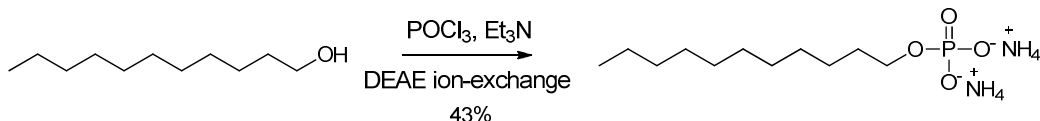


## Supporting Information

### 1. Chemical synthesis procedures of Glc $\alpha$ -PP-O(CH $_2$ ) $_{10}$ CH $_3$

#### 1.1 Chemical synthesis of 1-undecanol phosphate<sup>1</sup>



Et $_3$ N (2.18 mL, 15.64 mmol) was added to a solution of POCl $_3$  (1.43 mL, 15.62 mmol) in hexane (15 mL) at rt. for 5 min. Then a solution of undecanol (500 mg, 2.90 mmol) in hexane (15 mL) was added slowly to the mixture over a period of 15 min. After addition, the stirring was continued for another 15 min before the mixture was poured into 100 mL of a mixture of acetone/water/Et $_3$ N (88/10/2) and left for overnight. The mixture was concentrated on a rotary evaporator to 10 mL aqueous milky residue. And the evaporation was repeated after addition of 30 mL n-propanol. To the residue was then added 50 mL benzene and the mixture evaporated. Evaporation with benzene was repeated several times until a crystalline precipitate had formed. At this stage the sample in benzene was left for 1 h and the crystalline precipitate was removed by filtration. The clear benzene solution was evaporated to dryness and the residue was separated using DEAE cellulose ion-exchange resin. 33 mmol NH $_4$ HCO $_3$  in methanol was used as eluent and the product was detected by MS. After evaporation, 1-undecanol phosphate diammonium salt was afforded as a light yellow solid (360 mg, 43%).  $^1\text{H}$  NMR (500 MHz, CD $_3$ OD)  $\delta$  3.84 (app q,  $J$  = 6.5 Hz, 2H), 1.59-1.65 (m, 2H), 1.25-1.41 (m, 16H), 0.90 (t,  $J$  = 7.1 Hz, 3H); MS (ESI) calcd for C $_{11}$ H $_{24}$ O $_4$ P (M-H) $^-$  251.1, found 251  $m/z$ .

#### 1.2 *Synthesis of 2,3,4,6-tetra-O-acetyl-1-O-[bis(benzyloxy)phosphoryl]- $\alpha$ -D-glucopyranose*

2,3,4,6-tetra-*O*-acetyl-D-glucopyranose (0.48 g, 1.38 mmol) and tetrazole (10 equiv, 965 mg, 13.78 mmol) were dissolved in dry CH $_2$ Cl $_2$  (20 mL) and the solution was cooled to -40  $^\circ\text{C}$ . Bis(benzyloxy)diisopropylamino)phosphine (5 equiv, 2.57 mL, 6.89 mmol) was then added drop wise over a 2 min period. The mixture was stirred for 3 h while allowing the temperature to rise to 25  $^\circ\text{C}$ . The mixture was cooled to -78  $^\circ\text{C}$ , and 77% m-CPBA (10 equiv, 3.09 g, 13.78 mmol) was added slowly. The solution was stirred for 30 min at 0  $^\circ\text{C}$ , then overnight at room temperature. After addition of ethyl acetate (100 mL) the solution was washed with saturated Na $_2$ SO $_3$  (50 mL  $\times$  3), water (50 mL  $\times$  2), and saturated NaCl (50 mL  $\times$  2), dried over anhydrous Na $_2$ SO $_4$ , and concentrated to yield a yellow solid. The crude product was purified by flash column chromatography ((v/v) hexane - ethyl acetate 3:1-2:1-1:1) to give product as a clear oil. ( $\alpha$ : 620 mg, 74%;  $\beta$ : 80 mg, 10%). See ref 2 for NMR data.<sup>2</sup>

#### 1.3 Synthesis of 2,3,4,6-tetra-O-acetyl- $\alpha$ -D-glucopyranose-1-phosphate

To a solution of the above dibenzyl phosphate (450 mg, 0.739 mmol) in methanol (20 mL) was added 114 mg of 20% Pd(OH) $_2$ . The reaction vessel was filled with

hydrogen and stirred at room temperature. A total of 0.74 mL of diisopropylethylamine (DIPEA) was added after 30 min. The solution was diluted with 20 mL of MeOH and stirred for another 30 min. The catalyst was filtered off over Celite. The filtrate was concentrated to dryness to give the sugar monophosphate (480 mg, 95%) which was used in the next coupling step without further purification.

#### 1.4 Synthesis of Glc $\alpha$ -PP-O(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub>

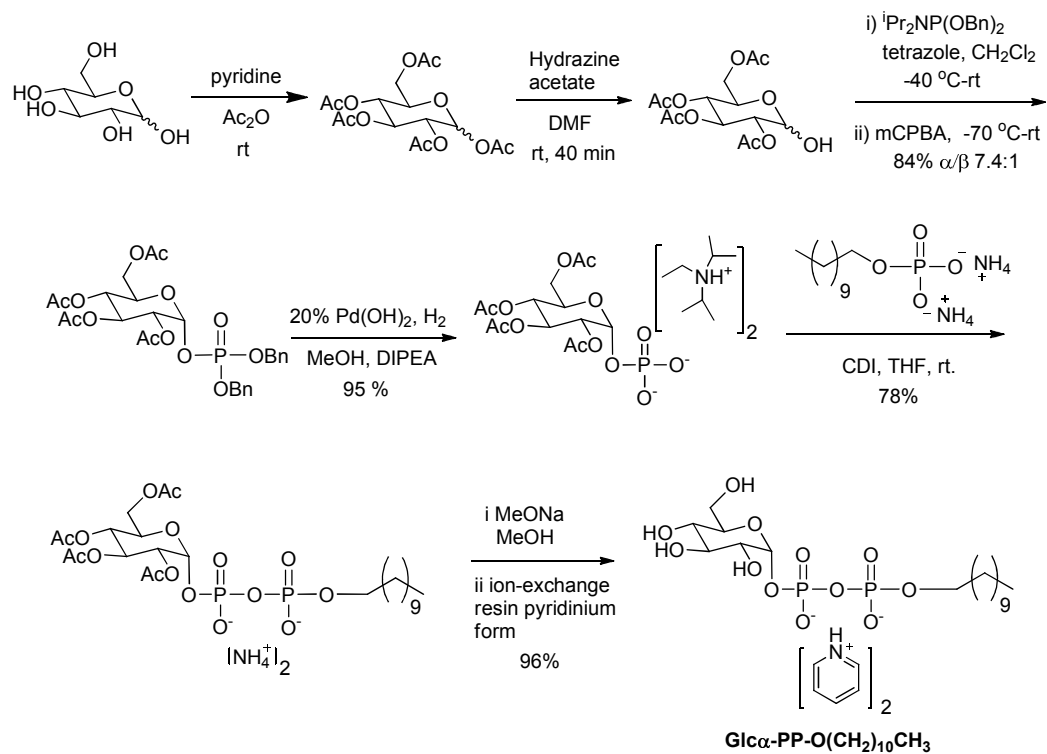
Monophosphate (480 mg, 0.699 mmol) was dissolved in 20 mL of dry THF and treated with carbonyldiimidazole (567 mg, 3.5 mmol). After 2 h, the intermediate was detected by MS (*m/e* 477.2, [M-H]<sup>-</sup>), 348  $\mu$ L of dry MeOH was added, and the reaction was stirred for another 1 h. The solvent was evaporated to give the phosphoimidazole intermediate. This intermediate was dissolved in 10 mL of dry THF and transferred to 1-undecanol phosphate (200 mg, 0.699 mmol), and the reaction progress was stirred at room temperature for 4 days (the reaction progress was monitored by MS). The solvent was evaporated and the residue was loaded on to a C18 reverse phase column (8 mm  $\times$  80 mm, particle size 40  $\mu$ m, pore size 60  $\text{\AA}$ , from Aldrich) and eluted with CH<sub>3</sub>CN/10 mM NH<sub>4</sub>HCO<sub>3</sub> in water. The product was detected by MS. The fractions containing desired product were combined and concentrated to give the coupling product as a white solid (380 mg, 78%). <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$  5.79 (dd, *J* = 7.8, 3.5 Hz, 1H), 5.52 (app t, *J* = 9.8 Hz, 1H), 5.21 (app t, *J* = 9.6 Hz, 1H), 5.09 (dt, *J* = 9.8, 3.2 Hz, 1H), 4.40-4.50 (m, 2H), 4.25 (dd, *J* = 13.0, 2.0 Hz, 1H), 3.95-4.03 (m, 2H), 2.18 (s, 3H), 2.16 (s, 3H), 2.14 (s, 3H), 2.11 (s, 3H), 1.65-1.72 (m, 2H), 1.28-1.42 (m, 16H), 0.90 (t, *J* = 7.0 Hz, 3H); <sup>31</sup>P NMR (162 MHz, D<sub>2</sub>O)  $\delta$  -10.76 (d, *J* = 19.9 Hz), -13.69 (d, *J* = 20.3 Hz); HRMS (ESI) calcd for C<sub>25</sub>H<sub>43</sub>NO<sub>16</sub>P<sub>2</sub> (M-H)<sup>-</sup> 661.2032, found 661.2047 *m/z*.

#### 1.5 Deacetylation

A solution of the above coupling product (364 mg) was treated with 0.13% NaOCH<sub>3</sub> in methanol (20 mL). After 2 hr, the reaction was complete (monitored by MS, *m/e* 493 [M-H]<sup>-</sup>) and cation-exchange resin (pyridinium form) was added and the reaction mixture was stirred very slowly for another 1 h. Then the resin was filtered off and washed with methanol. Evaporation of the filtrate gave Glc $\alpha$ -PP-O(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub> as a syrup (326 mg, >95%, pyridinium salt). HRMS (ESI) calcd for C<sub>17</sub>H<sub>35</sub>NO<sub>12</sub>P<sub>2</sub> (M-H)<sup>-</sup> 493.1609, found 493.1599 *m/z*.

#### References

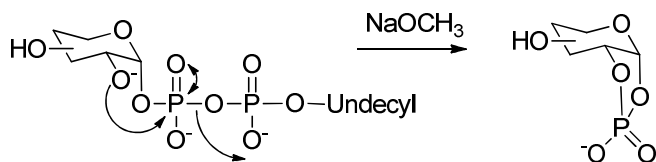
- (1) Danilov, L. L., and Chojnacki, T. (1981) A simple procedure for preparing dolichyl monophosphate by use of POC13. *FEBS Letters* 131, 310-312.
- (2) Sim, M. M., Kondo, H., and Wong, C. H. (1993) Synthesis of dibenzyl glycosyl phosphites using dibenzyl N,N-diethylphosphoramidite as phosphitylating reagent: An effective route to glycosyl phosphates, sugar nucleotides and glycosides *J. Am. Chem. Soc.* 115, 2260-2267.



**Scheme S1.** Synthesis of the Glc $\alpha$ -PP-O(CH $_2$ ) $_{10}$ CH $_3$  acceptor

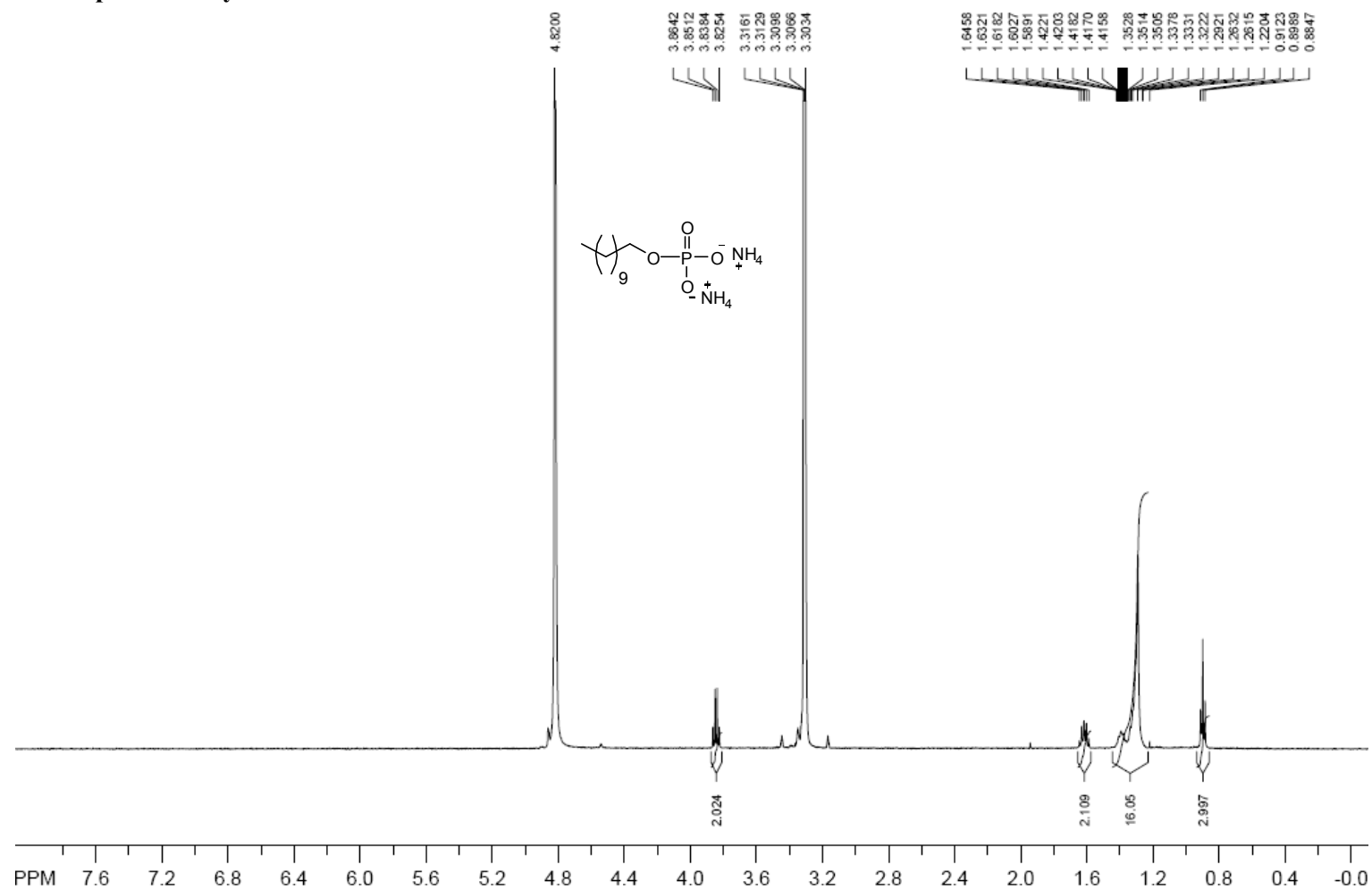
**Table S1. Oligonucleotide primers used in this study**

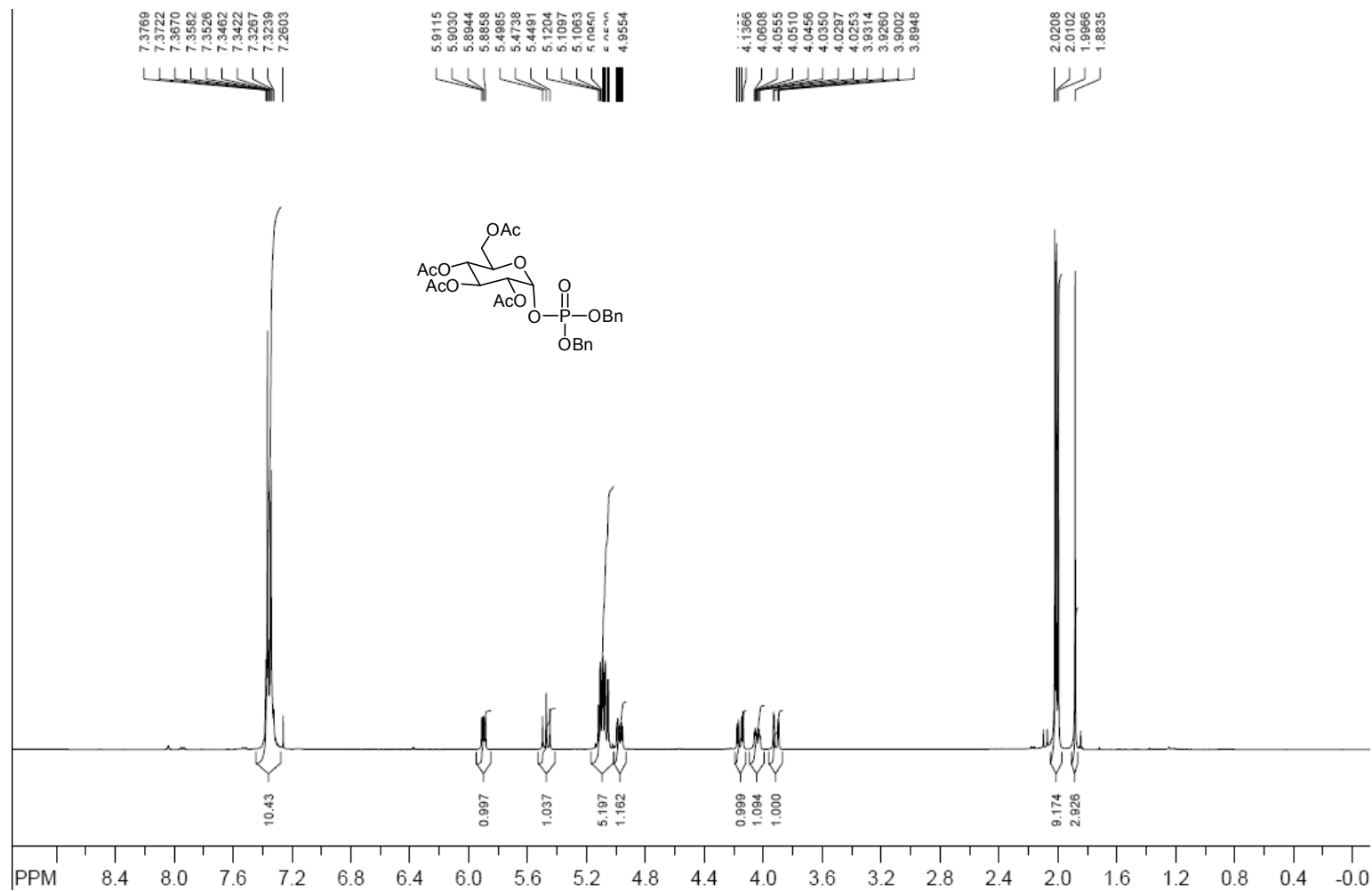
<b>Name</b>	<b>Sequence (5'-3')</b>
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WciN-BamHI-R	AGCTGGATCCTTATTTCAAAATTCTATACAATTTAGG
WciN-D28A-F	CTTCCATCAAATCACTTTACACTACTAATTCAGCTTTGGATTAAATTTATGGATTATT
WciN-D28A-R	AATAATCCATAAATTTAAATCCAAAGCTGAATTAGTAGTGTAAGTGATTTGATGGAAG
WciN-D30A-F	ATCACTTTACACTACTAATTCAGATTTGGCTTTAAATTTATGGATTATTGCTGATAAAG
WciN-D30A-R	CTTTATCAGCAATAATCCATAAATTTAAAGCCAAATCTGAATTAGTAGTGTAAGTGAT
WciN-D102A-F	CTTCAATGAGTAAAGTTCTTTATCTTGCCAGTGATATTATTGTTATGGATTCTTT
WciN-D102A-R	AAAGAATCCATAACAATAATATCACTGGCAAGATAAAGAACTTTACTCATTGAAG
WciN-D104A-F	GAGTAAAGTTCTTTATCTTGACAGTGCTATTATTGTTATGGATTCTTTACGAA
WciN-D104A-R	TTCGTAAAGAATCCATAACAATAATAGCACTGTCAAGATAAAGAACTTTACTC
WciN-D116A-F	TGTTATGGATTCTTTACGAAGTATTTTTGCTATTGATTTTAAGGGTAAAATTCTCTATG
WciN-D116A-R	CATAGAGAATTTTACCCTTAAAATCAATAGCAAAAATACTTCGTAAAGAATCCATAACA
WciN-D118A-F	ATTCTTTACGAAGTATTTTTGATATTGCTTTTAAGGGTAAAATTCTCTATGGGG
WciN-D118A-R	CCCCATAGAGAATTTTACCCTTAAAAGCAATATCAAAAATACTTCGTAAAGAAT

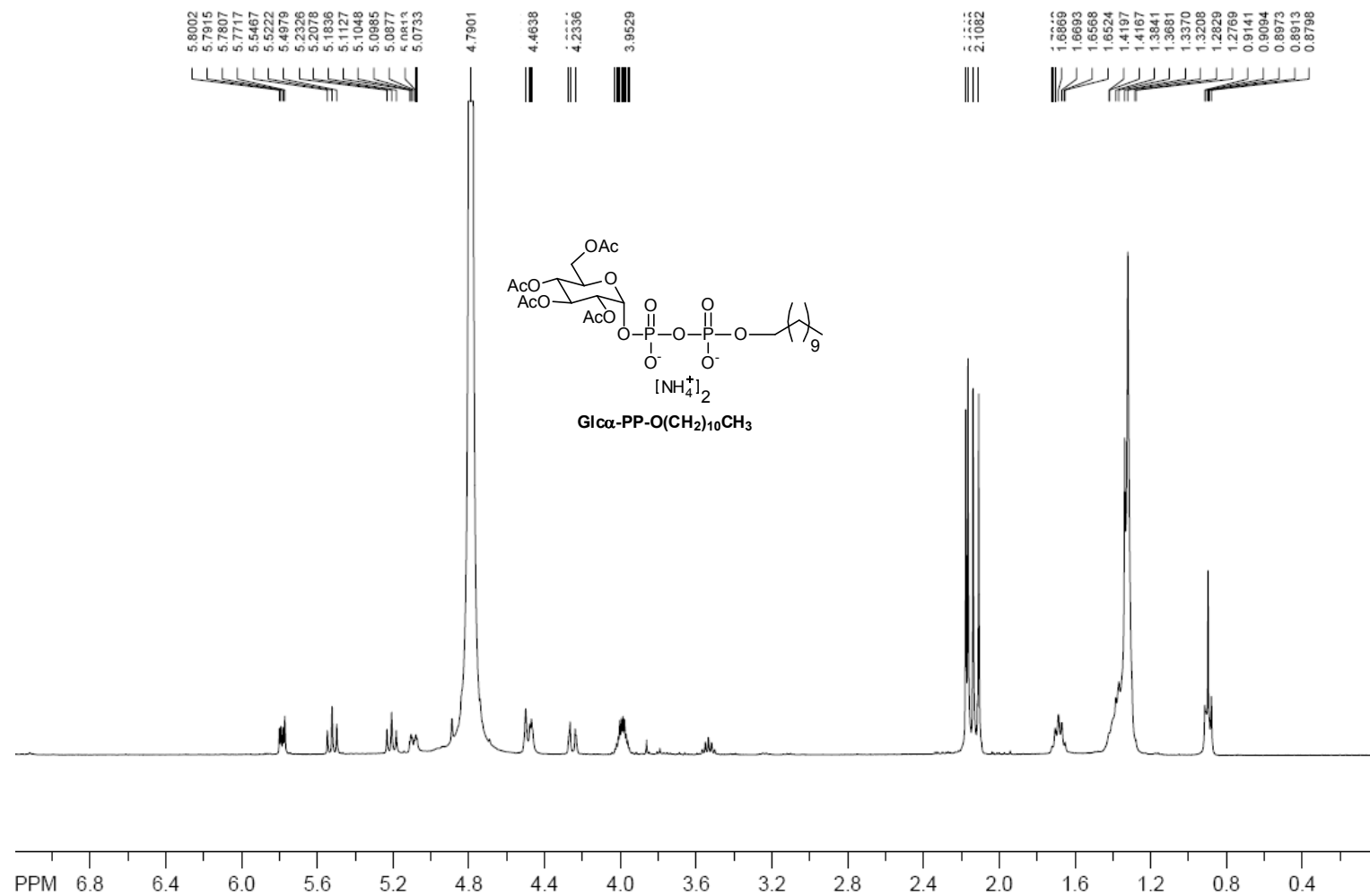


**Fig. S1** The possible reason leading to alkali-instability of the  $\text{Glc}\alpha\text{-PP-O(CH}_2\text{)}_{10}\text{CH}_3$  product during the final deacetylation step (formation of a 1,2 cyclic phosphate).

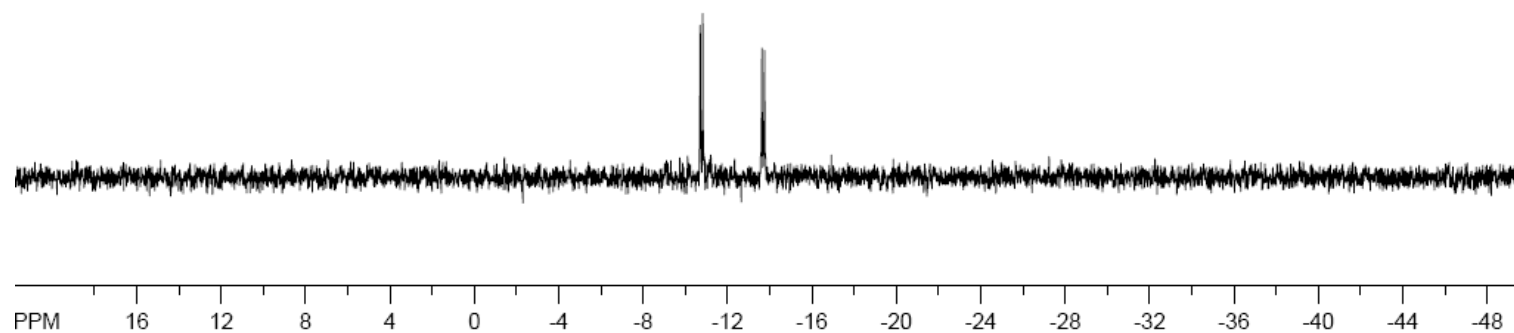
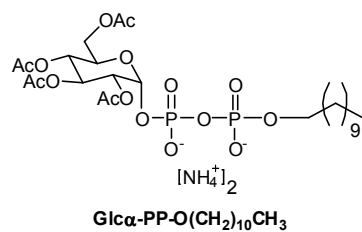
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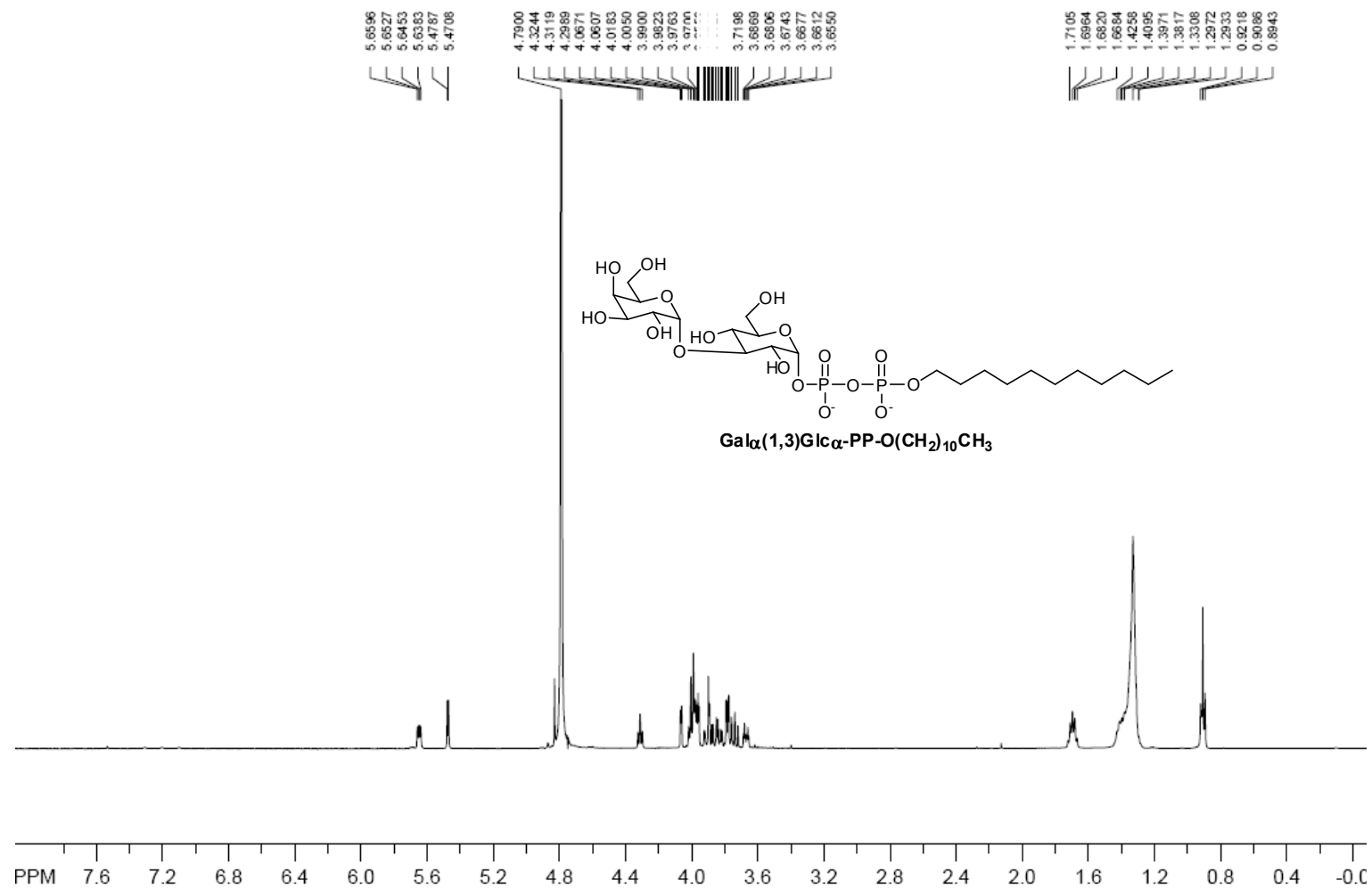


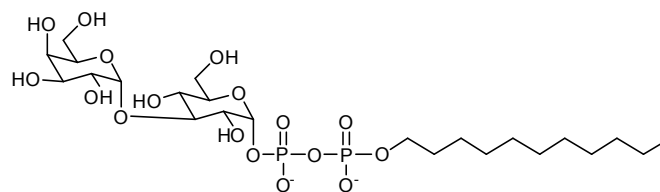
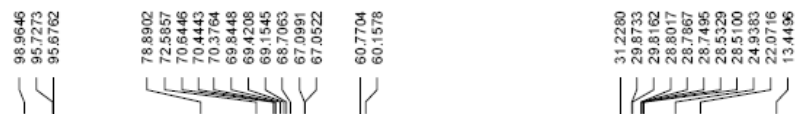




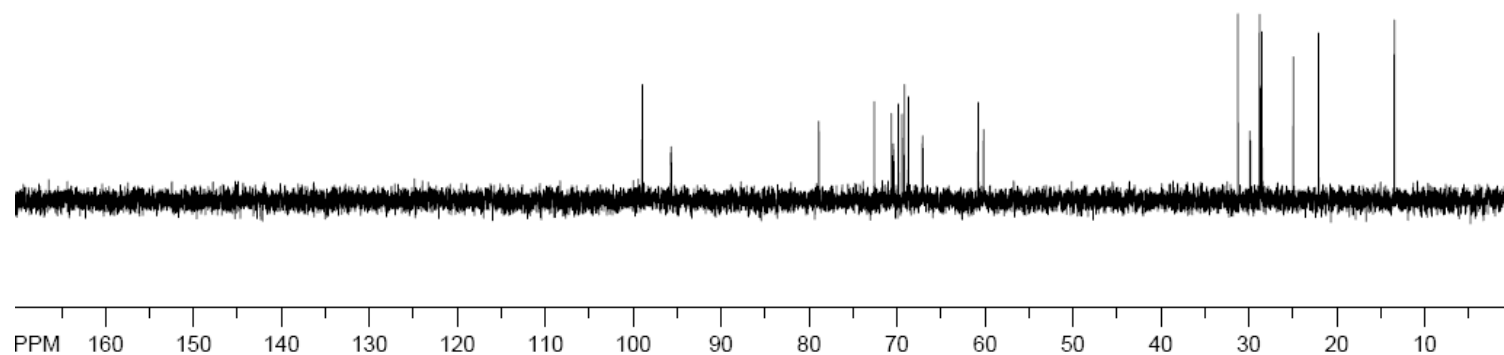


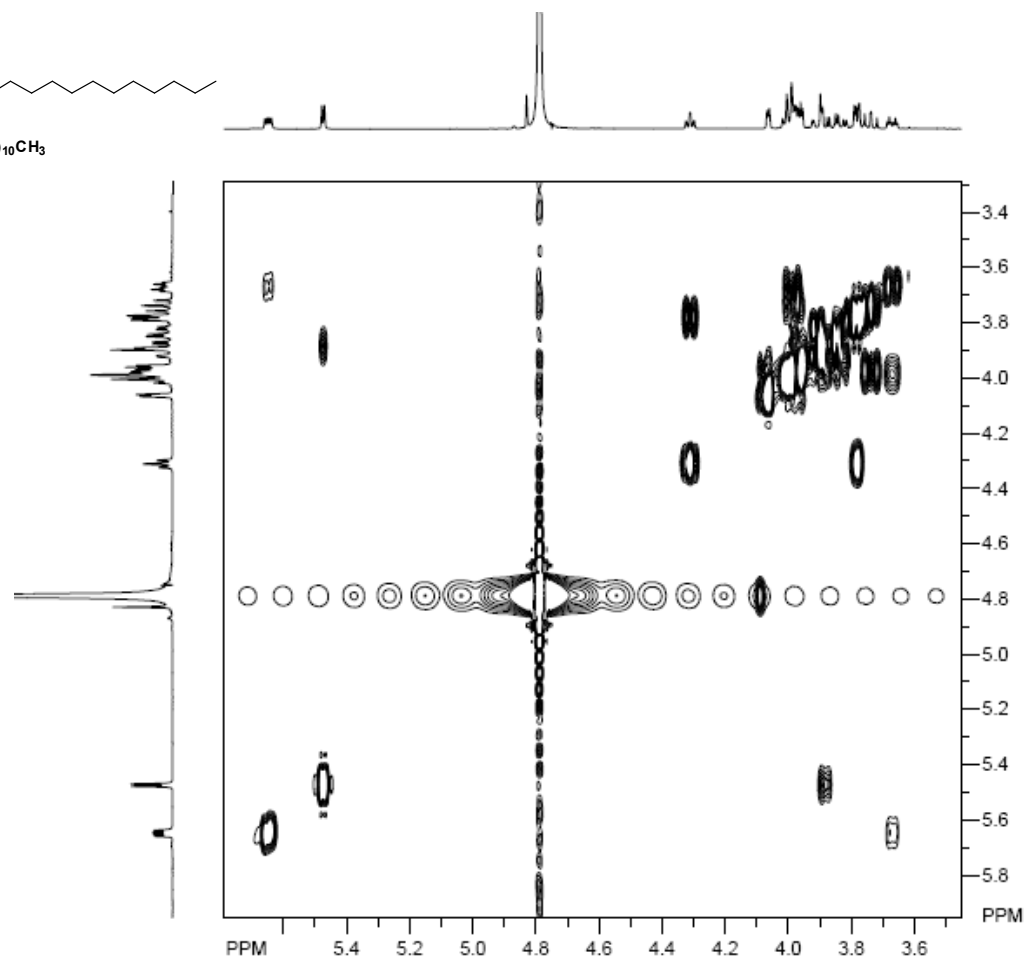
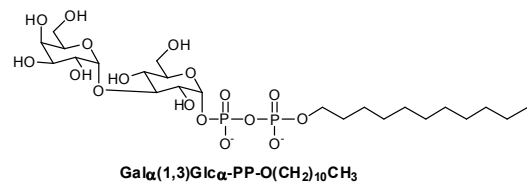


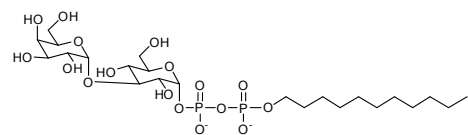




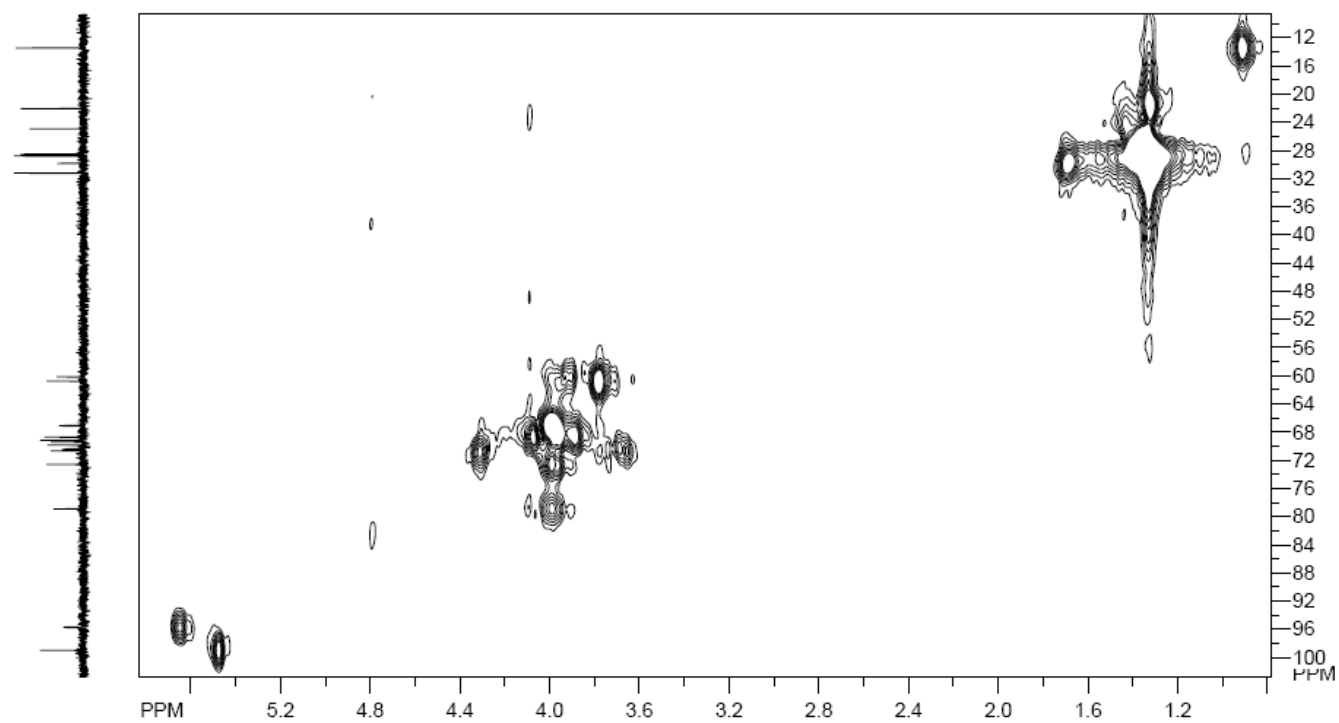
**Gal $\alpha$ (1,3)Glc $\alpha$ -PP-O(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub>**

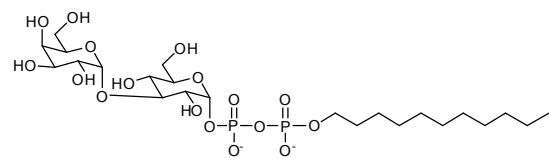






Gal $\alpha$ (1,3)Glc $\alpha$ -PP-O(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub>





Gal $\alpha$ (1,3)Glc $\alpha$ -PP-O(CH $_2$ ) $_{10}$ CH $_3$

