.5$ Hz, H-4), 4.76 (dd, 1H, $J_{4,5}=6.5$, $J_{5,6}=4.0$ Hz, H-5); FABMS (m/z, %): 360 (4), 359 (67), 329 (34), 271 (100). Anal. calcd for $C_{17}H_{28}O_8$: C, 56.66; H, 7.83. Found: C, 56.61; H, 7.78.

3.31. Ethyl 2-[6-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-4-ethoxy-2,2-dimethyl-(3a*S*,4*R*,6*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxol-4-yl]acetate 29

A solution of **26** and **26a** (0.2 g, 0.44 mmol), sodium cyanoborohydride (0.05 g, 0.88 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux, worked up and purified as described for **5**, to give **29** (0.11 g) in 68% yield as a colourless syrup; $[\alpha]_D = +55.1$ (c 2.15, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 1.20 (t, 3H, $-OCH_2CH_3$), 1.24 (t, 3H, $-OCH_2CH_3$), 1.34 (s, 6H, CH_3), 1.40, 1.46 (2s, 6H,

CH_3), 2.85 (s, 2H, H-2,2′), 3.48 (q, 2H, -O$CH_2$$CH_3$), 3.72 (dd, 1H, $J_{7,8}$ = 4.2, $J_{8,8'}$ = 7.6 Hz, H-8), 3.90 (dd, 1H, $J_{5,6}$ = 4.7, $J_{6,7}$ = 9.5 Hz, H-6), 4.05 (dd, 1H, $J_{7,8'}$ = 6.6, $J_{8,8'}$ = 9.5 Hz, H-8′), 4.13 (q, 2H, -O$CH_2$$CH_3$), 4.22–4.36 (m, 1H, H-7), 4.58 (d, 1H, $J_{4,5}$ = 6.6 Hz, H-4), 4.75 (dd, 1H, $J_{4,5}$ = 6.6, $J_{5,6}$ = 4.2 Hz, H-5); FABMS (*m*/*z*,%): 373 (M-1, 7), 359 (70), 329 (43), 271 (100), 213 (50). Anal. calcd for $C_{18}H_{30}O_8$: C, 57.74; H, 8.08. Found: C, 57.66; H, 8.01.

3.32. Ethyl 2-[6-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-4-(4-hydroxybutoxy)-2,2-dimethyl-(3a*S*,4*R*,6*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxol-4-yl]acetate 30

A solution of **27** and **27a** (0.2 g, 0.40 mmol), sodium cyanoborohydride (0.05 g, 0.80 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux, worked up and purified as described for **5**, to give **30** (0.11 g) in 65% yield as a colourless syrup; $[\alpha]_D$ = +3.4 (*c* 1.85, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.20–1.48 (m, 19H, CH_3, -O$CH_2$$CH_3$, H-10,10′,11,11′), 2.70 (d, 2H, *J* = 5.4 Hz, H-2,2′), 3.80–4.32 (m, 10H, H-6,7,8,8′,9,9′,12,12′, -O$CH_2$$CH_3$), 4.43 (d, 1H, $J_{4,5}$ = 5.0 Hz, H-4), 4.78 (dd, 1H, $J_{4,5}$ = 5.0, $J_{5,6}$ = 4.0 Hz, H-5); FABMS (*m*/*z*, %): 418 (M^+, 6), 403 (32), 271 (100), 181 (45). Anal. calcd for $C_{20}H_{34}O_9$: C, 57.40; H, 8.19. Found: C, 57.35; H, 8.14.

3.33. Ethyl 2-[3,4,5-tri(benzyloxy)-6-benzyloxymethyl-2-(3-butynyloxy)-(2*S*,3*R*,4*S*,5*R*,6*R*)-tetrahydr-2*H*-2-pyranyl]acetate 21

A solution of **17d** (0.1 g, 0.15 mmol), sodium cyanoborohydride (0.02 g, 0.317 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux for 2 h, worked up and purified as described for **5**, to give **21** (0.08 g) in 74% yield as a colourless syrup; $[\alpha]_D$ = +32.6 (*c* 1.5, $CHCl_3$); IR (neat): 750, 1060, 1280, 1640, 2960 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.22 (t, 3H, *J* = 4.5, 9.09 Hz, O$CH_2$$CH_3$), 1.90 (br.s, 1H, ≡CH), 2.45–2.60 (m, 2H, H-3,3′), 2.80 (s, 2H, H-2,2′), 3.50–3.80 (m, 6H), 4.90–4.15 (m, 4H), 4.40–4.70 (m, 3H), 4.75–5.00 (m, 5H), 7.10–7.35 (m, 20H); FABMS (*m*/*z*, %): 678 (M^+, 22), 581 (12), 271 (38), 243 (44), 91 (100). Anal. calcd for $C_{42}H_{46}O_8$: C, 74.31; H, 6.83. Found: C, 74.30; H, 6.80.

3.34. Ethyl 2-[3,4,5-tri(benzyloxy)-6-benzyloxymethyl-2-(3-butynyloxy)-(2*R*,3*R*,4*S*,5*R*,6*R*)-tetrahydr-2*H*-2-pyranyl]acetate 22

A solution of **18d** (0.1 g, 0.13 mmol), sodium cyanoborohydride (0.016 g, 0.26 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux for 2 h, worked up and purified as described for **5**, to give **22** (0.06 g) in 67% yield as a colourless syrup; $[\alpha]_D$ = +38.1 (*c* 0.25, $CHCl_3$); IR (neat): 700, 1080, 1280, 1610, 2960 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.26 (t, 3H, $J_{1,2}$ = 4.5, $J_{1,3}$ = 9.09 Hz, O$CH_2$$CH_3$), 2.02 (br.s, 1H, ≡CH), 2.40–2.60 (m, 2H), 2.85 (ABq, 2H, *J* = 9.09 Hz, H-2,2′), 3.45–3.80 (m, 6H), 3.90–4.10 (m, 4H), 4.40–4.65 (m, 3H), 4.70–4.96 (m, 5H), 7.08–7.35 (m, 20H); FABMS (*m*/*z*, %): 679 (M^++1, 5), 271 (45), 181 (50), 135 (46), 91 (100). Anal. calcd for $C_{42}H_{46}O_8$: C, 74.31; H, 6.83. Found: C, 74.27; H, 6.80.

3.35. Ethyl 2-[3,4,5-tri(benzyloxy)-6-benzyloxymethyl-2-methoxy-(2*S*,3*R*,4*S*,5*R*,6*R*)-tetrahydro-2*H*-2-pyranyl]-acetate 33a

A solution of **31a** (0.1 g, 0.13 mmol), sodium cyanoborohydride (0.018 g, 0.278 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux for 2 h, worked up and purified as described for **5**, to give **33a** (0.05 g) in 62% yield as a colourless syrup; $[\alpha]_D$ = +35.8 (*c* 1, $CHCl_3$); IR (neat): 770, 1100, 1680, 2880 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.22 (t, 3H, $J_{1,2}$ = 9.5, $J_{1,3}$ = 14.2 Hz, O$CH_2$$CH_3$), 2.80 (s, 2H, H-2, 2′), 3.30 (s, 3H, OCH_3), 3.70 (dd, 4H, *J* = 4.76, 9.5 Hz), 4.02–4.10 (m, 4H), 4.60 (ABq, 3H, *J* = 9.5 Hz), 4.80–5.05 (m, 5H), 7.15–7.45 (m, 20H); FABMS (*m*/*z*, %): 663 (M^++23, 6), 281 (66), 235 (24), 221 (64), 207 (100). Anal. calcd for $C_{39}H_{44}O_8$: C, 73.10; H, 6.92. Found: C, 73.08; H, 6.89.

3.36. Ethyl 2-[3,4,5-tri(benzyloxy)-6-benzyloxymethyl-2-methoxy-(2*R*,3*R*,4*S*,5*R*,6*R*)-tetrahydro-2*H*-2-pyranyl]acetate 34a

A solution of **32a** (0.1 g, 0.13 mmol), sodium cyanoborohydride (0.018 g, 0.278 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux for 2 h, worked up and purified as described for **5**, to give **34a** (0.06 g) in 67% yield as a colourless syrup; $[\alpha]_D$ = −28.5 (*c* 0.25, $CHCl_3$); IR (neat): 720, 1120, 1640, 2840 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.22 (t, 3H, $J_{1,2}$ = 9.5, $J_{1,3}$ = 14.2 Hz, O$CH_2$$CH_3$), 2.82 (ABq, 2H, *J* = 14.2 Hz, H-2,2′), 3.40 (s, 3H, OCH_3), 3.50–3.90 (m, 4H), 4.00–4.15 (m, 4H), 4.42–4.65 (m, 3H), 4.70–4.90 (m, 5H), 7.05–7.35 (m, 20H); FABMS (*m*/*z*, %): 641 (M^++1, 8), 341 (32), 281 (70), 235 (24), 267 (100). Anal. calcd for $C_{39}H_{44}O_8$: C, 73.10; H, 6.92. Found: C, 73.06; H, 6.90.

3.37. Ethyl 2-[3,4,5-tri(benzyloxy)-6-benzyloxymethyl-2-ethoxy-(2*S*,3*R*,4*S*,5*R*,6*R*)-tetrahydro-2*H*-2-pyranyl]-acetate 33b

A solution of **31b** (0.1 g, 0.13 mmol), sodium cyanoborohydride (0.017 g, 0.27 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux for 2 h, worked up and purified as described for **5**, to give **33b** (0.05 g) in 56% yield as a colourless syrup; $[\alpha]_D$ = +42.2 (*c* 0.80, $CHCl_3$); IR (neat): 700, 1100, 1280, 1660, 2950 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.10–1.30 (m, 6H, O$CH_2$$CH_3$, $CO_2CH_2CH_3$), 2.78 (s, 2H, H-2,2′), 3.50–3.80 (m, 5H), 3.76–4.14 (m, 4H), 4.40–4.65 (m, 4H), 4.72–5.02 (m, 5H), 7.10–7.38 (m, 20H); FABMS (*m*/*z*, %): 677 (M^++23, 6), 515 (54), 489 (72), 291 (41), 91 (100). Anal. calcd for $C_{40}H_{46}O_8$: C, 73.37; H, 7.08. Found: C, 73.33; H, 7.04.

3.38. Ethyl 2-[3,4,5-tri(benzyloxy)-6-benzyloxymethyl-2-ethoxy-(2*R*,3*R*,4*S*,5*R*,6*R*)-tetrahydro-2*H*-2-pyranyl]-acetate 34b

A solution of **32b** (0.1 g, 0.13 mmol), sodium cyanoborohydride (0.017 g, 0.27 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux for 2 h, worked up and purified as described for **5**, to give **34b** (0.05 g) in 58% yield as a colourless syrup; $[\alpha]_D = +6.8$ (*c* 0.4, $CHCl_3$); IR (neat): 760, 1080, 1650, 2940 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.10–1.30 (m, 6H, OCH_2CH_3, $CO_2CH_2CH_3$), 2.80 (ABq, 2H, $J = 14.2$ Hz, H-2, 2′), 3.58–3.84 (m, 7H), 4.05 (ABq, 2H, $J = 7.14$ Hz), 4.44–4.68 (m, 5H), 4.70–4.90 (m, 4H), 7.10–7.35 (m, 20H); FABMS (*m*/*z*, %): 654 (M^+, 6), 489 (72), 291 (38), 91 (100), 55 (40). Anal. calcd for $C_{40}H_{46}O_8$: C, 73.37; H, 7.08. Found: C, 73.35; H, 7.04.

3.39. Ethyl 2-[3,4,5-tri(benzyloxy)-6-benzyloxymethyl-2-[4-hydroxybutoxy)-(3*R*,4*S*,5*R*,6*R*)-tetrahydro-2*H*-2-pyranyl]acetate 33c/34c

A solution of **31c**/**32c** (0.1 g, 0.12 mmol), sodium cyanoborohydride (0.016 g, 0.27 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux for 2 h, worked up and purified as described for **5**, to give **33c**/**34c** (0.06 g) in 89% yield as a colourless syrup; $[\alpha]_D = +30.2$ (*c* 0.45, $CHCl_3$); IR (neat): 760, 1160, 1220, 1640, 3480 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.15 (t, 3H, $J_{1,2} = 6.8$, $J_{1,3} = 13.6$ Hz, $CO_2CH_2CH_3$), 1.52–1.72 (m, 4H, CH_2CH_2), 2.50, 2.72 (ABq, s, 2H, H-2, 2′), 3.40–3.70 (m, 5H), 3.84–4.20 (m, 6H), 4.35–4.64 (m, 4H), 4.68–5.00 (m, 5H), 7.02–7.40 (m, 20H); FABMS (*m*/*z*, %): 721 (M^++23, 4), 271 (16), 207 (18), 181 (16), 91 (100). Anal. calcd for $C_{42}H_{50}O_9$: C, 72.18; H, 7.21. Found: C, 72.17; H, 7.20.

3.40. Ethyl 2-[3,4,5-tri(benzyloxy)-6-benzyloxymethyl-2-[4-phenylbutoxy)-(3*R*,4*S*,5*R*,6*R*)-tetrahydro-2*H*-2-pyranyl]acetate 33d/34d

A solution of **31d**/**32d** (0.1 g, 0.12 mmol), sodium cyanoborohydride (0.015 g, 0.27 mmol) and tributyltin chloride (catalytic) in *t*-butanol (2 mL) was heated at reflux for 2 h, worked up and purified as described for **5**, to give **33d**/**34d** (0.035 g) in 59% yield as a colourless syrup; $[\alpha]_D = +24.4$ (*c* 1, $CHCl_3$); IR (neat): 740, 1060, 1680, 2940 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.18 (t, 3H, $J_{1,2} = 6.8$, $J_{1,3} = 13.6$ Hz, $CO_2CH_2CH_3$), 1.50–1.72 (m, 4H, CH_2CH_2), 2.40 (t, 2H, $J_{1,2} = 6.8$, $J_{1,3} = 13.6$ Hz, CH_2Ph), 2.75, 2.80 (s, ABq, 2H, H-2, 2′), 3.45–3.80 (m, 4H), 3.90–4.12 (m, 5H), 4.40–4.68 (m, 4H), 4.70–5.00 (m, 5H), 7.00–7.35 (m, 25H); FABMS (*m*/*z*, %): 781 (M^++23, 20), 501 (10), 181 (8), 133 (10), 91 (100). Anal. calcd for $C_{48}H_{54}O_8$: C, 75.96; H, 7.17; Found: C, 75.94; H, 7.12.

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