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A stereoselective approach to phosphodiester-linked oligomers of the repeating unit of *Escherichia coli* K52 capsular polysaccharide containing β-D-fructofuranosyl moieties

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Abstract—A stereoselective synthesis of a dimer, β-D-Fru*f*-(2→2)-α-D-Gal*p*-(1-PO_3H-3)-[β-D-Fru*f*-(2→2)]-D-Gal*p*, of the repeating unit of the K52 type CPS of *E. coli* is described. The β-fructofuranosyl residue was introduced in a DMTST-promoted coupling using a 1,4-TIPS-bridged thiofructofuranoside donor and a 2-OH TMSE galactoside acceptor affording exclusively the β-linked disaccharide. Protecting group manipulation of this disaccharide yielded both a 3-OH acceptor and a reducing disaccharide, which were linked via a phosphate diester bridge using H-phosphonate chemistry. The hemiacetal is present only as the α-anomer, why phosphonylation yielded stereoselectively the α-H-phosphonate monoester. Activation of the latter with pivaloyl chloride in the presence of the 3-OH disaccharide acceptor and subsequent I_2-oxidation gave the target dimer in good yield.

1. Introduction

Bacterial polysaccharides, even with small repeating units, often contain substantial structural complexity with many synthetic challenges. The capsular polysaccharide (CPS) of *E. coli* serotype K52 composed of disaccharide repeating units is no exception (Fig. 1).[1] Apart from a complex acylation pattern and being connected via anomeric phosphate diester linkages the repeating unit also contains a β-fructofuranosidic linkage, which so far has not been possible to synthesise chemically in a stereoselective manner. Hence, when synthesis of a dimer structure of the deacylated polysaccharide was attempted earlier the fructose part was omitted.[2] We have recently developed a method for stereoselective synthesis of β-fructofuranosides.[3] Herein we show that this method is applicable also to the synthesis of the repeating unit of *E. coli* K52 CPS, and that the resulting disaccharide allows conversion both to an acceptor and an anomeric H-phosphonate monoester to facilitate the formation of oligomers.

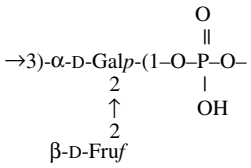

Figure 1. Structure of the deacylated repeating unit of *E. coli* K 52 CPS.[1]

2. Results and discussion

To make a convergent synthesis possible, where both the acceptor and the elongating monomer could be obtained from the same precursor, the trimethylsilylethyl (TMSE) glycoside of galactose[4] was chosen as starting material. Benzylidenation to give **1** followed by regioselective tin-mediated *p*-methoxybenzylation[5] or acetylation afforded **2** and **3**, respectively, with a free 2-OH ready for the introduction of the fructofuranosyl residue (Scheme 1). Attempts to use the internal aglycon delivery approach in this coupling proved fruitless.[6–8] However, employing our fructofuranosyl donor **4**,[3] in which the silane bridge prevents the donor attack from the α-side and thus the formation of α-glycosides, and DMTST as promoter, the β-linked disaccharides **5** and **6** were obtained stereoselectively in 80% and 89% yield, respectively. To stabilise the acid-labile fructofuranosidic linkage during subsequent manipulations, the silyl

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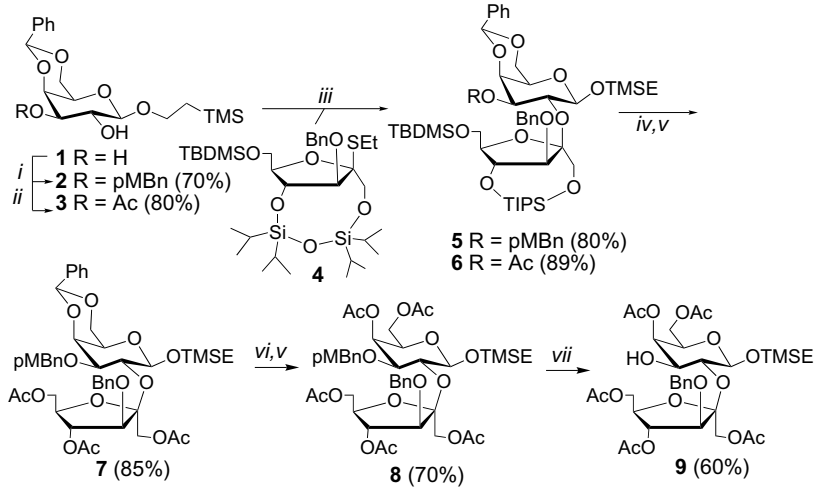


Scheme 1. Reagents and conditions: (i) Bu_2SnO, *p*-MBnCl, Bu_4NI, CH_3CN; (ii) AcCl, CH_2Cl_2/pyridine (4:1), 0 °C; (iii) DMTST, CH_2Cl_2, 4 Å MS; (iv) TBAF, THF; (v) AcCl, CH_2Cl_2/pyridine (1:1); (vi) 60% AcOH, 70 °C; (vii) DDQ, CH_2Cl_2.

groups in **5** were removed by fluoride treatment and the resulting triol acetylated (→**7**). The chemical shift of the fructofuranosidic anomeric C-2 in **7** is $\delta \approx 102$ ppm, clearly indicating a β-linkage.[3,9] The benzylidene acetal was also removed at this stage and substituted with acetyl protecting groups to give **8**. Subsequently the *p*-methoxybenzyl group was cleaved, without affecting any of the glycosidic linkages, by DDQ treatment to afford the key precursor **9**, which can either be used directly as an acceptor or converted into various donors.

If oligomers are to be constructed an acid-stable temporary protecting groups (e.g., a chloroacetate) can be introduced at the free 3-OH before further transformation. However, at this stage our main interest was to develop a methodology for the stereoselective construction of the phosphate diester linkage and **9** was consequently simply acetylated and the TMSE glycoside subsequently removed by TFA-treatment (Scheme 2). Fortunately, the resulting hemiacetal **10**, as is evident from NMR (δ 5.45 (d, J 3.4 Hz, H-1′)), was found to exist exclusively as the α-anomer, which could be phosphonylated[10] without anomerisation to give the α-H-phosphonate monoester **11** (δ 5.85 (dd, J 3.2 Hz, $J_{H,P}$ 8.5 Hz, H-1′)) in acceptable yield. Finally coupling of **9** and **11** using standard pivaloyl chloride activation followed by I_2/H_2O oxidation[10] smoothly afforded the target phosphate diester **12** in 55% yield, which can be compared to the 63% yield obtained in the formation of the non-fructosylated dimer.[2]

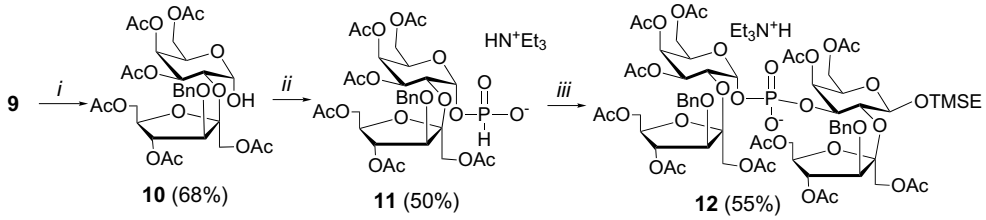
3. Conclusion

In conclusion, a stereoselective synthesis of a dimer of the repeating unit of the *E. coli* K52 CPS has been accomplished using a newly developed β-directing fructofuranosyl donor and H-phosphonate chemistry. The pathway also includes the possibility of continued synthesis of oligomers.

4. Experimental

4.1. General

CH_2Cl_2 was distilled from CaH_2 and stored over molecular sieves 4 Å. Organic solutions were dried over $MgSO_4$, before concentration under reduced pressure and at temperature below 40 °C (water bath). TLC was performed on silica gel F_{254} (E. Merck) with detection by UV-light and/or charring with 8% H_2SO_4 or AMC (ammonium molybdate 10 g, cerium(IV)sulfate 2 g, dissolved in aq 10% H_2SO_4 2 L). Silica gel (Si-60 35–70 μm, Millipore®) was used for column chromatography. NMR spectra were recorded in $CDCl_3$ (internal



Scheme 2. Reagents and conditions: (i) (a) AcCl, CH_2Cl_2/pyridine (1:1); (b) TFA–CH_2Cl_2 (2:1), 0 °C; (ii) (a) PCl_3, imidazole, Et_3N, MeCN; (b) Et_4NHCO_3, H_2O; (iii) (a) **9**, Piv-Cl, pyridine; (b) I_2, H_2O, −40 °C.

Me_4Si, $\delta = 0.00$) at 25 °C unless otherwise stated, using a Varian 300 MHz or 400 MHz instrument.

4.2. 2-(Trimethylsilyl)ethyl 4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl-β-D-galactopyranoside 2

Bu_2SnO (1.06 g, 2.25 mmol) was added to a solution of compound **1** (1.3 g, 3.53 mmol) in MeOH (40 mL). After refluxing for 1 h the reaction mixture became clear. The solution was allowed to attain room temperature, then concentrated, co-evaporated three times with toluene (20 mL) and dried in vacuum for 1 h. *p*-MBnCl (0.38 mL, 2.83 mmol) and Bu_4NI were added to a solution of the residue in dried MeCN (40 mL). The reaction mixture was warmed to 100 °C and then stirred for 2 h after which MeOH (5 mL) was added. The mixture was concentrated and the residue re-dissolved in CH_2Cl_2 (50 mL), washed with H_2O, dried, concentrated and the residue purified by silica gel chromatography (toluene–EtOAc 3:1) to afford **2** (1.2 g, 2.4 mmol, 70%). ^{13}C NMR, δ −1.40, 18.16, 55.27, 66.63, 67.01, 69.31, 70.03, 71.06, 73.21, 78.77, 101.16, 102.44, 113.83–159.33. ^1H NMR, 0.01 (s, 9H), 0.95 (m, 2H), 2.42 (d, 1H, *J* 1.6 Hz), 3.33 (d, 1H, *J* 1.1 Hz), 3.44 (dd, 1H, *J* 3.5 Hz, *J* 9.6 Hz), 3.52 (m, 1H), 3.78 (s, 3H), 3.93 (m, 4H), 4.28 (d, 1H, *J* 7.6 Hz), 4.67 (q, 2H), 5.45 (s, 1H), 6.80–7.55 (m, 9H).

4.3. 2-(Trimethylsilyl)ethyl 4,6-*O*-benzylidene-3-*O*-acetyl-β-D-galactopyranoside 3

Acetyl chloride (0.22 mL, 2.27 mmol) in CH_2Cl_2 (0.2 mL) was added, at 0 °C and under Ar atmosphere to a solution of compound **1** (856 mg, 2.32 mmol) in CH_2Cl_2–pyridine (4:1, 5 mL). After stirring for 1 h the reaction was diluted with CH_2Cl_2 (10 mL), the organic phase was washed with H_2O, $NaHCO_3$ (saturated aq), H_2O, dried, concentrated and the product purified by silica gel chromatography (toluene–EtOAc 3:1) to give **3** (769 mg, 1.87 mmol, 80%). ^{13}C NMR, δ −1.41, 18.11, 20.94, 66.21, 67.14, 68.25, 68.94, 73.40, 73.80, 100.71, 102.51, 126.26–137.81, 170.95. ^1H NMR, δ 0.01 (s, 9H), 0.95 (m, 2H), 2.14 (s, 3H), 3.51 (m, 2H), 4.00 (m, 3H), 4.37 (m, 3H), 4.83 (dd, 1H, *J* 3.6 Hz, *J* 10.4 Hz), 5.50 (s, 1H), 7.34–7.52 (m, 5H).

4.4. 2-(Trimethylsilyl)ethyl [3-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-1,4-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-β-D-fructofuranosyl]-(2→2)-4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl-β-D-galactopyranoside 5

A solution of **2** (327 mg, 0.67 mmol), **4**[3] (350 mg, 0.52 mmol) and DTBMP (105 mg, 0.52 mmol) in CH_2Cl_2 (8 mL) containing powdered molecular sieves (4 Å) was stirred for 15 min at room temperature under an Ar atmosphere. DMTST (346 mg, 1.34 mmol) was added and the stirring continued for 20 min. Et_3N (0.3 mL) was then added and the mixture was filtered through Celite and concentrated. The residue was applied to a silica gel column and eluted with toluene–EtOAc 18:1 to yield **5** (0.46 g, 0.42 mmol, 80%). ^{13}C NMR, δ −5.28, −5.24, −1.50, 12.29, 12.79, 13.36, 13.71, 17.01–18.01, 25.75, 36.05, 50.56, 63.08, 64.56, 65.99, 67.60, 68.39, 69.59, 71.67, 73.59, 76.61, 78.25, 82.83, 87.68, 99.94, 101.58, 110.25, 123.55–146.75. ^1H NMR, δ 0.02 (s, 9H), 0.09 (s, 6H), 0.82–1.18 (m, 39H), 3.29 (s, 1H), 3.50 (m, 3H), 3.74–4.01 (m, 6H), 3.79 (s, 3H), 4.22–4.32 (m, 2H), 4.34 (d, 1H, *J* 7.6 Hz), 4.44 (m, 2H), 4.56 (m, 4H), 4.94 (d, 1H, *J* 12.4 Hz), 5.38 (s, 1H), 6.8–7.6 (m, 14H).

4.5. 2-(Trimethylsilyl)ethyl [3-*O*-benzyl-6-*O*-*tert*-butyldimethylsilyl-1,4-*O*-(1,1,3,3-tetraisopropyldisiloxane-1,3-diyl)-β-D-fructofuranosyl]-(2→2)-4,6-*O*-benzylidene-3-*O*-acetyl-β-D-galactopyranoside 6

A solution of **3** (57 mg, 0.139 mmol), **4** (93 mg, 0.139 mmol) and DTBMP (28 mg, 0.139 mmol) in CH_2Cl_2 (8 mL) containing powdered molecular sieves (4 Å) was stirred for 15 min at room temperature under an Ar atmosphere. DMTST (144 mg, 0.56 mmol) was then added to the mixture and the stirring continued for 20 min. Et_3N (0.2 mL) was then added and the mixture was filtered through Celite and concentrated. The crude mixture was applied to a silica gel column and eluted with toluene–EtOAc 18:1 to yield **6** (126 mg, 0.124 mmol, 89%). ^{13}C NMR, δ −5.27, −5.23, −1.54, 15.43–16.68, 20.10–33.03, 63.39, 64.76, 67.08, 68.95, 70.66, 70.99, 74.91, 75.05, 75.15, 80.35, 84.40, 88.71, 102.00, 104.29, 111.43, 127.63–140.22, 172.01.

4.6. 2-(Trimethylsilyl)ethyl (1,4,6-tri-*O*-acetyl-3-*O*-benzyl-β-D-fructofuranosyl)-(2→2)-4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl-β-D-galactopyranoside 7

TBAF (1.4 mL, 1 M in THF) was added to a solution of disaccharide **5** (0.37 g, 0.34 mmol) in THF (5 mL). After stirring for 2 h the reaction mixture was diluted with CH_2Cl_2 (30 mL), washed with H_2O, dried, concentrated and the residue was subjected to silica gel chromatography ($CHCl_3$–MeOH 18:1) to afford 2-(trimethylsilyl)-ethyl (3-*O*-benzyl-β-D-fructofuranosyl)-(2→2)-4,6-*O*-benzylidene-3-*O*-*p*-methoxybenzyl-β-D-galactopyranoside, which was dissolved in pyridine–CH_2Cl_2 1:1 (5 mL) and acetyl chloride (0.24 mL, 3.4 mmol) in CH_2Cl_2 (0.5 mL) was added at 0 °C and under an Ar atmosphere. The reaction mixture was stirred for 2 h at room temperature, then diluted with CH_2Cl_2 (20 mL) and washed with $NaHCO_3$ (saturated aq) and H_2O, dried, concentrated and purified by silica gel chromatography (toluene–EtOAc 6:1) to give **7** (0.25 g, 0.29 mmol, 85% after two steps). ^{13}C NMR, δ −1.51, 20.85, 20.90, 55.26, 64.62, 65.00, 66.39, 66.99, 69.25, 69.75, 70.92, 72.43, 73.30, 75.10, 77.70, 78.55, 80.03, 101.07, 101.85, 102.17, 113.74–137.90, 169.48, 170.10, 170.82. ^1H NMR, δ 0.01 (s, 9H), 1.01 (m, 2H), 1.90 (s, 3H), 2.01 (s, 6H), 3.27 (s, 1H), 3.46 (dd, 1H, *J* 3.4 Hz, *J* 8.9 Hz), 3.58 (m, 1H), 3.75 (s, 3H), 3.89 (m, 4H), 4.11(d, 1H *J* 7.6 Hz), 4.14 (d, 1H, *J* 4.0 Hz), 4.25 (d, 1H, *J* 11.1 Hz), 4.32 (d, 1H, *J* 7.6 Hz), 4.37 (m, 4H), 4.52 (m, 4H), 5.34 (s, 1H), 5.67 (t, 1H, *J* 8.6 Hz), 6.78–7.5 (m, 14H).

4.7. 2-(Trimethylsilyl)ethyl (1,4,6-tri-*O*-acetyl-3-*O*-benzyl-β-D-fructofuranosyl)-(2→2)-4,6-di-*O*-acetyl-3-*O*-*p*-methoxybenzyl-β-D-galactopyranoside 8

Compound **7** (0.25 g, 0.29 mmol) in acetic acid (60%, 5 mL) was stirred at 70 °C for 1 h. The reaction mixture

was concentrated and co-evaporated three times with toluene (10 mL). The concentrate was dissolved in pyridine–CH_2Cl_2 1:1 (5 mL) and AcCl (0.2 mL 2.8 mmol) in CH_2Cl_2 (0.5 mL) was added at 0 °C and under an Ar atmosphere. After stirring for 1 h at room temperature, the reaction mixture was diluted with CH_2Cl_2 (20 mL), washed with $NaHCO_3$ (saturated aq), H_2O, dried and concentrated. The residue was purified by silica gel chromatography (toluene–EtOAc 4:1) to give **8** (0.18 g, 0.20 mmol, 70%). ^{13}C NMR, δ −1.50, 18.03, 20.80, 20.80, 21.94, 55.29, 62.22, 64.55, 64.99, 66.25, 67.49, 70.11, 70.74, 71.15, 72.52, 75.06, 77.74, 77.83, 79.96, 102.09, 102.18, 113.50, 137.50, 169.59, 170.00, 170.53, 170.59, 170.73. ^1H NMR, δ 0.01 (s, 9H), 1.00 (m, 2H), 1.87 (s, 3H), 1.98 (s, 3H), 1.99 (s, 3H), 2.03 (s, 3H), 2.09 (s, 3H), 3.47 (dd, 1H, *J* 2.8 Hz, *J* 9.2 Hz), 3.61, (m, 2H), 3.73 (s, 3H), 3.87 (m, 2H), 4.06 (m, 3H), 4.27 (m, 3H), 4.56 (m, 2H), 5.48 (d, 1H, *J* 2.9 Hz), 5.60 (t, 1H, *J* 8.6 Hz), 6.79–7.31 (m, 9H).

4.8. 2-(Trimethylsilyl)ethyl (1,4,6-tri-*O*-acetyl-3-*O*-benzyl-β-D-fructofuranosyl)-(2→2)-4,6-di-*O*-acetyl-β-D-galactopyranoside 9

DDQ (45 mg, 0.20 mmol) and H_2O (6 drops) were added to a solution of disaccharide **8** (0.132 g, 0.15 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred overnight, then diluted with CH_2Cl_2 (20 mL) and washed with $NaHCO_3$ (saturated aq) and H_2O, dried, concentrated and the residue purified on a silica gel column (toluene–EtOAc 4:1) to yield **9** (80 mg, 92 μmol, 60%). ^{13}C NMR, δ −1.49, 18.15, 20.72, 20.78, 20.82, 20.91, 61.97, 62.74, 65.86, 67.84, 68.88, 70.88, 72.10, 73.18, 74.50, 77.05, 78.78, 82.77, 101.80, 103.88, 128.19–128.61, 169.87, 170.5. ^1H NMR, δ 0.10 (s, 9H), 1.00 (m, 2H), 1.90 (s, 3H), 1.99(s, 3H), 2.05 (s, 6H), 2.1 (s, 3H), 3.50 (m, 1H), 3.70 (m, 6H), 4.08 (m, 7H), 4.61 (s, 2H), 5.35 (d, 1H, *J* 3.3 Hz), 5.40 (t, 1H, *J* 6.8 Hz), 7.20 (m, 5H).

4.9. (1,4,6-Tri-*O*-acetyl-3-*O*-benzyl-β-D-fructofuranosyl)-(2→2)-3,4,6-tri-*O*-acetyl-α-D-galactopyranose 10

Acetyl chloride (20 μL, 0.28 mmol) in CH_2Cl_2 (0.2 mL) was added, at 0 °C and under an Ar atmosphere, to a solution of compound **9** (52 mg, 70 μmol) in pyridine–CH_2Cl_2 (1:1, 2 mL). After stirring for 1 h at room temperature, the reaction mixture was diluted with CH_2Cl_2 (20 mL), washed with $NaHCO_3$ (saturated aq), dried, concentrated and purified by silica gel chromatography (toluene–EtOAc 3:1) to give 2-(trimethylsilyl)ethyl (1,4,6-tri-*O*-acetyl-3-*O*-benzyl-β-D-fructofuranosyl)-(2→2)-3,4,6-tri-*O*-acetyl-β-D-galactopyranoside (42 mg, 61 μmol, 90%). TFA (1 mL) was added, at 0 °C and under an Ar atmosphere, to a solution of the acetylated product (32 mg, 46 μmol) in CH_2Cl_2 (0.5 mL). After stirring for 1 h at 0 °C, *n*-propylacetate (1 mL) and toluene (1 mL) were added. The mixture was concentrated, co-evaporated with toluene (2 mL) and the residue purified on a silica gel column to afford **10** (21 mg, 30 μmol, 75%). ^{13}C NMR, δ 20.67, 20.74, 20.81, 61.81, 63.59, 63.77, 66.32, 68.35, 68.54, 68.79, 72.87, 76.14, 78.89, 81.52, 92.59, 104.34, 127.88–136.99, 169.83, 170.00, 170.22, 170.54, 170.81. ^1H NMR, δ 1.94 (s, 3H), 2.01 (s, 3H), 2.04 (s, 3H), 2.07 (s, 3H), 2.09 (s, 3H), 2.13 (s, 3H), 4.01 (m, 5H), 4.19 (m, 3H), 4.34 (m, 1H), 4.44 (m, 1H), 4.59 (dd, 2H, *J* 11.8 Hz, *J* 22.8 Hz), 5.29 (m, 2H), 5.43 (dd, 1H, *J* 1.7 Hz, *J* 3.3 Hz), 5.45 (d, 1H, *J* 3.4 Hz), 7.23 (m, 5H).

4.10. Triethylammonium (1,4,6-tri-*O*-acetyl-3-*O*-benzyl-β-D-fructofuranosyl)-(2→2)-3,4,6-tri-*O*-acetyl-α-D-galactopyranosyl hydrogenphosphonate 11

To a stirred solution of imidazole in MeCN (1 mL) at 0 °C was added PCl_3 (11 μL, 0.122 mmol) and Et_3N (59 μL, 0.428 mmol). The stirring was continued for 15 min at the same temperature and a solution of compound **10** (19 mg, 28 μmol) in MeCN (1 mL) was added dropwise. After stirring at room temperature for 20 min, the reaction was quenched by addition of 1 M TEAB (0.163 mL), concentrated and the residue re-dissolved in pyridine–Et_3N 4:1 (5 mL) and concentrated. The residue was taken up in $CHCl_3$ and washed four times with 0.5 M TEAB, filtered through Na_2SO_4 (s), concentrated and the residue was purified on a silica gel column ($CHCl_3$–MeOH 9:1+1% Et_3N) to give **11** (12 mg, 14 μmol, 50%). ^{13}C NMR, δ 8.51, 20.67, 20.71, 20.74, 20.79, 20.90, 45.46, 61.57, 64.13, 65.03, 67.09, 67.99, 68.36, 68.72, 77.46, 80.83, 94.50 (d, $J_{C\text{-}1,P}$ 5.3 Hz), 103.20, 128.06–137.50, 169.79, 170.19, 170.31, 170.52, 170.80. ^1H NMR, δ 1.29 (t, 9H), 2.00 (s, 3H), 2.02 (s, 3H), 2.03 (s, 3H), 2.05 (s, 3H), 2.08 (s, 3H), 2.14 (s, 3H), 2.96 (q, 6H), 3.82 (d, 1H, *J* 11.8 Hz), 3.95 (m, 8H), 4.27 (m, 2H), 4.42 (m, 7H), 5.34 (dd, 1H), 5.45 (d, 1H, *J* 2.7 Hz), 5.51 (t, 1H, *J* 7.9 Hz), 5.85 (dd, 1H, $J_{1,2}$ 3.2 Hz, $J_{H\text{-}1,P}$ 8.5 Hz), 7.05 (d, 1H, *J* 640 Hz, PO_3H^-), 7.24 (m, 5H). ^{31}P NMR, δ 1.36 (dd, *J* 640 Hz, *J* 8.5 Hz).

4.11. 2-(Trimethylsilyl)ethyl (1,4,6-tri-*O*-acetyl-3-*O*-benzyl-β-D-fructofuranosyl)-(2→2)-(3,4,6-tri-*O*-acetyl-α-D-galactopyranosyl phosphate)-(1→3)-[(1,4,6-tri-*O*-acetyl-3-*O*-benzyl-β-D-fructofuranosyl)-(2→2)]-4,6-di-*O*-acetyl-β-D-galactopyranoside triethylammonium salt 12

Pivaloyl chloride (4.3 μL, 35 μmol) was added, under an Ar atmosphere, to a solution of compounds **9** (12 mg, 16.2 μmol) and **11** (12 mg, 14.8 μmol) in pyridine (0.4 mL). After stirring for 30 min the mixture was cooled to − 40 °C and water (15 μL) and iodine (4 mg, 16.6 mol) were added. The temperature was allowed to raise to 0 °C, when the reaction mixture was partitioned between $CHCl_3$ and 1 M $Na_2S_2O_3$. The organic phase was washed twice with 1 M TEAB, filtered through Na_2SO_4 (s) and concentrated. The product was purified using silica gel chromatography ($CHCl_3$–MeOH 9:1+0.5% Et_3N) to yield **12** (13 mg, 8.18 μmol, 55%). ^{13}C NMR, −1.5, 8.7, 17.79, 20.76, 20.88, 21.01, 45.32, 61.20, 63.56, 64.03, 64.78, 65.16, 65.36, 66.64, 67.00, 68.10, 68.71, 69.05, 69.85, 70.35, 71.22, 71.91, 72.56, 73.92, 74.09, 74.60, 75.64, 77.23, 80.20, 80.37, 94.70 ($J_{C-1,P}$ 5.3 Hz), 101.55, 101.99, 103.3, 127.49–138.49, 169.40, 169.51, 170.12, 170.22, 170.40, 170.59, 170.75. ^1H NMR (assorted signals), δ 0.01 (s, 9H), 0.82 (m, 2H), 1.01 (t, Et_3N), 1.98–2.19 (m, 33H), 3.6–4.85 (m, 28H), 5.63 (t, 1H, *J* 8.6 Hz), 5.78 (d, 1H, *J* 2.2 Hz), 5.89 (dd, 1H, $J_{1,2}$ 3.2 Hz, $J_{H,P}$

8 Hz). ^{31}P NMR, δ −1.49 (dd, *J* 6.0 Hz, *J* 8.0 Hz). MALDI-TOF MS: Calcd for $C_{65}H_{88}O_{35}PSi$: 1488.43; Found: 1511.43 [M+Na]; 1527.50 [M+K].

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