Supporting Information

A Highly Efficient Approach to the Synthesis of Complex α-Glycosyl Phosphosaccharides

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1. General Methods.

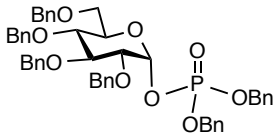
All reactions were carried out at room temperature (RT) under argon atmosphere in glassware with magnetic stirring unless otherwise stated. Unless otherwise stated, all reagents were commercially available and used as received without further purification. Proton nuclear magnetic resonance (^{1}H NMR), carbon nuclear magnetic resonance (^{13}C NMR) and phosphorus nuclear magnetic resonance (^{31}P NMR) spectra were recorded on Brüker DRX 400 spectrometer at 400, 100 and 162 MHz, respectively. Chemical shifts are reported in parts per million (ppm) in $CDCl_3$, D_2O. NMR data are presented as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet and/or multiple resonances); coupling constant are reported in Hertz (Hz). NMR signals were assigned on the basis of ^{1}H NMR, ^{13}C NMR, COSY and HSQC experiments. High resolution mass spectra were recorded on AB QSTAR Pulsar mass spectrometer. Column chromatography was performed on silica gel G60 (Silicycle, 60-200 μm, 60 Å). TLC analysis was conducted on Silica gel 60 F254 (EMD Chemicals Inc.) with detection by UV light (254 nm) where applicable, and by charring with 10% sulfuric acid in ethanol followed by heating. Molecular sieves were flame-dried under vacuum immediately prior to use.

2. Synthesis and characterization

2.1. Glycosylation procedure (A) and glycosyl phosphates 3a-3o

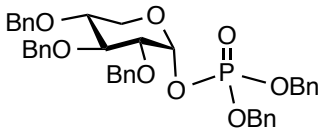
General procedure (A) for the gold(I)-catalyzed glycosylation reaction of glycosyl *ortho*-alkynylbenzoate donors and phosphoric acid acceptors. To a solution of donor (0.075 mmol, 1.5 equiv.) and acceptor (0.05 mmol, 1.0 equiv.) in $ClCH_2CH_2Cl$ (1.0 mL) was added $Ph_3PAuNTf_2$ (3.7 mg, 0.005 mmol, 0.1 equiv.) at 0 °C. After the mixture was stirred for 0.5 h, the reaction temperature was elevated to 60 °C when donor **1a** was used, 100 °C when donor **1d** or **1l** was used, and 25 °C when the other donors were used. After stirring at elevated temperature for 2.0 h, the mixture was cooled down and quenched with Et_3N. Then the mixture was filtrated, and the filtrate was concentrated to give a residue, which was loaded to a silica gel column which was neutralized prior to use by using Hexanes/Et_3N (100/1), then purified to give the desired product of glycosyl phosphosaccharide.

dibenzyl 2,3,4,6-tetra-*O*-benzyl-*α*-D-glucopyranosyl phosphate (3a)



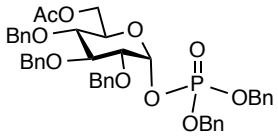
3a, prepared via general procedure (A), eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 2/1/0.01), R_f= 0.2 (Hexanes/EtOAc, 2/1), colorless oil, 37.2 mg, 93% yield, α/β = 16/1. $[\alpha]_D^{25}$ = 40.2 (*c* 3.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.12 (m, 30H, Ar*H*), 5.96 (dd, *J* = 6.8, 3.2 Hz, 1H, H-1), 5.04 (dd, *J* = 11.9, 7.7 Hz, 4H, C*H*$_2$Ph x 2), 4.91 (d, *J* = 10.9 Hz, 1H, C*H*Ph), 4.82 (d, *J* = 10.8 Hz, 1H, C*H*Ph), 4.78 (d, *J* = 11.3 Hz, 2H, C*H*Ph x 2), 4.67 (d, *J* = 11.4 Hz, 1H, C*H*Ph), 4.54 (d, *J* = 12.1 Hz, 1H, C*H*Ph), 4.48 (d, *J* = 10.8 Hz, 1H, C*H*Ph), 4.41 (d, *J* = 12.1 Hz, 1H, C*H*Ph), 3.92 (t, *J* = 9.3 Hz, 2H, H-4, H-5), 3.71 (t, *J* = 9.6 Hz, 1H, H-3), 3.65-3.63 (m, 2H, H-2, H-6), 3.47 (dd, *J* = 10.9, 1.9 Hz, 1H, H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.7, 138.2, 137.9, 137.7, 136.0, 135.9, 128.63, 128.58, 128.52, 128.45, 128.3, 128.06, 128.03, 128.00, 127.94, 127.88, 127.85, 127.79, 95.8 (d, *J* = 6.1 Hz), 81.3, 79.4 (d, J = 7.4 Hz), 75.8, 75.3, 73.6, 73.1, 72.6, 69.4 (d, *J* = 5.4 Hz), 69.2 (d, *J* = 5.4 Hz), 68.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.2; HR ESI-MS: $[M+H^+]^+$calcd for $[C_{48}H_{50}O_9P]^+$, 801.3187; found, 801.3188.

dibenzyl 2,3,4-tri-*O*-benzyl-*α*-D-xylopyranosyl phosphate (3b)



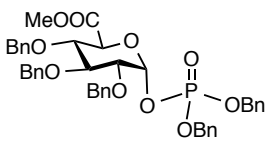
3b, prepared via general procedure (A), eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 2/1/0.01), R_f= 0.2 (Hexanes/EtOAc, 2/1), colorless oil, 26.5 mg, 78% yield, α/β = 11/1. $[\alpha]_D^{25}$ = 53.3 (*c* 2.3 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 25H, Ar*H*), 5.85 (dd, *J* = 6.8, 3.3 Hz, 1H, H-1), 5.04 (ddd, *J* = 17.7, 7.4, 2.8 Hz, 4H, 4 x C*H*Ph), 4.90-4.81 (m, 2H, 2 x C*H*Ph), 4.72 (dt, *J* = 22.1, 11.2 Hz, 3H, 3 x C*H*Ph), 4.60 (d, *J* = 11.6 Hz, 1H, C*H*Ph), 3.83 (t, *J* = 8.9 Hz, 1H, H-3), 3.72-3.57 (m, 3H, H-4, H-5, H-5'), 3.53 (dt, *J* = 9.5, 3.1 Hz, 1H, H-2); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.6, 138.1, 137.7, 135.9, 135.84, 135.80, 135.77, 134.3, 134.1, 128.55, 128.49, 128.47, 128.44, 128.41, 128.38, 128.35, 128.1, 128.0, 127.90, 127.87, 127.8, 127.7, 95.8 (d, *J* = 6.1 Hz), 80.5, 79.1 (d, J = 7.2 Hz), 77.2, 75.7, 73.6, 73.3, 69.4 (d, *J* = 5.4 Hz), 69.2 (d, *J* = 5.4 Hz), 61.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.2; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{40}H_{41}NaO_8P]^+$, 703.2431; found, 703.2428.

dibenzyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosyl phosphate (3c)



3c, prepared via general procedure (A), eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 2/1/0.01), R_f= 0.2 (Hexanes/EtOAc, 5/3), colorless oil, 33.1 mg, 88% yield, α/β = 12/1. $[\alpha]_D^{25}$ = 55.2 (*c* 1.2 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.25 (m, 25H, Ar*H*), 5.94 (dd, *J* = 7.0, 3.3 Hz, 1H, H-1), 5.06 (ddd, *J* = 13.7, 7.4, 2.0 Hz, 4H, 2 x CH_2Ph), 4.94 (d, *J* = 10.8 Hz, 1H, C*H*Ph), 4.87 (d, *J* = 10.8 Hz, 1H, C*H*Ph), 4.82-4.75 (m, 2H, 2 x C*H*Ph), 4.67 (d, *J* = 11.3 Hz, 1H, C*H*Ph), 4.55 (d, *J* = 10.7 Hz, 1H, C*H*Ph), 4.19 (dd, *J* = 12.1, 4.4 Hz, 1H, H-6), 4.11 (dd, *J* = 12.2, 2.2 Hz, 1H, H-6'), 4.01-3.86 (m, 2H, H-3, H-5), 3.62 (dt, *J* = 9.6, 3.1 Hz, 1H, H-2), 3.52 (t, *J* = 9.5 Hz, 1H, H-4), 1.92 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.7, 138.4, 137.8, 137.6, 135.8, 128.73, 128.67, 128.62, 128.58, 128.52, 128.3, 128.2, 128.13, 128.10, 128.07, 128.0, 127.92, 127.86, 81.2, 79.4 (d, J = 7.3 Hz), 76.6, 75.8, 75.3, 73.2, 70.9, 69.5 (d, *J* = 5.4 Hz), 69.3 (d, *J* = 5.4 Hz), 62.7, 20.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.2; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{43}H_{45}NaO_{10}P]^+$, 775.2643; found, 775.2641.

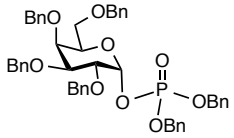
dibenzyl methyl-2,3,4-tri-*O*-benzyl-*α*-D-glucopyranuronatosyl phosphate (3d)



3d, prepared via general procedure (A), eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 2/1/0.01), R_f= 0.2 (Hexanes/EtOAc, 5/3), colorless oil, 32.1 mg, 87% yield, α/β = 9.7/1.

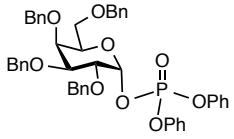
$[\alpha]_D^{25}$ = 40 (*c* 3.2 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.13 (m, 25H, Ar*H*), 5.86 (dd, *J* = 7.1, 3.2 Hz, 1H, H-1), 5.05-4.91 (m, 4H, 2 x CH_2Ph), 4.82 (d, *J* = 11.0 Hz, 1H, C*H*Ph), 4.76-4.66 (m, 3H, 3 x C*H*Ph), 4.59 (d, *J* = 11.4 Hz, 1H, C*H*Ph), 4.49 (d, *J* = 10.8 Hz, 1H, C*H*Ph), 4.31 (d, *J* = 10.0 Hz, 1H, H-5), 3.84 (t, *J* = 9.3 Hz, 1H, H-3), 3.71 (t, *J* = 9.6 Hz, 1H, H-4), 3.61-3.57 (m, 4H, H-2, OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 169.2, 138.4, 137.8, 137.4, 135.83, 135.77, 135.70, 128.65, 128.59, 128.54, 128.52, 128.3, 128.21, 128.05, 128.01, 128.00, 127.93, 127.89, 127.8, 95.5 (d, *J* = 6.1 Hz), 80.6, 78.9, 78.8 (d, *J* = 7.2 Hz), 75.9, 75.4, 73.3, 72.0, 69.6 (d, *J* = 5.5 Hz), 69.5 (d, *J* = 5.5 Hz), 52.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.4; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{42}H_{44}O_{10}P]^+$, 739.2667; found, 739.2664.

dibenzyl 2,3,4,6-tetra-*O*-benzyl-*α*-D-galactopyranosyl phosphate (3e)



3e, prepared via general procedure (A), eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 2/1/0.01), R_f = 0.2 (Hexanes/EtOAc, 2/1), colorless oil, 38.9 mg, 99% yield, α/β = 11/1. $[\alpha]_D^{25}$ = 37 (*c* 0.44, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.20 (m, 30H, Ar*H*), 5.96 (dd, *J* = 6.6, 3.4 Hz, 1H, H-1), 5.07-4.91 (m, 5H, C*H*Ph x 5), 4.81-4.65 (m, 4H, C*H*Ph x 4), 4.56 (d, *J* = 11.3 Hz, 1H, C*H*Ph), 4.35 (q, *J* = 11.7 Hz, 2H, C*H*Ph x 2), 4.16 – 4.06 (m, 2H, H-2, H-3), 3.99 (d, *J* = 2.8 Hz, 1H, H-4), 3.87 (dd, *J* = 10.1, 2.8 Hz, 1H, H-5), 3.52 (dd, *J* = 9.3, 7.1 Hz, 1H, H-6), 3.43 (dd, *J* = 9.3, 5.9 Hz, 1H, H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.61, 138.56, 138.2, 137.9, 136.14, 136.06, 136.02, 128.6, 128.5, 128.43, 128.40, 128.35, 128.3, 128.2, 127.95, 127.87, 127.85, 127.8, 127.7, 127.63, 127.57, 96.7 (d, *J* = 6.3 Hz), 78.2, 75.9 (d, *J* =7.0 Hz), 75.0, 74.7, 73.6, 73.4, 73.1, 71.6, 69.3 (d, *J* = 5.3 Hz), 69.1 (d, *J* = 5.2 Hz), 68.6; ^{31}P NMR (162 MHz, CDCl3) δ = -2.1. HR ESI-MS: $[M+H^+]^+$calcd for $[C_{48}H_{50}O_9P]^+$, 801.3187; found, 801.3188.

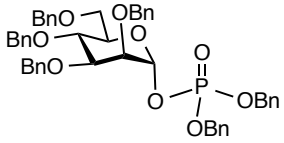
diphenyl 2,3,4,6-tetra-*O*-benzyl-*α*-D-galactopyranosyl phosphate (3e')



3e', prepared via general procedure (A), eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/1/0.01), R_f = 0.2 (Hexanes/EtOAc, 3/1), colorless oil, 35.9 mg, 93% yield, α/β = 10/1. $[\alpha]_D^{25}$ = 24.6 (*c* 1.6 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.09 (m, 30H, Ar*H*), 6.07 (dd, *J* = 6.2, 3.3 Hz, 1H, H-1), 4.92 (d, *J* = 11.4 Hz, 1H, C*H*Ph), 4.78-4.65 (m, 4H, 4 x C*H*Ph), 4.55 (d, *J* = 11.4 Hz, 1H, C*H*Ph), 4.36 (d, *J* = 1.4 Hz, 2H), 4.13 (dt,

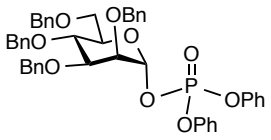
J = 10.0, 3.3 Hz, 1H, H-2), 4.04-3.95 (m, 2H, H-4, H-5), 3.83 (dd, *J* = 10.0, 2.7 Hz, 1H, H-3), 3.52 (t, *J* = 8.6 Hz, 1H, H-6), 3.29 (dd, *J* = 9.0, 5.2 Hz, 1H, H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.73, 150.68, 150.65, 150.61, 138.6, 138.5, 138.0, 137.8, 129.8, 129.6, 128.5, 128.4, 128.35, 128.26, 128.20, 128.17, 128.00, 127.7, 127.88, 127.85, 127.81, 127.73, 127.67, 127.62, 127.5, 125.32, 125.28, 120.53, 120.48, 120.3, 120.2, 98.1, 78.1, 75.7, 75.0, 74.5, 73.5, 73.4, 73.1, 71.7, 68.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -13.2; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{46}H_{46}O_9P]^+$, 773.2874; found, 773.2875.

dibenzyl 2,3,4,6-tetra-*O*-benzyl-*α*-D-mannopyranosyl phosphate (3f)



3f, prepared via general procedure (A), eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 2/1/0.01), R_f = 0.2 (Hexanes/EtOAc, 2/1), colorless oil, 36.8 mg, 92% yield, α/β > 20/1. $[\alpha]_D^{25}$ = 11.3 (*c* 0.8 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.15 (m, 30H, Ar*H*), 5.78 (dd, *J* = 6.2, 2.0 Hz, 1H, H-1), 5.02 (d, *J* = 8.2 Hz, 2H, C*H*$_2$Ph), 4.96 (d, *J* = 8.5 Hz, 2H, C*H*$_2$Ph), 4.86 (d, *J* = 10.8 Hz, 1H, C*H*Ph), 4.66 (s, 2H, C*H*$_2$Ph), 4.60 (d, *J* = 12.1 Hz, 1H, C*H*Ph), 4.55-4.40 (m, 4H, C*H*Ph x 4), 4.04 (t, *J* = 9.7 Hz, 1H, H-4), 3.89 (ddd, *J* = 10.0, 4.6, 1.7 Hz, 1H, H-5), 3.81 (dd, *J* = 9.4, 3.1 Hz, 1H, H-3), 3.73-3.69 (m, 2H, H-2, H-6), 3.56 (dd, *J* = 11.0, 1.8 Hz, 1H, H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.5, 138.33, 138.31, 137.9, 135.85, 135.78, 135.71, 128.7, 128.6, 128.5, 128.44, 128.40, 128.1, 128.08, 128.03, 127.99, 127.92, 127.8, 127.6, 96.5 (d, *J* = 6.2 Hz), 79.0, 75.3, 74.5 (d, *J* = 9.5 Hz), 74.2, 74.0, 73.5, 72.9, 72.3, 69.6 (d, *J* = 5.3 Hz), 69.5 (d, *J* = 5.4 Hz), 68.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.7; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{48}H_{49}NaO_9P]^+$, 823.3006; found, 823.3000.

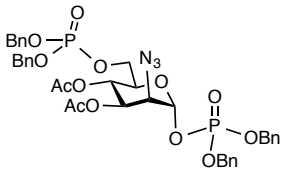
diphenyl 2,3,4,6-tetra-*O*-benzyl-*α*-D-mannopyranosyl phosphate (3e')



3f', prepared via general procedure (A), eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/1/0.01), R_f = 0.2 (Hexanes/EtOAc, 3/1), colorless oil, 34.4 mg, 89% yield, α/β > 20/1. $[\alpha]_D^{25}$ = 25.7 (*c* 1.8 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-71.3 (m, 30H, Ar*H*), 6.00 (dd, *J* = 6.0, 2.7 Hz, 1H, H-1), 4.91-4.81 (m, 1H, C*H*Ph), 4.69 (s, 2H, C*H*$_2$Ph), 4.62 (d, *J* = 11.8 Hz, 1H, C*H*Ph), 4.55-4.37 (m, 4H, 4 x C*H*Ph), 4.09 (td, *J* = 9.7, 4.9 Hz, 1H, H-4), 3.93-3.79 (m, 2H, H-3, H-5), 3.78-3.67 (m, 2H, H-2, H-6), 3.53 (dd, *J* =

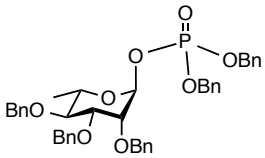
11.4, 2.3 Hz, 1H, H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.4, 138.35, 138.30, 138.2, 137.7, 129.91, 129.88, 128.5, 128.42, 128.38, 128.1, 127.92, 127.89, 127.84, 127.78, 127.71, 127.6, 125.6, 125.5, 120.22, 120.17, 97.8, 78.9, 75.3, 74.4, 74.3, 74.2, 74.0, 73.5, 72.9, 72.3, 68.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -13.9; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{46}H_{46}O_9P]^+$, 773.2874; found, 773.2876.

dibenzyl 3,4-di-*O*-acetyl-2-azido-6-*O*-dibenzyloxyphosphoryl-2-deoxy-*α*-D-mannopyranosyl phosphate (3g)



3g, prepared via general procedure (A), eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/2/0.01), R_f = 0.2 (Hexanes/EtOAc, 3/2), colorless oil, 36.0 mg, 89% yield, α/β > 20/1. $[\alpha]_D^{25}$ = 24.6 (*c* 2.2 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.31 (m, 30H, Ar*H*), 5.51 (dd, *J* = 6.6, 1.8 Hz, 1H, H-1), 5.33 (t, *J* = 9.7 Hz, 1H, H-4), 5.27 (dd, *J* = 9.9, 3.6 Hz, 1H, H-3), 5.13-4.97 (m, 8H, 4 x C*H*$_2$Ph), 4.00-3.85 (m, 3H, H-5, H-6, H-6'), 3.67 (t, *J* = 2.5 Hz, 1H, H-2), 2.09 (s, 3H, CH_3), 1.98 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 169.8, 169.4, 135.9, 135.8, 135.43, 135.37, 129.0, 128.9, 128.7, 128.6, 128.4, 128.3, 128.1, 128.0, 95.6 (d, *J* = 5.0 Hz), 70.9 (d, *J* = 8.4 Hz), 70.21, 70.15 (d, 2^{13}C, *J* = 6.5 Hz), 69.6 (d, 2^{13}C, *J* = 5.3 Hz), 65.1, 65.0 (d, *J* = 4.8 Hz), 61.4 (d, *J* = 9.9 Hz), 20.7, 20.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -1.4, -3.2; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{38}H_{42}N_3O_{13}P_2]^+$, 810.2187; found, 810.2183.

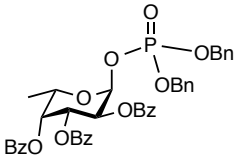
dibenzyl 2,3,4-tri-*O*-benzyl-*α*-L-rhamnopyranosyl phosphate (3h)



3h, prepared via general procedure (A), eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/1/0.01), R_f = 0.2 (Hexanes/EtOAc, 3/1), colorless oil, 29.5 mg, 85% yield, α/β > 20/1. $[\alpha]_D^{25}$ = -39.5 (*c* 1.4 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.25 (m, 25H, Ar*H*), 5.66 (dd, *J* = 6.0, 2.0 Hz, 1H, H-1), 5.01 (d, *J* = 8.1 Hz, 2H, C*H*$_2$Ph), 4.96 (d, *J* = 8.4 Hz, 2H, C*H*$_2$Ph), 4.92 (d, *J* = 10.9 Hz, 1H C*H*Ph), 4.65 (s, 2H, C*H*$_2$Ph), 4.61 (d, *J* = 10.9 Hz, 1H, C*H*Ph), 4.56-4.43 (m, 2H, C*H*$_2$Ph), 3.88-3.79 (m, 1H, H-5), 3.76 (dd, *J* = 9.4, 3.1 Hz, 1H, H-3), 3.70 (t, *J* = 2.6 Hz, 1H, H-2), 3.61 (t, *J* = 9.5 Hz, 1H, H-4), 1.25 (d, *J* = 6.3 Hz, 3H, C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.5, 138.4, 137.9, 135.81, 135.77, 135.73, 128.7, 128.54, 128.50, 128.1, 128.08, 128.03, 127.82, 127.77, 96.5 (d,

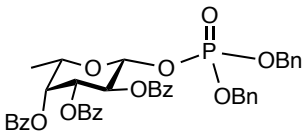
J = 6.0 Hz), 79.8, 78.9, 75.5, 74.7 (d, *J* = 9 Hz), 73.0, 72.3, 70.3, 69.5 (d, 2C, *J* = 5.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.7; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{41}H_{43}NaO_8P]^+$, 717.2588; found, 717.2588.

dibenzyl 2,3,4-tri-*O*-benzoyl-*α*-L-fucopyranosyl phosphate (3hα)



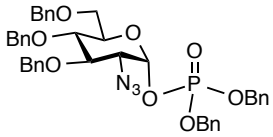
3lα, prepared via general procedure (A), eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 2/1/0.01), R_f = 0.2 (Hexanes/EtOAc, 2/1), colorless oil, 31.3 mg, 85% yield, α/β = 9.7/1. $[\alpha]_D^{25}$ = -188 (*c* 2.7 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09-7.23 (m, 25H, Ar*H*), 6.22 (dd, *J* = 6.2, 3.4 Hz, 1H, H-1), 5.93 (dd, *J* = 10.8, 3.3 Hz, 1H, H-3), 5.75 (td, *J* = 5.5, 4.7, 3.2 Hz, 2H, H-2, H-4), 5.14-4.90 (m, 4H, 2 x C*H*$_2$Ph), 4.52-4.36 (m, 1H, H-5), 1.18 (d, *J* = 6.5 Hz, 3H, H-6); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.0, 165.9, 165.6, 135.7, 135.6, 135.5, 133.7, 133.5, 133.3, 130.03, 129.96, 129.8, 129.3, 129.2, 129.0, 128.8, 128.73, 128.71, 128.69, 128.6, 128.4, 127.94, 127.91, 95.4, 71.5, 69.7, 69.6, 68.4, 68.3, 67.5, 16.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.4; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{41}H_{37}NaO_{11}P]^+$, 759.1966; found, 759.1965.

dibenzyl 2,3,4-tri-*O*-benzoyl-*β*-L-fucopyranosyl phosphate (3hβ)



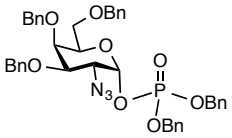
3lβ, prepared via general procedure (A) with additional ^{i}Pr$_2$NEt (0.2 equiv.), eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/2/0.01), R_f = 0.2 (Hexanes/EtOAc, 3/2), colorless oil, 34.2 mg, 93% yield, α/β = 1/20. $[\alpha]_D^{25}$ = -120 (*c* 3.4 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-7.00 (m, 25H, Ar*H*), 5.89 (dd, *J* = 10.4, 8.0 Hz, 1H, H-2), 5.75 (dd, *J* = 3.5, 1.1 Hz, 1H, H-4), 5.67 (dd, *J* = 8.0, 7.2 Hz, 1H, H-1), 5.57 (dd, *J* = 10.4, 3.4 Hz, 1H, H-3), 5.20-5.04 (m, 2H, 2 x C*H*$_2$Ph), 4.86 (dd, *J* = 11.7, 6.6 Hz, 1H, H-6), 4.77 (dd, *J* = 11.7, 7.1 Hz, 1H, H-6'), 4.21 (qd, *J* = 6.4, 1.2 Hz, 1H, H-5), 1.35 (d, *J* = 6.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.0, 165.6, 165.4, 135.7, 135.6, 135.3, 133.7, 133.6, 133.4, 130.1, 130.0, 129.9, 129.3, 129.1, 128.9, 128.8, 128.62, 128.60, 128.49, 128.46, 128.40, 128.1, 127.6, 97.2 (d, *J* = 4.9 Hz), 71.9 (bs), 71.0, 70.8, 69.9 (d, *J* = 9.2 Hz), 69.8 (d, *J* = 9.2 Hz), 69.5 (d, *J* = 9.2 Hz), 16.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.9; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{41}H_{37}NaO_{11}P]^+$, 759.1966; found, 759.1965.

dibenzyl 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl phosphate (3j)



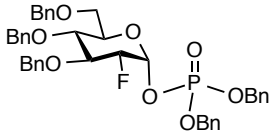
3j, prepared via general procedure (A), eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 2/1/0.01), R_f= 0.2 (Hexanes/EtOAc, 2/1), colorless oil, 34.2 mg, 93% yield, α/β = 8.6/1. $[\alpha]_D^{25}$ = 25.8 (*c* 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.14 (m, 30H, Ar*H*), 5.81 (dd, *J* = 6.2, 3.3 Hz, 1H, H-1), 5.17-5.01 (m, 4H, C*H*Ph x 4), 4.87-4.77 (m, 3H, C*H*Ph), 4.55-4.51 (m, 2H, C*H*Ph x 2), 4.40 (d, *J* = 12.0 Hz, 1H, C*H*Ph), 4.00-3.83 (m, 2H, H-3, H-4), 3.78 (t, *J* = 9.5 Hz, 1H, H-5), 3.64 (dd, *J* = 11.0, 3.0 Hz, 1H, H-6'), 3.55 (dt, *J* = 10.1, 3.3 Hz, 1H, H-2), 3.43 (dd, *J* = 11.1, 1.9 Hz, 1H, H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.0, 137.8, 137.7, 135.83, 135.76, 128.71, 128.66, 128.63, 128.59, 128.56, 128.2, 128.12, 128.08, 128.02, 127.99, 127.93, 127.8, 96.4 (d, *J* = 5.7 Hz), 80.1, 75.7, 75.2, 73.6, 73.0, 69.7 (d, *J* = 5.4 Hz), 69.6 (d, *J* = 5.4 Hz), 67.8, 63.6 (d, *J* = 8.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.5; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{41}H_{42}N_3NaO_8P]^+$, 758.2602; found, 758.2604.

dibenzyl 2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-*α*-D-galactopyranosyl phosphate (3k)



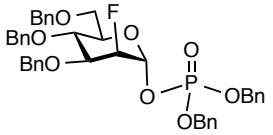
3k, prepared via general procedure (A), eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 2/1/0.01), R_f= 0.2 (Hexanes/EtOAc, 2/1), colorless oil, 34.9 mg, 95% yield, α/β = 7.3/1. $[\alpha]_D^{25}$ = 51.6 (*c* 2.0 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.21 (m, 25H, Ar*H*), 5.78 (dd, *J* = 6.0, 3.4 Hz, 1H, H-1), 5.13-5.04 (m, 4H, CH_2Ph x 2), 4.86 (d, *J* = 11.2 Hz, 1H, C*H*Ph), 4.71 (d, *J* = 11.4 Hz, 1H, C*H*Ph), 4.65 (d, *J* = 11.3 Hz, 1H, C*H*Ph), 4.51 (d, *J* = 11.2 Hz, 1H, C*H*Ph), 4.38 (d, *J* = 11.7 Hz, 1H, C*H*Ph), 4.32 (d, *J* = 11.7 Hz, 1H, C*H*Ph), 4.10 (dd, *J* = 7.4, 5.9 Hz, 1H, H-5), 4.07-4.04 (m, 2H, H-2, H-4), 3.86 (dd, *J* = 10.5, 2.6 Hz, 1H, H-3), 3.55 (dd, *J* = 9.2, 7.6 Hz, 1H, H-6), 3.40 (dd, *J* = 9.2, 5.7 Hz, 1H, H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.2, 137.8, 137.4, 135.9, 135.8, 128.68, 128.66, 128.62, 128.58, 128.55, 128.46, 128.18, 128.16, 128.07, 127.98, 127.96, 127.92, 96.8 (d, *J* = 6.0 Hz), 75.0, 73.6, 72.9, 72.3, 71.6, 69.6 (d, *J* = 5.3 Hz), 69.4 (d, *J* = 5.3 Hz), 68.2, 59.9 (d, *J* = 8.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ -2.34; HR ESI-MS: $[M+H^+]^+$calcd for $[C_{41}H_{43}N_3O_8P]^+$, 736.2782; found, 736.2778.

dibenzyl 3,4,6-tri-*O*-benzyl-2-fluoro-2-deoxy-*α*-D-glucopyranosyl phosphate (3l)



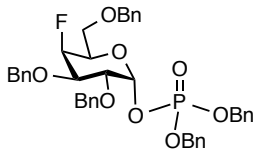
3l, prepared via general procedure (A), eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 2/1/0.01), R_f= 0.2 (Hexanes/EtOAc, 2/1), colorless oil, 24.6 mg, 69% yield, α/β = 7.7/1. $[\alpha]_D^{25}$ = 59.5 (*c* 1.4 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.13 (m, 25H, Ar*H*), 5.94 (dd, *J* = 6.4, 3.6 Hz, 1H, H-1), 5.09-5.06 (m, 4H, 2 x CH_2Ph), 4.83 (dd, *J* = 11.0, 7.3 Hz, 2H, 2 x C*H*Ph), 4.71 (d, *J* = 11.2 Hz, 1H, C*H*Ph), 4.65-4.48 (m, 3H, 2 x C*H*Ph, H-2), 4.40 (d, *J* = 12.1 Hz, 1H, C*H*Ph), 4.00 (dt, *J* = 12.2, 9.1 Hz, 1H, H-3), 3.91 (ddd, *J* = 10.1, 3.4, 2.0 Hz, 1H, H-5), 3.72 (t, *J* = 9.6 Hz, 1H, H-4), 3.63 (dd, *J* = 11.0, 3.4 Hz, 1H, H-6), 3.46 (dd, *J* = 10.9, 2.0 Hz, 1H, H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.2, 138.1, 137.8, 135.8, 135.7, 128.70, 128.66, 128.6, 128.55, 128.52, 128.13, 128.07, 128.01, 127.95, 127.91, 94.9 (dd, *J* = 5.5 Hz, *J* = 23 Hz), 90.6 (dd, *J* = 8.1 Hz, *J* = 194 Hz), 80.1 (d, *J* = 16.3 Hz), 76.2 (d, *J* = 8.6 Hz), 75.4, 75.2 (d, *J* = 2.3 Hz), 73.6, 72.5, 69.7 (d, *J* = 5.5 Hz), 69.5 (d, *J* = 5.5 Hz), 67.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.5; ^{19}F NMR (377 MHz, CDCl3) δ = -197.8; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{41}H_{43}FO_8P]^+$, 713.2672; found, 713.2674.

dibenzyl 3,4,6-tri-*O*-benzyl-2-fluoro-2-deoxy-*α*-D-mannopyranosyl phosphate (3m)



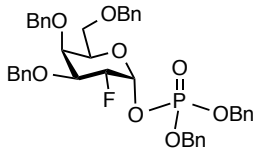
3m, prepared via general procedure (A), eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 2/1/0.01), R_f= 0.2 (Hexanes/EtOAc, 2/1), colorless oil, 32.8 mg, 92% yield, α/β = 11/1. $[\alpha]_D^{25}$ = 19.0 (*c* 1.8 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.15 (m, 25H, Ar*H*), 5.79 (td, *J* = 6.1, 2.1 Hz, 1H, H-1), 5.06-4.99 (m, 4H, 2 x CH_2Ph), 4.83 (d, *J* = 10.8 Hz, 1H, C*H*Ph), 4.66-4.47 (m, 5H, 4 x C*H*Ph, H-2), 4.43 (d, *J* = 12.1 Hz, 1H, C*H*Ph), 4.00-3.91 (m, 1H, H-4), 3.87 (ddd, *J* = 10.0, 4.3, 1.6 Hz, 1H, H-5), 3.78 (ddd, *J* = 28.9, 9.4, 2.5 Hz, 1H, H-3), 3.67 (dd, *J* = 11.0, 4.1 Hz, 1H, H-6), 3.51 (dd, *J* = 11.0, 1.8 Hz, 1H, H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.2, 138.1, 137.8, 135.6, 135.5, 134.4, 134.2, 128.9, 128.83, 128.78, 128.6, 128.50, 128.47, 128.2, 128.1, 128.0, 127.9, 127.8, 95.4 (dd, *J* = 5.7 Hz, *J* = 32 Hz), 86.2 (dd, *J* = 11 Hz, *J* = 180 Hz), 77.7, 73.74, 73.70, 73.6, 72.4, 69.9 (d, 2^{13}C, *J* = 5.5 Hz), 68.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -203; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{41}H_{43}FO_8P]^+$, 713.2672; found, 713.2674.

dibenzyl 2,3,6-tri-*O*-benzyl-4-fluoro-4-deoxy-*α*-D-galactopyranosyl phosphate (3n)



3n, prepared via general procedure (A), eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 2/1/0.01), R_f= 0.2 (Hexanes/EtOAc, 2/1), colorless oil, 33.5 mg, 94% yield, α/β = 13/1. $[\alpha]_D^{25}$ = 35.1 (*c* 2.6 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.23-7.17 (m, 25H, Ar*H*), 5.86 (dd, *J* = 6.8, 3.3 Hz, 1H, H-1), 5.01-4.86 (m, 4H, C*H*$_2$Ph x 2), 4.80 (dd, *J* = 50.0, 2.4 Hz, 1H, H-4), 4.69 (s, 2H, C*H*$_2$Ph), 4.66 (s, 2H, C*H*$_2$Ph), 4.39 (s, 2H, C*H*$_2$Ph), 4.00 (dt, *J* = 29.7, 6.7 Hz, 1H, H-5), 3.90 (dt, *J* = 10.1, 3.2 Hz, 1H, H-2), 3.74 (ddd, *J* = 27.9, 10.0, 2.5 Hz, 1H, H-3), 3.56 (dd, *J* = 9.5, 7.3 Hz, 1H, H-6), 3.42 (ddd, *J* = 9.4, 6.0, 1.4 Hz, 1H, H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.0, 137.9, 137.8, 136.0, 135.94, 135.89, 135.86, 134.4, 134.2, 129.4, 129.3, 128.7, 128.63, 128.57, 128.56, 128.52, 128.46, 128.2, 128.1, 128.0, 127.94, 127.89, 127.87, 127.84, 96.2 (d, *J* = 6.2 Hz), 87.8, 86.0, 75.2, 75.1, 73.75, 73.67, 72.6, 70.3, 69.5 (d, *J* = 5.2 Hz), 69.3 (d, *J* = 5.2 Hz), 67.6 (d, *J* = 5.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.1; ^{19}F NMR (377 MHz, $CDCl_3$) δ = -218; HR ESI-MS: $[M+H^+]^+$calcd for $[C_{41}H_{43}FO_8P]^+$, 713.2672; found, 713.2674.

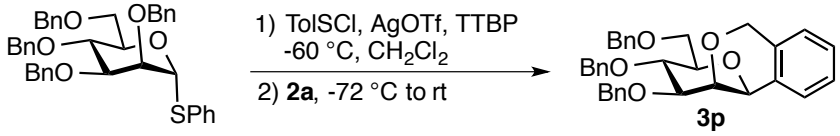
dibenzyl 3,4,6-tri-*O*-benzyl-2-fluoro-2-deoxy-*α*-D-galactopyranosyl phosphate (3o)



3o, prepared via general procedure (A), eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 2/1/0.01), R_f= 0.2 (Hexanes/EtOAc, 2/1), colorless oil, 31.3 mg, 88% yield, α/β = 9/1. $[\alpha]_D^{25}$ = 41.6 (*c* 3.5 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.20 (m, 25H, Ar*H*), 5.94 (dd, *J* = 6.2, 3.7 Hz, 1H, H-1), 5.07-4.94 (m, 5H, H-2, 2 x C*H*$_2$Ph), 4.97-4.86 (m, 1H, C*H*Ph), 4.76 (d, *J* = 11.9 Hz, 1H, C*H*Ph), 4.65 (d, *J* = 11.9 Hz, 1H, C*H*Ph), 4.54 (d, *J* = 11.2 Hz, 1H, C*H*Ph), 4.40-4.31 (m, 2H, C*H*$_2$Ph), 4.11 (t, *J* = 6.6 Hz, 1H, H-5), 4.01 (bs, 1H, H-4), 3.94 (td, *J* = 10.0, 2.8 Hz, 1H, H-3), 3.53 (dd, *J* = 9.3, 7.3 Hz, 1H, H-6), 3.42 (dd, *J* = 9.2, 5.8 Hz, 1H, H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.2, 138.0, 137.7, 135.8, 135.7, 128.6, 128.52, 128.49, 128.43, 128.3, 128.2, 128.0, 127.9, 127.84, 127.82, 127.80, 127.5, 95.4 (dd, *J* = 6.2 Hz, *J* = 23 Hz,), 88.4 (dd, *J* = 7.8 Hz, *J* = 191

Hz), 76.3 (d, *J* = 16 Hz), 75.1, 75.0, 73.5, 73.0, 71.5, 69.5 (d, *J* = 5.3 Hz), 69.3 (d, *J* = 5.3 Hz), 68.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -206.7; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{41}H_{43}FO_8P]^+$, 713.2672; found, 713.2670.

(2*R*,3*R*,4*R*,4a*R*,10b*S*)-3,4-bis(benzyloxy)-2-((benzyloxy)methyl)-2,3,4,4a,6,10b-hexahydropyrano[3,2-*c*] isochromene (3p)



3p

To a mixture of phenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-mannoside (38 mg, 0.06 mmol), TTBP (18.6 mg, 0.075 mmol) and freshly activated 4 Å molecular sieves (50 mg) in anhydrous CH_2Cl_2 (2 mL) under argon atmosphere was added *p*-TolSCl (7.9 μL, 0.06 mmol) and AgOTf (15 mg, 0.06 mmol) at -60 °C. After stirring 5 min, **2a** (14 mg, 0.05 mmol) was added in one portion at -60 °C. The resulting mixture was slowly warmed to room temperature within 2 h, and then quenched with Et_3N (1 mL) and filtered through Celite. After concentration, the residue was purified through flash silica gel column chromatography (Hexanes/EtOAc, 10/1) to give compound **3p** as colorless oil (22.6 mg, 87% yield). R_f = 0.2 (Hexanes/EtOAc, 7/1), $[\alpha]_D^{25}$ = 31.9 (*c* 1.6 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.12 (m, 20H, Ar*H*), 5.12 (d, *J* = 1.8 Hz, 1H, H-1), 4.81 (d, *J* = 10.6 Hz, 1H, C*H*Ph), 4.59-4.43 (m, 3H, 3 x C*H*Ph), 3.90 (t, *J* = 9.6 Hz, 1H, H-4), 3.66-3.62 (m, 2H, H-3, H-6), 3.57-3.49 (m, 2H, H-2, H-6'), 3.48 (dd, *J* = 10.1, 4.7 Hz, 1H, H-5); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.5, 138.47, 138.4, 138.1, 128.6, 128.52, 128.47, 128.2, 128.1, 127.92, 127.89, 127.86, 127.82, 127.80, 127.7, 93.5, 79.6, 75.4, 74.8, 74.2, 73.6, 72.8, 72.6, 72.2, 69.2; HR ESI-MS: $[M+H^+]^+$calcd for $[C_{34}H_{35}O_5]^+$, 523.2479; found, 523.2478.

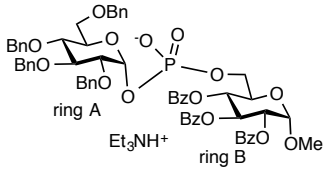
2.2. Hydrogenolysis procedure (B) and phosphosaccharides 4a-4zb

To clearly characterize the products of bis-glycosyl benzyl phosphotriester by using NMR analysis, the chirality of phosphorus atom was eliminated by removing the benzyl group on phosphorus. The deprotection reaction was straightforward to perform, in quantitative yield and free of purification. Notably, the azido groups of **4t**-**4z**, **4za**, **4e**, **4j** and **4o** were simultaneously reduced to amino groups.

General procedure (B) for removal of benzyl group of benzyl phosphate. To a solution of phosphotriester (40 mg) in EtOAc/MeOH (2.0 mL/2.0 mL) was added Et_3N (40 μL) and Pd/C (40 mg). Then, the mixture was stirred under an atmosphere of H_2 at room temperature for 0.5 h until TLC showed the completion of hydrogenolysis. After filtration through syringe filter, the filtrate was concentrated to afford a colorless oil, which was tested via NMR analysis to determine the structure and α/β ratio (by ^{31}P

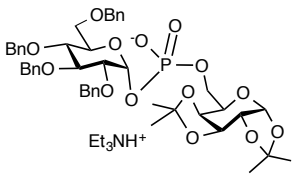
NMR). Notably, because the diastereomeric anomers with amino group on sugar ring (**4t**-**4z** and **4za**) do not show separated ^{31}P signals, the α/β ratio was determined before hydrogenolysis by using ^{31}P NMR spectra of phosphotriester.

methyl 2,3,4,6-tetra-*O*-benzyl-*α*-D-glucopyranosyl-phosphoryl-(→6)-2,3,4-tri-*O*-benzoyl-*α*-D-glucopyranoside triethylammonium salt (4a)



4a, prepared first via procedure (A), purified via flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 2/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 2/1), 53.3 mg, 89% yield); then procedure (B), quantitative yield, colorless oil, α/β = 20/1. $[\alpha]_D^{25}$ = 54.3 (*c* 2.7 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.91-7.08 (m, 35H, Ar*H*), 6.02 (t, *J* = 9.7 Hz, 1H, H-3^A), 5.80 (dd, *J* = 8.2, 3.2 Hz, 1H, H-1^B), 5.39 (t, *J* = 9.8 Hz, 1H, H-4^A), 5.12-5.02 (m, 2H, H-1^A, H-2^A), 4.85 (d, *J* = 10.9 Hz, 1H, C*H*Ph), 4.80 (d, *J* = 11.8 Hz, 1H, C*H*Ph), 4.75 (d, *J* = 11.1 Hz, 1H, C*H*Ph), 4.67 (d, *J* = 10.9 Hz, 1H, C*H*Ph), 4.56 (d, *J* = 11.8 Hz, 1H, C*H*Ph), 4.43 (t, *J* = 12.5 Hz, 2H, C*H*Ph x 2), 4.31 (d, *J* = 12.2 Hz, 1H, C*H*Ph), 4.19 (ddd, *J* = 9.6, 6.8, 1.8 Hz, 1H, H-5^A), 4.14-4.07 (m, 1H, H-6^A), 4.06 – 3.86 (m, 3H, H-5^B, H-6'^{A}, H-3^B), 3.63 (t, *J* = 9.6 Hz, 1H, H-4^B), 3.57 (dd, *J* = 10.7, 2.9 Hz, 1H, H-6^B), 3.50 (d, *J* = 11.5 Hz, 2H, H-2^B, H-6'^{B}), 3.34 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.0, 165.9, 165.3, 139.0, 138.9, 138.8, 138.3, 133.4, 133.2, 133.1, 130.03, 129.96, 129.8, 129.5, 129.33, 129.30, 128.5, 128.4, 128.3, 128.1, 127.87, 127.85, 127.7, 127.6, 127.5, 96.6, 93.1 (d, *J* = 6.1 Hz), 81.6, 80.0 (d, *J* = 7.5 Hz), 75.6, 74.8, 73.4, 72.3, 72.1, 71.3, 71.0, 69.5, 69.1 (d, *J* = 8.4 Hz), 68.5, 64.3 (bs), 55.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -1.6; HR ESI-MS: $[M\text{-}Et_3NH^+ + Na^+ + H^+]^+$calcd for $[C_{62}H_{61}NaO_{17}P]^+$, 1131.3539; found, 1131.3533.

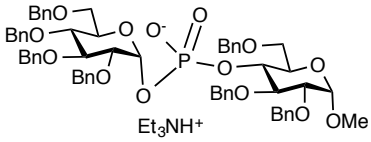
2,3,4,6-tetra-*O*-benzyl-*α*-D-glucopyranosyl-phosphoryl-(→6)-1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose triethylammonium salt (4b)



4b, prepared first via procedure (A), purified via flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 2/1/0.01) to give an intermediate product (R_f = 0.2

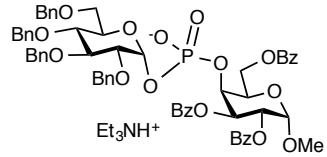
(Hexanes/EtOAc, 2/1), 41 mg, 86% yield); then procedure (B), quantitative yield, colorless oil, α/β = 12/1. $[\alpha]_D^{25}$ = 17.1 (*c* 3.0 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.08 (m, 20H, Ar*H*), 5.83 (dd, *J* = 8.1, 3.3 Hz, 1H, H-1^B), 5.41 (d, *J* = 5.0 Hz, 1H, H-1^A), 4.88 (d, *J* = 10.9 Hz, 1H, C*H*Ph), 4.83 (d, *J* = 11.8 Hz, 1H, C*H*Ph), 4.77 (d, *J* = 11.1 Hz, 1H, C*H*Ph), 4.70 (d, *J* = 10.9 Hz, 1H, C*H*Ph), 4.58-4.52 (m, 2H, C*H*Ph x 2), 4.45-4.43 (m, 2H, C*H*Ph, H-3^A), 4.37 (d, *J* = 12.2 Hz, 1H, C*H*Ph), 4.19-4.15 (m, 2H, H-2^A, H-4^A), 4.09-3.92 (m, 5H, H-3^B, H-5^B, H-5^A, H-6^A, H-6'^{A}), 3.71-3.63 (m, 2H, H-4^B, H-6^B), 3.60 (dd, *J* = 10.9, 2.0 Hz, 1H, H-6'^{B}), 3.53 (dt, *J* = 9.7, 2.9 Hz, 1H, H-2^B), 1.42 (s, 3H, C*H*$_3$), 1.30 (s, 3H, C*H*$_3$), 1.21 (s, 3H, C*H*$_3$), 1.16 (s, 3H, C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.1, 138.9, 138.7, 138.4, 128.5, 128.4, 128.3, 128.1, 128.04, 128.00, 127.65, 127.61, 127.53, 127.46, 109.1, 108.5, 96.4, 93.1, 81.8, 80.1, 75.6, 74.8, 73.5, 72.0, 71.3, 71.0, 68.7; HR ESI-MS: $[M\text{-}Et_3NH^+ + Na^+ + H^+]^+$calcd for $[C_{46}H_{55}NaO_{14}P]^+$, 885.3222; found, 885.3226.

methyl 2,3,4,6-tetra-*O*-benzyl-*α*-D-glucopyranosyl-phosphoryl-(→4)-2,3,6-tri-*O*-benzyl-*α*-D-glucopyranoside triethylammonium salt (4c)



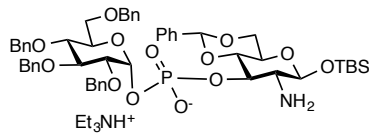
4c, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 2/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 2/1), 48.6 mg, 84% yield); then procedure (B), quantitative yield, colorless oil, α/β = 13/1. $[\alpha]_D^{25}$ = 48.6 (*c* 2.2 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.06 (m, 35H, Ar*H*), 5.86 (dd, *J* = 7.9, 3.2 Hz, 1H, H-1^B), 5.13 (d, *J* = 11.3 Hz, 1H, C*H*Ph), 4.75 (t, *J* = 12.1 Hz, 4H), 4.63 (d, *J* = 12.2 Hz, 1H, C*H*Ph), 4.58 (d, *J* = 12.1 Hz, 1H, C*H*Ph), 4.52-4.42 (m, 8H, CHPh x 7, H-1^A), 4.34 (d, *J* = 12.0 Hz, 1H, C*H*Ph), 4.31-4.21 (m, 1H, H-4^A), 4.11-3.99 (m, 2H, H-6^A, H-5^B), 3.93-3.72 (m, 4H, H-3^B, H-3^A, H-5^A, H-6'^{A}), 3.67-3.50 (m, 4H, H-2^B, H-4^B, H-6^B, H-6'^{B}), 3.38 (dd, *J* = 9.7, 3.7 Hz, 1H, H-2^A), 3.27 (s, 3H, C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 140.3, 139.4, 139.1, 138.9, 138.7, 138.5, 138.3, 128.41, 128.37, 128.3, 128.2, 128.12, 128.9, 128.05, 128.00, 129.97, 127.9, 127.83, 127.78, 127.73, 127.66, 127.52, 127.49, 127.42, 127.0, 126.9, 98.0, 93.3 (d, *J* = 6.0 Hz), 81.9, 81.5 (d, *J* = 2.9 Hz), 80.5 (d, *J* = 8.0 Hz), 79.4, 77.8, 75.5, 75.2, 74.9, 74.7 (d, *J* = 6.4 Hz), 73.54, 73.51, 72.3, 71.3, 70.6 (d, *J* = 3.8 Hz), 70.0, 69.0, 55.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.5; HR ESI-MS: $[M\text{-}Et_3NH^+ + Na^+ + H^+]^+$calcd for $[C_{62}H_{67}NaO_{14}P]^+$, 1089.4161; found, 1089.4163.

methyl 2,3,4,6-tetra-*O*-benzyl-*α*-D-glucopyranosyl-phosphoryl-(→4)-2,3,6-tri-*O*-benzoyl-*α*-D-galactopyranoside triethylammonium salt (4d)



4d, prepared via first procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 2/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 2/1), 52.7 mg, 88% yield); then procedure (B), quantitative yield, colorless oil, α/β = 13/1. $[\alpha]_D^{25}$ = 96.8 (*c* 2.4 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-7.11 (m, 35H, Ar*H*), 5.78 (dd, *J* = 7.7, 3.4 Hz, 1H, H-1^B), 5.60 (d, *J* = 2.0 Hz, 2H, H-2^A, H-3^A), 5.11 (d, *J* = 2.3 Hz, 1H, H-1^A), 4.97 (d, *J* = 10.3 Hz, 1H, H-4^A), 4.84 (d, *J* = 11.1 Hz, 1H, C*H*Ph), 4.76 (d, *J* = 11.0 Hz, 2H, C*H*Ph, H-6^A), 4.72-4.57 (m, 3H, H-6'^{A}, 2 x C*H*Ph), 4.51-4.44 (m, 3H, 3 x C*H*Ph), 4.34 (d, *J* = 12.0 Hz, 1H, C*H*Ph), 4.09 (dt, *J* = 10.2, 2.4 Hz, 1H, H-5^B), 3.97 (t, *J* = 9.3 Hz, 1H, H-3^B), 3.94-3.87 (m, 1H, H-5^A), 3.74 (dd, *J* = 11.0, 3.2 Hz, 1H, H-6^B), 3.69-3.57 (m, 2H, H-4^B, H-6'^{B}), 3.45 (dt, *J* = 9.6, 3.0 Hz, 1H, H-2^B), 3.29 (s, 3H, OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.5, 166.3, 166.2, 139.3, 139.1, 138.6, 133.1, 132.9, 132.6, 130.9, 130.5, 130.3, 130.0, 129.82, 129.78, 128.5, 128.42, 128.37, 128.32, 128.29, 128.22, 127.93, 127.89, 127.7, 127.50, 127.45, 127.39, 97.3, 93.6 (d, *J* = 5.9 Hz), 81.9, 80.3 (d, J = 7.7 Hz), 75.5, 74.7, 73.4, 72.5, 71.7 (d, J = 5.4 Hz), 71.4, 69.8, 69.7 (d, *J* = 2.3 Hz), 69.0, 68.6 (d, *J* = 3.6 Hz), 65.3, 55.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -1.4; HR ESI-MS: [M-Et_3NH^++Na^++H^+]$^+$calcd for [$C_{62}H_{61}NaO_{17}P$]$^+$, 1131.3539; found, 1131.3537.

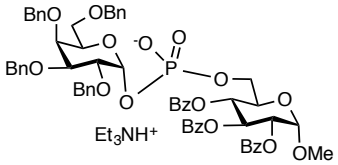
***tert*-butyldimethylsilyl 2,3,4,6-tetra-*O*-benzyl-*α*-D-glucopyranosyl-phosphoryl-(→3)-2-amino-4,6-*O*-benzylidene-2-deoxy-*β*-D-glucopyranoside triethylammonium salt (4e)**



4e, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 4/1), 44 mg, 80% yield); then procedure (B), quantitative yield, colorless oil, α/β = 17/1. $[\alpha]_D^{25}$ = 25.4 (*c* 1.9 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.04 (m, 25H, Ar*H*), 5.83 (dd, *J* = 8.0, 3.3 Hz, 1H, H-1^B), 5.30 (s, 1H, C*H*Ph), 4.74-4.69 (m, 3H, 3 x C*H*Ph), 4.54-4.33 (m, 6H, H-1^A, 5 x C*H*Ph), 4.03 (d, *J* = 10.2 Hz,

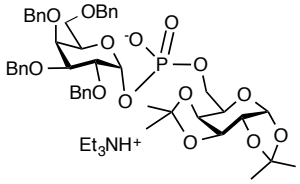
2H, H-5^{B}, H-6^{A}), 3.87 (t, *J* = 9.3 Hz, 1H, H-3^{B}), 3.69-3.39 (m, 7H, H-2^{B}, H-3^{A}, H-4^{A}, H-4^{B},H-6^{B}, H-6'^{B}, H-6'^{A}), 3.27 (t, *J* = 8.4 Hz, 1H, H-5^{A}), 2.74 (t, *J* = 8.6 Hz, 1H, H-2^{A}), 0.78 (s, 9H), 0.01 (s, 3H), 0.00 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.1, 138.8, 138.5, 138.2, 137.9, 129.4, 128.8, 128.5, 128.45, 128.39, 128.33, 128.28, 128.2, 128.04, 128.01, 127.98, 127.91, 127.8, 127.73, 127.66, 127.5, 126.7, 119.1, 116.0, 101.6, 93.4 (bs), 81.7, 80.5, 80.2, 77.7, 75.5, 74.8, 73.5, 72.1, 71.3, 69.0, 68.7, 66.6, 60.0, 8.5, -4.0, -4.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -1.9; HR ESI-MS: [M-Et_3NH^++2H$^+$]$^+$calcd for [$C_{53}H_{67}NO_{13}PSi$]$^+$, 984.4114; found, 984.4111.

methyl 2,3,4,6-tetra-*O*-benzyl-*α*-D-galactopyranosyl-phosphoryl-(→6)-2,3,4-tri-*O*-benzoyl-*α*-D-glucopyranoside triethylammonium salt (4f)



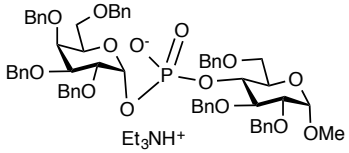
4f, prepared first via general procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 2/1), 57.5 mg, 96% yield); then procedure (B), quantitative yield, colorless oil, α/β = 14/1. $[\alpha]_D^{25}$ = 48.0 (*c* 4.5 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-71.6 (m, 35H, Ar*H*), 6.02 (t, *J* = 9.8 Hz, 1H, H-3^{A}), 5.76 (dd, *J* = 8.0, 3.3 Hz, 1H, H-1^{B}), 5.37 (t, *J* = 9.8 Hz, 1H, H-4^{A}), 5.10 (dd, *J* = 10.1, 3.6 Hz, 1H, H-2^{A}), 5.05 (d, *J* = 3.7 Hz, 1H, H-1^{A}), 4.84 (d, *J* = 11.4 Hz, 1H, C*H*Ph), 4.76 (d, *J* = 11.8 Hz, 1H, C*H*Ph), 4.68 (d, *J* = 11.9 Hz, 1H, C*H*Ph), 4.59 (dd, *J* = 11.9, 6.3 Hz, 2H, C*H*Ph x 2), 4.47 (d, *J* = 11.4 Hz, 1H, C*H*Ph), 4.41 (d, *J* = 11.7 Hz, 1H, C*H*Ph), 4.33 (d, *J* = 11.7 Hz, 1H, C*H*Ph), 4.19-4.07 (m, 3H, H-5^{B}, H-5^{A}, H-6^{A}), 4.03-3.99 (m, 1H, H-6'^{A}), 3.97-3.94 (m, 1H, H-2^{B}), 3.87-3.85 (m, 2H, H-3^{B}, H-4^{B}), 3.47 (d, *J* = 6.7 Hz, 2H, H-6^{B}, H-6'^{B}), 3.32 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.9, 165.8, 165.2, 139.2, 139.1, 139.0, 138.3, 133.3, 133.1, 129.98, 129.94, 129.7, 129.5, 129.4, 129.3, 128.44, 128.39, 128.34, 128.31, 128.27, 128.22, 128.16, 128.0, 127.8, 127.7, 127.5, 127.44, 127.39, 127.2, 96.6, 93.9 (d, *J* = 6.3 Hz), 78.6, 76.6 (d, *J* = 7.2 Hz), 75.3, 74.9, 73.4, 73.0, 72.34, 72.28, 71.1, 69.9, 69.6, 69.2 (d, *J* = 8.6 Hz), 68.9, 64.3 (d, *J* = 5.3 Hz), 55.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -1.5; HR ESI-MS: [M-Et_3NH^++2H$^+$]$^+$calcd for [$C_{62}H_{62}O_{17}P$]$^+$, 1109.3719; found, 1109.3724.

2,3,4,6-tetra-*O*-benzyl-*α*-D-galactopyranosyl-phosphoryl-(→6)-1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose triethylammonium salt (4g)



4g, prepared first via general procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 2/1), 45.7 mg, 96% yield); then procedure (B), quantitative yield, colorless oil, α/β > 20/1. $[\alpha]_D^{25}$ =10.8 (*c* 1.7 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.14 (m, 20H, Ar*H*), 5.77 (dd, *J* = 7.8, 3.2 Hz, 1H, H-1^B), 5.41 (d, *J* = 5.0 Hz, 1H, H-1^A), 4.85 (d, *J* = 11.4 Hz, 1H, C*H*Ph), 4.81 (d, *J* = 11.9 Hz, 1H, C*H*Ph), 4.74 (d, *J* = 11.9 Hz, 1H, C*H*Ph), 4.64 (d, *J* = 12.0 Hz, 1H, C*H*Ph), 4.61 (d, *J* = 11.9 Hz, 1H, C*H*Ph), 4.49 (d, *J* = 11.4 Hz, 1H, C*H*Ph), 4.45-4.37 (m, 2H, C*H*Ph), 4.32 (d, *J* = 11.8 Hz, 1H, C*H*Ph), 4.25-3.90 (m, 10H, H-2^A, H-3^A, H-4^A,H-5^A, H-6^A, H-6'^{A}, H-2^B, H-3^B, H-4^B, H-5^B), 3.55-3.46 (m, 2H, H-6^B, H-6'^{B}), 1.42 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.17 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.2, 139.14, 139.05, 138.4, 128.5, 128.4, 128.29, 128.27, 128.21, 128.0, 127.9, 127.7, 127.52, 127.50, 127.4, 127.3, 109.1, 108.5, 96.5, 93.9 (d, *J* = 6.4 Hz), 78.7, 76.53, 76.45, 75.3, 75.0, 73.4, 73.0, 72.3, 71.0, 70.8 (d, *J* = 1.8 Hz), 69.9, 68.9, 67.9 (d, *J* = 8.2 Hz), 64.6 (d, *J* = 5.2 Hz), 26.3, 26.2, 25.2, 24.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -1.2; HR ESI-MS: $[M\text{-}Et_3NH^+\text{+}2H^+]^+$calcd for $[C_{46}H_{56}O_{14}P]^+$, 863.3402; found, 863.3404.

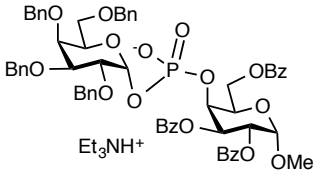
methyl 2,3,4,6-tetra-*O*-benzyl-*α*-D-galactopyranosyl-phosphoryl-(→4)-2,3,6-tri-*O*-benzyl-*α*-D-glucopyranoside triethylammonium salt (4h)



4h, prepared first via general procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 3/1), 53.8 mg, 93% yield); then procedure (B), quantitative yield, colorless oil, α/β > 20/1. $[\alpha]_D^{25}$ = 46.8 (*c* 2.5 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.10 (m, 35H, Ar*H*), 5.85 (dd, *J* = 8.0, 3.2 Hz, 1H, H-1^B), 5.08 (d, *J* = 10.9 Hz, 1H, C*H*Ph), 4.83-4.72 (m, 3H, 3 x C*H*Ph), 4.64 (d, *J* = 12.2 Hz, 1H, C*H*Ph), 4.58-4.39 (m, 8H, H-1^A, 7 x C*H*Ph), 4.33 (td, *J* = 13.3, 12.6, 7.6 Hz, 4H, 3 x C*H*Ph, H-4^A), 4.15 (t, *J* = 6.5 Hz, 1H, H-5^B), 4.05 (d, *J* = 10.5 Hz, 1H, H-6^B), 3.93 (dt, *J* = 10.0, 2.9 Hz, 1H, H-2^B), 3.86 (t, *J* = 9.3 Hz, 1H, H-3^A), 3.78 (dd, *J* = 10.1, 2.7 Hz, 1H, H-3^B), 3.76-3.62 (m, 3H, H-4^B, H-6'^{B}, H-5^A), 3.49-3.29 (m, 3H, H-2^A, H-6^A, H-6'^{A}), 3.26

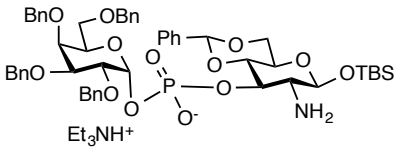
(s, 3H, OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 140.2, 139.4, 139.3, 139.0, 138.9, 138.6, 138.3, 128.5, 128.4, 128.33, 128.29, 128.6, 128.22, 128.15, 128.1, 128.05, 127.98, 127.8, 127.6, 127.5, 127.4, 127.31, 127.26, 127.1, 127.0, 98.0, 94.2 (d, *J* = 6.1 Hz), 81.5 (d, *J* = 3.1 Hz), 79.5, 78.7, 75.4, 75.3, 74.9, 74.6 (d, *J* = 6.4 Hz), 73.6, 73.4, 73.2, 73.1, 72.5, 70.7 (d, *J* = 3.4 Hz), 70.2, 70.0, 69.4, 55.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.4; HR ESI-MS: $[M\text{-}Et_3NH^+ + 2H^+]^+$ calcd for $[C_{62}H_{68}O_{14}P]^+$, 1067.4341; found, 1067.4341.

methyl 2,3,4,6-tetra-*O*-benzyl-*α*-D-galactopyranosyl-phosphoryl-(→4)-2,3,6-tri-*O*-benzoyl-*α*-D-galactopyranoside triethylammonium salt (4i)



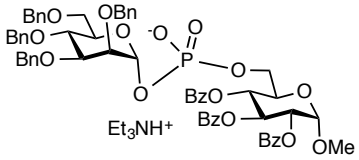
4i, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 3/1), 54 mg, 90% yield); then procedure (B), quantitative yield, colorless oil, 90% yield, α/β > 20/1. $[\alpha]_D^{25}$ = 85.6 (*c* 2.5 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.13 (m, 35H, Ar*H*), 5.79 (dd, *J* = 7.1, 3.4 Hz, 1H, H-1^B), 5.58 (dd, *J* = 10.8, 3.6 Hz, 1H, H-2^A), 5.46 (dd, *J* = 10.8, 3.1 Hz, 1H, H-3^A), 5.03 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.89 (dd, *J* = 14.9, 11.2 Hz, 2H, H-4^A, C*H*Ph), 4.79 – 4.73 (m, 2H, C*H*Ph, H-6^A), 4.67-4.58 (m, 4H, 3 x C*H*Ph, H-6'^{A}), 4.50 (d, *J* = 11.4 Hz, 1H, C*H*Ph), 4.41-4.35 (m, 2H, CH_2Ph), 4.31 (t, *J* = 6.7 Hz, 1H, H-5^B), 4.05 (dd, *J* = 10.0, 2.9 Hz, 1H, H-3^B), 3.98-3.94 (m, 2H, H-2^B, H-4^B), 3.57 (d, *J* = 8.8 Hz, 1H, H-5^A), 3.53-3.45 (m, 2H, H-6^B, H-6'^{B}), 3.27 (s, 3H, OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.4, 166.3, 166.2, 139.4, 139.1, 138.9, 138.5, 133.1, 132.8, 132.5, 131.2, 130.6, 130.2, 130.0, 129.9, 129.7, 128.7, 128.43, 128.37, 128.30, 128.27, 128.2, 128.0, 127.6, 127.5, 127.4, 127.2, 97.1, 94.6 (d, *J* = 6.0 Hz), 79.4, 76.6, 75.4, 75.0, 73.2, 73.1, 72.9, 71.4 (d, *J* = 5.5 Hz), 69.8 (d, *J* = 1.5 Hz), 69.7, 69.6, 69.2, 68.6 (d, *J* = 3.8 Hz), 65.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -1.3; HR ESI-MS: $[M\text{-}Et_3NH^+]^-$ calcd for $[C_{62}H_{60}O_{17}P]^-$, 1108.3719; found, 1108.3721.

***tert*-butyldimethylsilyl 2,3,4,6-tetra-*O*-benzyl-*α*-D-galactopyranosyl-phosphoryl-(→3)-2-amino-4,6-*O*-benzylidene-2-deoxy-*β*-D-glucopyranoside triethylammonium salt (4j)**



4j, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (4/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 4/1), 52.2 mg, 95% yield); then procedure (B), quantitative yield, colorless oil, α/β > 20/1. $[\alpha]_D^{25}$ = 22 (*c* 2.4 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.14 (m, 25H, Ar*H*), 5.78 (dd, *J* = 7.2, 3.3 Hz, 1H, H-1^B), 5.30 (s, 1H, C*H*(O)$_2$Ph), 4.77 (d, *J* = 11.5 Hz, 1H, C*H*Ph), 4.69 (d, *J* = 11.3 Hz, 1H, C*H*Ph), 4.56-4.47 (m, 3H, 2 x C*H*Ph, H-1^A), 4.43-4.27 (m, 4H, 4 x C*H*Ph), 4.15 (t, *J* = 6.7 Hz, 1H, H-3^A), 4.03 (dd, *J* = 10.4, 4.9 Hz, 1H, H-6^B), 3.91 (dt, *J* = 10.0, 3.0 Hz, 1H, H-2^B), 3.80 (d, *J* = 10.2 Hz, 1H, H-3^B), 3.72-3.65 (m, 1H, H-4^B), 3.51-3.37 (m, 5H, H-4^A, H-5^A, H-6'^{B}, H-6^A, H-6'^{A}), 3.29-3.22 (m, 1H, H-5^B), 2.74-2.67 (m, 1H, H-2^A), 0.78 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.1, 138.73, 138.66, 138.0, 137.8, 128.9, 128.5, 128.3, 128.22, 128.16, 128.13, 128.09, 128.04, 127.9, 127.8, 127.62, 127.56, 127.34, 127.28, 126.5, 101.3, 97.0 (bs), 94.1 (d, *J* = 6.5 Hz), 80.2 (d, *J* = 3.7 H), 78.6, 74.9, 74.8, 73.4, 72.8, 72.6, 70.1, 69.1, 68.5, 66.4, 59.7, 25.8, 1.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.1; HR ESI-MS: [M-Et_3NH^+]$^-$ calcd for $[C_{53}H_{65}NO_{13}PSi]^-$, 982.3968; found, 982.3966.

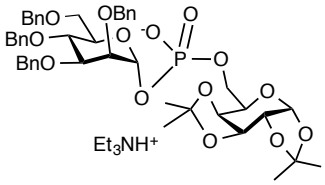
methyl 2,3,4,6-tetra-*O*-benzyl-*α*-D-mannopyranosyl-phosphoryl-(→6)-2,3,4-tri-*O*-benzoyl-*α*-D-glucopyranoside triethylammonium salt (4k)



4k, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/1/0.01) to give an intermediate product (R_f= 0.2 (Hexanes/EtOAc, 2/1), 54 mg, 90% yield); then procedure (B), quantitative yield, colorless oil, α/β > 20/1. $[\alpha]_D^{25}$ = 33.9 (*c* 3.6 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.11 (m, 35H, Ar*H*), 6.03 (dd, *J* = 10.2, 9.4 Hz, 1H, H-3^A), 5.67 (dd, *J* = 7.8, 2.0 Hz, 1H, H-1^B), 5.49-5.40 (m, 1H, H-4^A), 5.14 (dd, *J* = 10.2, 3.6 Hz, 1H, H-2^A), 5.03 (d, *J* = 3.6 Hz, 1H, H-1^A), 4.83 (d, *J* = 11.1 Hz, 1H, C*H*Ph), 4.68 (s, 2H, C*H*$_2$Ph), 4.55-4.45 (m, 4H, 4 x C*H*Ph), 4.35 (d, *J* = 11.9 Hz, 1H, C*H*Ph), 4.17 (ddd, *J* = 10.2, 5.9, 2.0 Hz, 1H, H-5^A), 4.04 (ddd, *J* = 11.5, 5.8, 2.1 Hz, 1H, H-6^A), 3.99-3.92 (m, 5H, H-2^B, H-3^B, H-4^B, H-5^B, H-6'^{A}), 3.66 (dd, *J* = 10.7, 3.5 Hz, 1H, H-6^B), 3.56 (dd, *J* = 10.9, 1.3 Hz,

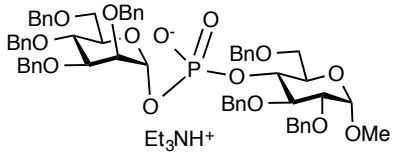
1H, H-6'^{B}), 3.29 (s, 3H, OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.9, 165.8, 165.3, 139.1, 138.9, 138.8, 138.7, 133.4, 133.3, 129.98, 129.88, 129.7, 129.5, 129.2, 128.5, 128.4, 128.34, 128.29, 128.25, 128.22, 128.0, 127.8, 127.7, 127.6, 127.44, 127.41, 127.3, 96.7, 94.3 (d, *J* = 5.5 Hz), 79.8, 75.7 (d, *J* = 7.2 Hz), 74.9, 74.8, 73.4, 72.9, 72.5, 72.2, 71.9, 71.0, 69.6, 69.4, 69.0 (d, *J* = 8.7 Hz), 64.3 (d, *J* = 4.9 Hz), 55.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.5; HR ESI-MS: $[M\text{-}Et_3NH^+\text{+}2H^+]^+$ calcd for $[C_{62}H_{62}O_{17}P]^+$, 1109.3719; found, 1109.3716.

2,3,4,6-tetra-*O*-benzyl-*α*-D-mannopyranosyl-phosphoryl-(→6)-1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose triethylammonium salt (4l)



4l, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 2/1), 46.7 mg, 98% yield); then procedure (B), quantitative yield, colorless oil, 98% yield, α/β > 20/1. $[\alpha]_D^{25}$ = -14.3 (*c* 2.8 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.10 (m, 20H, Ar*H*), 5.69 (d, *J* = 8.0 Hz, 1H, H-1^{B}), 5.40 (d, *J* = 5.0 Hz, 1H, H-1^{A}), 4.84 (d, *J* = 11.1 Hz, 1H, C*H*Ph), 4.76-4.64 (m, 2H, CH_2Ph), 4.58 (d, *J* = 12.0 Hz, 1H, C*H*Ph), 4.55-4.39 (m, 6H, 5 x C*H*Ph, H-4^{A}), 4.19 (dd, *J* = 5.2, 2.3 Hz, 1H, H-2^{A}), 4.14 (d, *J* = 8.0 Hz, 1H, H-3^{A}), 4.03-3.93 (m, 7H, H-2^{B}, H-3^{B}, H-4^{B}, H-5^{B}, H-5^{A}, H-6^{A}, H-6'^{A}), 3.71 (dd, *J* = 10.9, 3.3 Hz, 1H, H-6^{B}), 3.63 (d, *J* = 10.8 Hz, 1H, H-6'^{B}); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.1, 138.9, 138.9, 138.7, 128.33, 128.27, 128.0, 127.8, 127.6, 127.5, 127.40, 127.35, 109.2, 108.5, 96.4, 94.3 (d, *J* = 5.3 Hz), 79.8, 75.7 (d, *J* = 7.0 Hz), 74.9, 74.8, 73.4, 72.9, 72.5, 71.8, 71.1, 70.8, 70.7, 69.7, 67.9 (d, *J* = 8.9 Hz), 64.8 (d, *J* = 5.2 Hz), 26.3, 26.1, 25.1, 24.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.0; HR ESI-MS: $[M\text{-}Et_3NH^+\text{+}2H^+]^+$ calcd for $[C_{46}H_{56}O_{14}P]^+$, 863.3402; found, 863.3406.

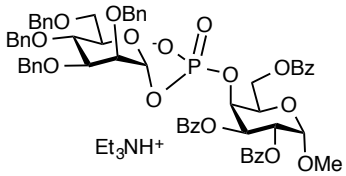
methyl 2,3,4,6-tetra-*O*-benzyl-*α*-D-mannopyranosyl-phosphoryl-(→4)-2,3,6-tri-*O*-benzyl-*α*-D-glucopyranoside triethylammonium salt (4m)



4m, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/1/0.01) to give an intermediate product (R_f = 0.2

(Hexanes/EtOAc, 2/1), 52.0 mg, 90% yield); then procedure (B), quantitative yield, colorless oil, α/β > 20/1. $[\alpha]_D^{25}$ = 19.3 (*c* 2.2 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.10 (m, 35H, Ar*H*), 5.72 (dd, *J* = 7.6, 1.7 Hz, 1H, H-1^B), 5.08 (d, *J* = 11.0 Hz, 1H, C*H*Ph), 4.79 (d, *J* = 11.1 Hz, 1H, C*H*Ph), 4.73 (d, *J* = 11.1 Hz, 1H, C*H*Ph), 4.69-4.61 (m, 3H, 3 x C*H*Ph), 4.58-4.36 (m, 7H, H-1^A, 6 x C*H*Ph), 4.34-4.17 (m, 2H, CH_2Ph), 4.13-3.95 (m, 2H, H-3^B, H-4^A), 3.95-3.80 (m, 5H, H-2^B, H-3^A, H-5^B, H-6^B, H-6'^{B}), 3.74 (ddd, *J* = 10.1, 6.3, 1.8 Hz, 1H, H-5^A), 3.68-3.62 (m, 2H, H-6^A, H-6'^{A}), 3.59 (dd, *J* = 10.8, 1.9 Hz, 1H, H-4^B), 3.36-3.26 (m, 4H, H-2^A, OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.9, 139.0, 138.8, 138.6, 138.50, 138.45, 128.43, 128.36, 128.35, 128.28, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.52, 127.47, 127.42, 127.35, 127.20, 127.16, 98.0, 94.6, 81.4, 80.0, 79.3, 75.5, 75.0, 74.9, 74.8, 73.52, 73.46, 73.43, 72.8, 72.4, 71.8, 70.8, 70.0, 69.8, 55.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -3.3; HR ESI-MS: $[M\text{-}Et_3NH^+]^-$ calcd for $[C_{62}H_{66}O_{14}P]^-$, 1065.4196; found, 1065.4193.

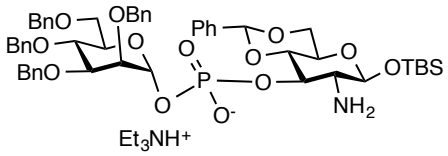
methyl 2,3,4,6-tetra-*O*-benzyl-*α*-D-mannopyranosyl-phosphoryl-(→4)-2,3,6-tri-*O*-benzoyl-*α*-D-galactopyranoside triethylammonium salt (4n)



4n, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 4/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 3/1), 55.7 mg, 93% yield); then procedure (B), quantitative yield, colorless oil, α/β > 20/1. $[\alpha]_D^{25}$ = 56.4 (*c* 2.3 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04-7.11 (m, 35H, Ar*H*), 5.79-5.67 (m, 2H, H-1^B, H-3^A), 5.56 (dd, *J* = 10.7, 3.6 Hz, 1H, H-2^A), 5.12 (d, *J* = 3.6 Hz, 1H, H-1^A), 5.03 (dd, *J* = 10.2, 3.1 Hz, 1H, H-4^A), 4.81 (d, *J* = 11.1 Hz, 1H, C*H*Ph), 4.67-4.51 (m, 5H, H-6^A, H-6'^{A}, 3 x C*H*Ph), 4.46 (d, *J* = 11.5 Hz, 2H, 2 x C*H*Ph), 4.34 (t, *J* = 12.6 Hz, 2H, 2 x C*H*Ph), 4.24 (dd, *J* = 8.2, 4.2 Hz, 1H, H-5^A), 3.99 (s, 2H, H-2^B, H-5^B), 3.94-3.91 (m, 2H, H-3^B, H-4^B), 3.70 (dd, *J* = 10.9, 4.7 Hz, 1H, H-6^B), 3.62 (d, *J* = 10.7 Hz, 1H, H-6'^{B}), 3.33 (s, 3H, OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.42, 166.36, 166.1, 139.2, 139.0, 138.7, 133.2, 133.1, 132.8, 130.4, 130.3, 130.2, 130.0, 129.8, 129.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 127.4, 127.3, 127.2, 97.5, 94.8 (d, *J* = 5.0 Hz), 79.8, 75.8 (d, *J* = 7.9 Hz), 74.8, 73.4, 72.84, 72.77, 72.3 (d, *J* = 5.3 Hz), 71.6, 69.9, 69.7, 69.5 (d, *J* = 2.7 Hz), 68.6 (d, *J* = 3.2

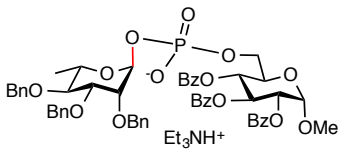
Hz), 64.7, 55.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.9; HR ESI-MS: $[M\text{-}Et_3NH^+\text{+}2H^+]^+$ calcd for $[C_{62}H_{62}O_{17}P]^+$, 1109.3719; found, 1109.3714.

***tert*-butyldimethylsilyl 2,3,4,6-tetra-*O*-benzyl-*α*-D-mannopyranosyl-phosphoryl-(→3)-2-amino-4,6-*O*-benzylidene-2-deoxy-*β*-D-glucopyranoside triethylammonium salt (4o)**



4o, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (4/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 4/1), 52.8 mg, 96% yield); then procedure (B), quantitative yield, colorless oil, α/β > 20/1. $[\alpha]_D^{25}$ = -9.5 (*c* 2.0 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.01 (m, 25H, Ar*H*), 5.57 (dd, *J* = 7.2, 1.6 Hz, 1H, H-1^B), 5.32 (s, 1H, C*H*Ph), 4.69 (d, *J* = 11.2 Hz, 1H, C*H*Ph), 4.54 (s, 2H, CH_2Ph), 4.49-4.43 (m, 2H, H-1^A, C*H*Ph), 4.38-4.16 (m, 6H, 5 x C*H*Ph, H-3^A), 4.06 (dd, *J* = 10.4, 4.9 Hz, 1H, H-6^A), 3.98-3.91 (m, 1H, H-5^B), 3.79-3.77 (m, 3H, H-2^B, H-3^B, H-4^B), 3.62-3.48 (m, 4H, H-4^A, H-6^B, H-6'^{B}, H-6'^{A}), 3.23-3.14 (m, 2H, H-2^A, H-5^A), 0.78 (s, 9H), -0.00 (s, 3H), -0.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.2, 139.0, 138.8, 138.7, 137.7, 129.0, 128.4, 128.29, 128.25, 128.2, 128.1, 127.9, 127.8, 127.6, 127.53, 127.50, 127.43, 127.38, 127.3, 126.8, 101.7, 97.7, 94.7 (d, *J* = 5.9 Hz), 80.14 (d, *J* = 2.9 Hz), 80.09, 75.4 (d, *J* = 4.7 Hz), 75.3, 75.1, 74.8, 73.5, 72.7, 72.5, 71.9, 70.0, 69.0 (d, *J* = 3.0 Hz), 68.6, 66.6, 25.7, -4.3, -5.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -3.3; HR ESI-MS: $[M\text{-}Et_3NH^+\text{+}2H^+]^+$ calcd for $[C_{53}H_{67}NO_{13}PSi]^+$, 984.4110; found, 984.4114.

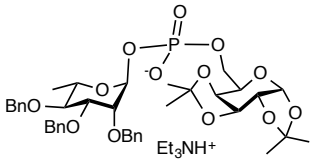
methyl 2,3,4-tri-*O*-benzyl-*α*-L-rhamnopyranosyl-phosphoryl-(→6)-2,3,4-tri-*O*-benzoyl-*α*-D-glucopyranoside triethylammonium salt (4p)



4p, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 2/1), 48.6 mg, 89% yield); then procedure (B), quantitative yield, colorless oil, α/β > 20/1. $[\alpha]_D^{25}$ = 27.0 (*c* 2.1 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.15 (m, 30H, Ar*H*), 6.04 (t, *J* = 9.9 Hz, 1H, H-3^A), 5.61-5.50 (m, 2H, H-4^A, H-1^B), 5.16 (dd, *J* = 10.2, 3.5 Hz, 1H, H-2^A), 5.06 (d, *J* = 3.5 Hz, 1H, H-1^A), 4.86 (d, *J* =

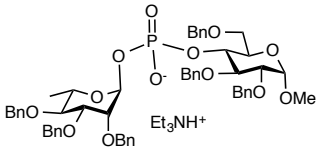
11.2 Hz, 1H, C*H*Ph), 4.76-4.62 (m, 2H, CH_2Ph), 4.54 (d, *J* = 11.2 Hz, 1H, C*H*Ph), 4.49 (s, 2H, CH_2Ph), 4.22-4.14 (m, 1H, H-5^A), 4.09-4.04 (m, 1H, H-6^A), 3.97 (dt, *J* = 11.1, 5.2 Hz, 1H, H-6'^{A}), 3.93-3.80 (m, 3H, H-2^B, H-3^B, H-5^B), 3.51 (t, *J* = 9.7 Hz, 1H, H-4^B), 3.35 (s, 3H, OCH_3), 1.09 (d, *J* = 6.2 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.0, 165.9, 165.3, 139.1, 139.0, 138.8, 133.4, 133.2, 133.1, 130.05, 130.01, 129.8, 129.6, 129.5, 129.3, 128.5, 128.4, 128.3, 128.0, 127.9, 127.6, 127.49, 127.46, 127.4, 96.9, 94.2 (d, *J* = 5.7 Hz), 80.4, 79.7, 75.8 (d, *J* = 7.7 Hz), 75.1, 72.5, 72.3, 71.9, 71.1, 69.2, 69.1, 69.0, 68.9, 64.1 (d, *J* = 5.4 Hz), 55.7, 18.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.4; HR ESI-MS: [M-Et_3NH^+]$^-$ calcd for [$C_{55}H_{54}O_{16}P$]$^-$, 1001.3155; found, 1001.3160.

2,3,4-tri-*O*-benzyl-*α*-L-rhamnopyranosyl-phosphoryl-(→6)-1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose triethylammonium salt (4q)



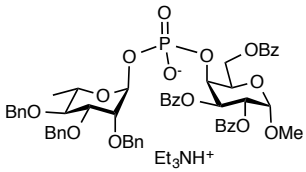
4q, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 2/1), 38.6 mg, 91% yield); then procedure (B), quantitative yield, colorless oil, 91% yield, α/β > 20/1. $[\alpha]_D^{25}$ = -14.8 (*c* 1.9 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-71.6 (m, 15H, Ar*H*), 5.59 (dd, *J* = 7.8, 1.7 Hz, 1H, H-1^B), 5.41 (d, *J* = 5.0 Hz, 1H, H-1^A), 4.88 (d, *J* = 11.1 Hz, 1H, C*H*Ph), 4.72-4.65 (m, 2H, CH_2Ph), 4.57-4.48 (m, 4H, 3 x C*H*Ph, H-4^A), 4.27-4.16 (m, 2H, H-2^A, H-3^A), 4.05-3.81 (m, 6H, H-2^B, H-3^B, H-5^B, H-5^A, H-6^A, H-6'^{A}), 3.62-3.49 (m, 1H, H-4^B), 1.42 (s, 3H), 1.32 (s, 3H, Me), 1.24 (s, 3H, Me), 1.23 (s, 3H, Me), 1.22 (m, 6H, 2 x Me), 1.20 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.1, 139.0, 138.8, 128.4, 128.3, 128.0, 127.9, 127.6, 127.5, 127.4, 109.3, 108.5, 96.5, 94.5 (d, *J* = 5.6 Hz), 80.4, 79.8, 75.9 (d, *J* = 8.2 Hz), 75.2, 72.7, 71.9, 71.0, 70.8, 70.75, 70.73, 69.0, 67.7 (d, *J* = 9.5 Hz), 64.5 (d, J = 5.2 Hz), 26.3, 26.1, 25.1, 24.5, 18.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.1; HR ESI-MS: [M-Et_3NH^++Na^++H^+]$^+$calcd for [$C_{39}H_{49}NaO_{13}P$]$^+$, 779.2803; found, 779.2798.

methyl 2,3,4-tri-*O*-benzyl-*α*-L-rhamnopyranosyl-phosphoryl-(→4)-2,3,6-tri-*O*-benzyl-*α*-D-glucopyranoside triethylammonium salt (4r)



4r, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 2/1), 46.2 mg, 88% yield); then procedure (B), quantitative yield, colorless oil, α/β > 20/1. $[\alpha]_D^{25}$ = 9.9 (*c* 3.3 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.10 (m, 30H, Ar*H*), 5.61 (dd, *J* = 7.1, 2.0 Hz, 1H, H-1^B), 5.06 (d, *J* = 11.0 Hz, 1H, C*H*Ph), 4.89-4.81 (m, 1H, C*H*Ph), 4.71 (d, *J* = 11.1 Hz, 1H, C*H*Ph), 4.69- 4.64 (m, 1H, C*H*Ph), 4.62 (s, 2H, CH_2Ph), 4.57-4.47 (m, 5H, H-1^A, 4 x C*H*Ph), 4.41-4.34 (m, 2H, CH_2Ph), 4.19-4.12 (m, 1H, H-4^B), 4.00-3.90 (m, 3H, H-2^B, H-3^B, H-5^B, H-6^A), 3.88-3.78 (m, 3H, H-3^A, H-5^A), 3.71 (dd, *J* = 10.9, 6.4 Hz, 1H, H-6'^{A}), 3.60-3.48 (m, 1H, H-4^A), 3.46-3.38 (m, 1H, H-2^A), 3.33 (s, 3H, OMe), 1.19 (d, *J* = 6.3 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.7, 139.0, 138.9, 138.71, 138.68, 138.3, 128.3, 128.29, 128.18, 128.1, 128.07, 128.04, 128.01, 127.72, 127.68, 127.3, 127.2, 127.1, 127.0, 97.8, 94.5 (d, *J* = 5.3 Hz), 81.1 (d, *J* = 3.1 Hz), 80.3 , 79.8, 79.0, 75.7 (d, *J* = 8.1 Hz), 75.0, 74.9, 74.5 (d, *J* = 6.4 Hz), 73.3, 72.5, 71.7, 70.6 (d, *J* = 3.4 Hz), 69.9, 68.9, 55.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -3.6; HR ESI-MS: $[M\text{-}Et_3NH^+ + H^+ + Na^+]^+$ calcd for $[C_{55}H_{61}NaO_{13}P]^-$, 983.3742; found, 983.3749.

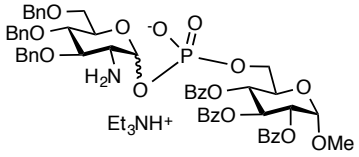
methyl 2,3,4-tri-*O*-benzyl-*α*-L-rhamnopyranosyl-phosphoryl-(→4)-2,3,6-tri-*O*-benzoyl-*α*-D-galactopyranoside triethylammonium salt (4s)



4s, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (4/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 4/1), 44.3 mg, 81% yield); then procedure (B), quantitative yield, colorless oil, α/β > 20/1. $[\alpha]_D^{25}$ = 61.5 (*c* 1.8 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02-7.12 (m, 30H, Ar*H*), 5.72-5.65 (m, 1H, H-3^A), 5.62 (dd, *J* = 7.2, 1.9 Hz, 1H, H-1^B), 5.57 (dd, *J* = 10.8, 3.6 Hz, 1H, H-2^A), 5.14 (d, *J* = 3.6 Hz, 1H, H-1^A), 5.03 (dd, *J* = 10.2, 3.1 Hz, 1H, H-4^A), 4.84 (d, *J* = 11.2 Hz, 1H, C*H*Ph), 4.71-4.53 (m, 5H, 3 x CHPh, H-6^A, H-6'^{A}), 4.50-4.38 (m, 2H, CH_2Ph), 4.31 (dd, *J* = 8.3, 3.9 Hz, 1H, H-5^A), 3.98 (bs, 1H, H-2^B), 3.93 (ddd, *J* = 12.4, 7.8, 4.8 Hz, 1H, H-5^B), 3.86 (dd, *J* = 9.5, 3.1 Hz, 1H, H-3^B), 3.52 (t, *J* = 9.5 Hz, 1H, H-4^B), 3.31 (s, 3H, OMe), 1.18 (d, *J* = 6.1 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.4, 166.3, 166.1, 139.2, 139.1, 138.9, 133.2, 133.0, 132.8, 130.34, 130.29, 130.0, 129.8, 129.7, 128.5, 128.4, 128.34, 128.29, 128.25, 128.0,

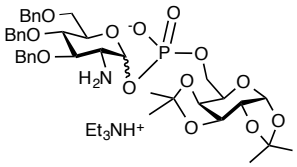
127.8, 127.6, 127.40, 127.36, 127.3, 97.4, 95.0 (d, *J* = 5.4 Hz), 80.4, 79.9, 76.0 (d, *J* = 8.4 Hz), 75.0, 72.9, 72.4 (d, *J* = 5.3 Hz), 71.8, 69.8 (d, *J* = 2.8 Hz), 69.6, 69.1, 68.6 (bs), 64.8, 55.3, 18.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.9; HR ESI-MS: [M-Et_3NH^++Na^++H^+]$^+$calcd for $[C_{55}H_{55}NaO_{16}P]^+$, 1025.3120; found, 1025.3112.

methyl 2-amino-3,4,6-tri-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl-phosphoryl-(→6)-2,3,4-tri-*O*-benzoyl-*α*-D-glucopyranoside triethylammonium salt (4t)



4t, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 2/1), 56.1 mg, 99% yield, α/β = 7.6/1); then procedure (B), quantitative yield, colorless oil. $[\alpha]_D^{25}$ = 66.6 (*c* 2.2 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.15 (m, 30H, Ar*H*), 6.09 (t, *J* = 9.8 Hz, 1H, H-3^A), 5.70 (dd, *J* = 7.5, 3.2 Hz, 1H, H-1^B), 5.51 (t, *J* = 9.8 Hz, 1H, H-4^A), 5.18 (dd, *J* = 10.2, 3.6 Hz, 1H, H-2^A), 5.09 (d, *J* = 3.7 Hz, 1H, H-1^A), 4.88 (d, *J* = 11.2 Hz, 1H, C*H*Ph), 4.81-4.69 (m, 2H, 2 x C*H*Ph), 4.54 (d, *J* = 11.7 Hz, 2H, 2 x C*H*Ph), 4.41 (d, *J* = 12.1 Hz, 1H, C*H*Ph), 4.25-3.98 (m, 4H, H-5^A, H-5^B, H-6^B, H-6'^{B}), 3.79 (t, *J* = 9.5 Hz, 1H, H-3^B), 3.73-3.53 (m, 3H, H-4^B, H-6^A, H-6'^{A}), 3.35 (s, 3H), 2.95-2.91 (m, 1H, H-2^B); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.79, 165.77, 165.2, 138.6, 138.4, 138.2, 133.3, 133.2, 133.0, 129.92, 129.88, 129.81, 129.6, 129.4, 129.20, 129.16, 128.4, 128.34, 128.28, 128.23, 128.19, 128.0, 127.90, 127.86, 127.84, 127.7, 127.6, 127.6, 127.5, 96.7, 95.1, 78.4, 75.4, 74.5, 73.4, 72.1, 72.0, 70.9, 69.3, 68.9, 68.8, 68.4, 64.2, 55.6, 55.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.2; HR ESI-MS: [M-Et_3NH^+]$^-$ calcd for $[C_{55}H_{55}NO_{16}P]^-$, 1106.3264; found, 1106.3259.

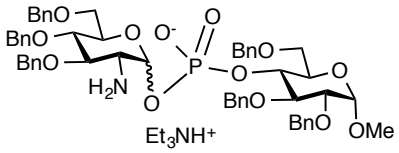
2-amino-3,4,6-tri-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl-phosphoryl-(→6)-1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose triethylammonium salt (4u)



4u, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 2/1), 44 mg, 99% yield, α/β = 8.4/1); then procedure (B), quantitative yield, colorless oil. $[\alpha]_D^{25}$ = 19.0 (*c* 1.8 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-

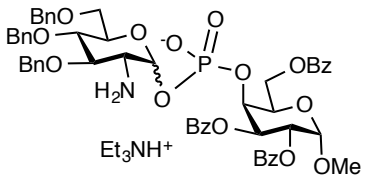
7.06 (m, 15H, Ar*H*), 5.68 (dd, *J* = 7.7, 3.3 Hz, 1H, H-1^{B}), 5.35 (d, *J* = 5.0 Hz, 1H, H-1^{A}), 4.85-4.73 (m, 2H, C*H*$_2$Ph), 4.67 (d, *J* = 11.2 Hz, 1H, C*H*Ph), 4.51 (d, *J* = 12.1 Hz, 1H, C*H*Ph), 4.47 (d, *J* = 11.2 Hz, 1H, C*H*Ph), 4.41 (dd, *J* = 7.9, 2.4 Hz, 1H, H-3^{A}), 4.36 (d, *J* = 12.1 Hz, 1H, C*H*Ph), 4.15 (dd, *J* = 5.0, 2.3 Hz, 1H, H-2^{A}), 4.06 (dd, *J* = 7.9, 1.6 Hz, 1H, H-4^{A}), 3.99-3.89 (m, 4H, H-5^{B}, H-5^{A}, H-6^{A}, H-6'^{A}), 3.84 (t, *J* = 9.6 Hz, 1H, H-3^{B}), 3.71-3.65 (m, 1H, H-6^{B}), 3.65-3.60 (m, 1H, H-4^{B}), 3.56 (dd, *J* = 11.1, 1.9 Hz, 1H, H-6'^{B}), 3.07-3.00 (m, 1H, H-2^{B}), 1.38 (s, 3H, CH$_3$), 1.28 (s, 3H, CH$_3$), 1.18 (s, 3H, CH$_3$), 1.16 (s, 3H, CH$_3$); ^{13}C NMR (101 MHz, CDCl$_3$) δ = 137.4, 137.2, 137.1, 127.4, 127.3, 127.3, 127.0, 126.9, 126.6, 126.5, 108.1, 107.6, 95.2, 93.2 (bs), 79.1, 77.4, 74.3, 73.5, 72.4, 71.0, 69.8, 69.6, 69.5, 67.4, 66.4 (d, *J* = 8.8 Hz), 63.4 (d, *J* = 5.2 Hz), 53.9, 25.0, 24.9, 23.9, 23.3; ^{31}P NMR (162 MHz, CDCl$_3$) δ = -1.9; HR ESI-MS: [M-Et$_3$NH$^+$]$^-$ calcd for [C$_{39}$H$_{49}$NO$_{13}$P]$^-$, 770.2947; found, 770.2945.

methyl 2-amino-3,4,6-tri-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl-phosphoryl-(→4)-2,3,6-tri-*O*-benzyl-*α*-D-glucopyranoside triethylammonium salt (4v)



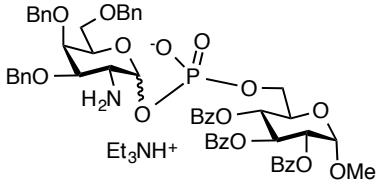
4v, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et$_3$N (5/1/0.01 to 3/1/0.01) to give an intermediate product (R$_f$ = 0.2 (Hexanes/EtOAc, 2/1), 52.9 mg, 97% yield, α/β = 6.6/1); then procedure (B), quantitative yield, colorless oil. [α]$_D^{25}$ = 34.2 (*c* 2.4 CHCl$_3$); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41-7.02 (m, 30H, Ar*H*), 5.71 (dd, *J* = 6.7, 3.2 Hz, 1H, H-1^{B}), 5.02 (d, *J* = 11.1 Hz, 1H, C*H*Ph), 4.74 (d, *J* = 11.2 Hz, 1H, C*H*Ph), 4.68-4.40 (m, 9H, 8 x C*H*Ph, H-1^{A}), 4.32 (d, *J* = 12.1 Hz, 1H, C*H*Ph), 4.26-4.11 (m, 2H, C*H*Ph, H-4^{A}), 4.01 (d, *J* = 9.4 Hz, 1H, H-5^{B}), 3.94 (dd, *J* = 11.0, 1.8 Hz, 1H, H-6^{A}), 3.84 (t, *J* = 9.3 Hz, 1H, H-3^{A}), 3.80-3.73 (m, 1H, H-5^{A}), 3.71-3.59 (m, 2H, H-6'^{A}, H-6^{B}), 3.59-3.47 (m, 3H, H-3^{B}, H-4^{B}, H-6'^{B}), 3.39 (dd, *J* = 9.7, 3.7 Hz, 1H, H-2^{A}), 3.30 (s, 3H, OMe), 2.82-2.78 (m, 1H, H-2^{B}); ^{13}C NMR (101 MHz, CDCl$_3$) δ = 138.4, 137.8, 137.4, 137.2, 136.9, 127.4, 127.3, 127.25, 127.19, 127.1, 127.0, 126.8, 126.63, 126.58, 126.52, 126.47, 126.3, 126.24, 126.18, 96.7, 93.8 (bs), 80.2, 80.0, 78.2, 77.3, 74.4, 74.1, 73.4, 73.4, 72.4, 72.3, 72.2, 70.9, 69.6 (bs), 68.7 (bs), 67.3 (bs), 54.4, 54.1; ^{31}P NMR (162 MHz, CDCl$_3$) δ = -2.5; HR ESI-MS: [M-Et$_3$NH$^+$]$^-$ calcd for [C$_{55}$H$_{61}$NO$_{13}$P]$^-$, 974.3886; found, 974.3882.

methyl 2-amino-3,4,6-tri-*O*-benzyl-2-deoxy-*α*-D-glucopyranosyl-phosphoryl-(→4)-2,3,6-tri-*O*-benzoyl-*α*-D-galactopyranoside triethylammonium salt (4w)



4w, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (4/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 4/1), 56.1 mg, 99% yield, α/β = 3/1); then procedure (B), quantitative yield, colorless oil. $[\alpha]_D^{25}$ = 82.1 (*c* 3.5 $CHCl_3$); α anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-7.13 (m, 30H, Ar*H*), 5.84-5.69 (m, 2H, H-1^B, H-3^A), 5.57 (dd, *J* = 10.7, 3.6 Hz, 1H, H-2^A), 5.16 (d, *J* = 3.7 Hz, 1H, H-1^A), 5.00 (dd, *J* = 10.0, 3.1 Hz, 1H, H-4^A), 4.73 (s, 2H, C*H*$_2$Ph), 4.70-4.49 (m, 5H, H-6^A, H-6'^{A}, 3 x C*H*Ph), 4.42 (d, *J* = 11.8 Hz, 1H, C*H*Ph), 4.28-4.20 (m, 1H, H-5^A), 4.08 (d, *J* = 10.1 Hz, 1H, H-5^B), 3.85-3.59 (m, 4H, H-3^B,H-4^B, H-6^B, H-6'^{B}), 3.41 (s, 3H, OMe), 2.87-2.85 (m, 1H, H-2^B); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.7, 166.3, 166.0, 138.6, 138.4, 138.3, 133.2, 133.1, 133.0, 130.3, 130.0, 129.9, 129.8, 129.7, 129.6, 128.45, 128.41, 128.35, 128.30, 128.26, 128.1, 127.9, 127.8, 127.59, 127.57, 127.50, 97.3, 94.7, 80.3, 78.5, 75.3, 74.4, 73.5, 72.2, 72.1, 69.6, 69.3, 68.8, 68.2, 65.2, 55.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.3; HR ESI-MS: [M-Et_3NH^+]$^-$ calcd for [$C_{55}H_{55}NO_{16}P$]$^-$, 1016.3264; found, 1016.3285.

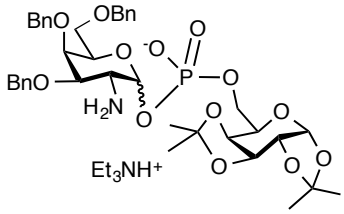
methyl 2-amino-3,4,6-tri-*O*-benzyl-2-deoxy-*α*-D-galactopyranosyl-phosphoryl-(→6)-2,3,4-tri-*O*-benzoyl-*α*-D-glucopyranoside triethylammonium salt (4x)



4x, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 2/1), 56.1 mg, 99% yield, α/β = 9.7/1); then procedure (B), quantitative yield, colorless oil. $[\alpha]_D^{25}$ = 59.1 (*c* 1.9 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.14 (m, 30H, Ar*H*), 5.98 (t, *J* = 9.8 Hz, 1H, H-2^A), 5.69 (bs, 1H, H-1^B), 5.39 (t, *J* = 10 Hz, 1H, H-3^A), 5.07 (d, *J* = 10.0 Hz, 1H, H-1^A), 4.97 (s, 1H, H-4^B), 4.66 (d, *J* = 11.3 Hz, 1H, C*H*Ph), 4.45-4.27 (m, 5H, C*H*Ph, C*H*$_2$Ph x 2), 4.07-3.98 (m, 5H, H-5^B, H-4^A, H-5^A, H-6^A, H-6'^{A}), 3.78 (s, 1H, H-3^B), 3.49-3.43 (m, 3H, H-2^B, H-6^B, H-6'^{B}), 3.20 (s, 3H, C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.9, 165.3, 138.6, 138.3, 138.0, 133.4, 133.3, 133.0, 130.1, 130.0, 129.8, 129.6, 129.4, 129.3, 128.6, 128.5, 128.5, 128.3, 128.2, 128.0, 127.8, 127.7, 96.7, 93.9 (bs), 74.7, 73.5, 72.3, 71.9, 71.1, 70.6, 69.5, 68.9

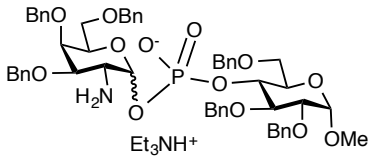
(d, J = 7.9 Hz), 68.5, 64.5 (bs), 55.6, 45.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.5; HR ESI-MS: [M-Et_3NH^+]$^-$ calcd for [$C_{55}H_{55}NO_{16}P$]$^-$, 1016.3264; found, 1016.3264.

2-amino-3,4,6-tri-*O*-benzyl-2-deoxy-*α*-D-galactopyranosyl-phosphoryl-(→6)-1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose triethylammonium salt (4y)



4y, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 2/1), 44 mg, 99% yield, α/β = 7.9/1); then procedure (B), quantitative yield, colorless oil. $[\alpha]_D^{25}$ = 13.5 (*c* 2.6 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.15 (m, 15H, Ar*H*), 5.68 (bs, 1H, H-1^B), 5.32 (d, J = 5.0 Hz, 1H, H-1^A), 4.68 (d, J = 11.1 Hz, 2H, 2 x C*H*Ph), 4.58 (d, J = 11.0 Hz, 1H, C*H*Ph), 4.42-4.28 (m, 4H, 3 x C*H*Ph, H-3^A), 4.18 (td, J = 6.3, 3.3 Hz, 1H, H-5^A), 4.08 (ddd, J = 15.2, 6.5, 2.5 Hz, 2H, H-2^A, H-4^A), 4.02-3.82 (m, 5H, H-3^B, H-4^B, H-5^B, H-6^A, H-6'^{A}), 3.61-3.39 (m, 3H, H-2^B, H-6^B, H-6'^{B}), 1.34 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.12 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.8, 138.3, 138.1, 128.55, 128.46, 128.41, 128.3, 127.9, 127.84, 127.79, 127.68, 127.5, 109.2, 108.7, 96.3, 93.6, 74.7, 73.4, 72.5 (bs), 72.0 (bs), 70.9, 70.7, 70.3, 68.4, 67.4 (d, J = 7.6 Hz), 64.6 (bs), 51.0, 26.2, 26.1, 25.0, 24.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.0; HR ESI-MS: [M-Et_3NH^+]$^-$ calcd for [$C_{39}H_{49}NO_{13}P$]$^-$, 770.2947; found, 770.2947.

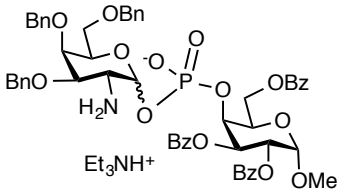
methyl 2-amino-3,4,6-tri-*O*-benzyl-2-deoxy-*α*-D-galactopyranosyl-phosphoryl-(→4)-2,3,6-tri-*O*-benzyl-*α*-D-glucopyranoside triethylammonium salt (4z)



4z, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (5/1/0.01 to 3/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 2/1), 54 mg, 99% yield, α/β = 11/1); then procedure (B), quantitative yield, colorless oil. $[\alpha]_D^{25}$ = 39.7 (*c* 2.3 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (dd, J = 6.8, 3.2 Hz, 1H, H-1^B), 4.97 (d, J = 10.8 Hz, 1H, C*H*Ph), 4.72 (d, J = 10.9 Hz, 1H, C*H*Ph), 4.58 (d, J = 11.8 Hz, 2H, 2 x C*H*Ph), 4.53-4.37 (m, 4H, H-1^A, 3 x C*H*Ph), 4.37-4.16 (m, 6H, 5 x C*H*Ph, H-4^A), 4.11 (dd, J = 8.3, 5.6 Hz, 1H, H-5^B), 3.85 (t, J =

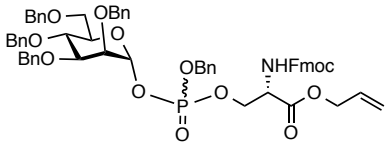
9.3 Hz, 2H, H-5^{A}, H-6^{A}), 3.80-3.65 (m, 3H, H-3^{A}, H-4^{B}, H-6'^{B}), 3.64-3.56 (m, 1H, H-3^{B}), 3.46 (t, *J* = 8.6 Hz, 1H, H-6^{B}), 3.39-3.26 (m, 6H, H-2^{B}, H-6'^{A}, H-2^{A}, OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 139.5, 138.9, 138.4, 138.3, 137.9, 137.7, 128.4, 128.34, 128.26, 128.23, 128.19, 128.0, 127.9, 127.81, 127.78, 127.73, 127.66, 127.55, 127.4, 127.2, 97.8, 93.9 (bs), 81.0, 79.4, 77.2, 75.1, 74.6, 74.4 (d, *J* = 7.0 Hz), 73.3, 73.2, 72.0, 71.5, 70.6 (d, *J* = 3.9 Hz), 70.3, 69.5, 68.1, 55.1, 51.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.3; HR ESI-MS: [M-Et_3NH^+]$^-$ calcd for [$C_{55}H_{61}NO_{13}P$]$^-$, 974.3886; found, 974.3882.

methyl 2-amino-3,4,6-tri-*O*-benzyl-2-deoxy-*α*-D-galactopyranosyl-phosphoryl-(→4)-2,3,6-tri-*O*-benzoyl-*α*-D-galactopyranoside triethylammonium salt (4za)



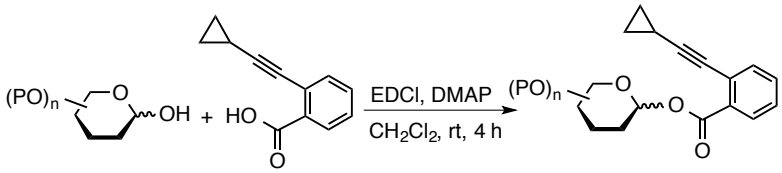
4za, prepared first via procedure (A), purified by flash chromatography by eluting with Hexanes/EtOAc/Et_3N (4/1/0.01) to give an intermediate product (R_f = 0.2 (Hexanes/EtOAc, 4/1), 56.0 mg, 99% yield, α/β = 8/1); then procedure (B), quantitative yield, colorless oil. $[\alpha]_D^{25}$ = 78.4 (*c* 2.4 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12-7.22 (m, 30H, Ar*H*), 5.85-5.71 (m, 2H, H-1^{B}, H-3^{A}), 5.59 (dd, *J* = 10.6, 3.6 Hz, 1H, H-2^{A}), 5.12 (d, *J* = 3.6 Hz, 1H, H-1^{A}), 5.04 (dd, *J* = 10.1, 3.0 Hz, 1H, H-4^{A}), 4.81 (dd, *J* = 11.8, 8.8 Hz, 1H, H-6^{A}), 4.76 (d, *J* = 11.4 Hz, 1H, C*H*Ph), 4.62-4.42 (m, 6H, 5 x C*H*Ph, H-6'^{A}), 4.31 (t, *J* = 6.8 Hz, 1H, H-5^{B}), 4.17 (d, *J* = 7.9 Hz, 1H, H-5^{A}), 3.88 (bs, 1H, H-4^{B}), 3.75 (d, *J* = 10.5 Hz, 1H, H-3^{B}), 3.67 (dd, *J* = 9.1, 6.0 Hz, 1H, H-6^{B}), 3.59 (t, *J* = 8.4 Hz, 1H, H-6^{B}), 3.45 (dd, *J* = 8.3, 4.9 Hz, 1H, H-2^{B}), 3.33 (s, 3H, OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.7, 166.04, 166.00, 138.8, 138.5, 138.2, 133.15, 133.09, 130.28, 130.26, 130.21, 130.0, 129.8, 129.7, 128.5, 128.42, 128.38, 128.29, 128.1, 128.0, 127.7, 127.6, 127.5, 97.3, 95.4, 74.7, 73.4, 72.6, 72.4 (d, *J* = 4.9 Hz), 71.7, 70.5, 69.9, 69.4 (d, *J* = 3.9 Hz), 69.1, 68.3, 65.2, 55.3, 51.4 (d, *J* = 6.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.3; HR ESI-MS: [M-Et_3NH^+]$^-$ calcd for [$C_{55}H_{55}NO_{16}P$]$^-$, 1106.3264; found, 1106.3259.

2,3,4,6-tetra-*O*-benzyl-*α*-D-mannopyranosyl-phosphoryl-(→3)-*N*-(9-fluorenylmethoxycarbonyl)-L-serine allyl ester (4zb)



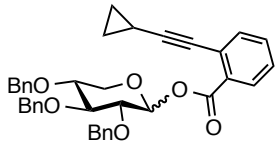
4zb prepared via procedure (A), colorless oil, 31.8 mg, 60% yield, α/β > 8/1, R_f= 0.2 (Hexanes/EtOAc, 3/2). Compound **4zb** was characterized without hydrogenolysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.13 (m, 76H, Ar*H*), 6.16 (d, *J* = 8.5 Hz, 1H, N*H*), 6.09 (d, *J* = 8.4 Hz, 1H, N*H'*), 5.89-5.78 (m, 3H, C*H*=CH_2, C*H'*=CH_2, H-1), 5.68 (dd, *J* = 6.2, 2.1 Hz, 1H, H-1'), 5.29-5.25 (2H, CH=C*H*H, CH=C*H'*H), 5.21-5.18 (m, 2H, CH=CH*H*, CH=CH*H'*), 5.05 (d, *J* = 8.6 Hz, 2H, CH_2Ph), 4.97 (d, *J* = 8.9 Hz, 2H, CH_2Ph), 4.85 (dd, *J* = 10.8, 2.1 Hz, 2H, CH_2Ph), 4.74-4.17 (m, 30H, 2 x CH (Fmoc), 2 x C*H*NH, 7 x CH_2Ph, 2 x CH_2OP, 2 x CH_2(Fmoc), 2 x C*H*$_2$CH=CH_2), 4.03-3.60 (m, 12H, 2 x H-2, 2 x H-3, 2 x H-4, 2 x H-5, 2 x H-6, 2 x H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.7, 156.1, 143.9, 143.9, 141.4, 138.33, 138.27, 138.2, 137.9, 135.6, 135.51, 135.45, 131.5, 131.4, 128.9, 128.8, 128.53, 128.49, 128.45, 128.44, 128.23, 128.16, 128.11, 128.09, 128.05, 128.01, 127.99, 127.96, 127.92, 127.85, 127.82, 127.79, 127.74, 127.70, 127.67, 127.3, 125.41, 125.38, 120.1, 120.0, 119.2, 96.9 (d, *J* = 6.8 Hz), 96.6 (d, *J* = 6.0 Hz), 93.0, 79.8, 78.9, 75.34, 75.30, 75.24, 75.18, 75.0, 74.8, 74.7, 74.6, 74.32, 74.25, 74.19, 73.5, 73.4, 73.1, 73.0, 72.9, 72.5, 72.41, 72.37, 72.0, 70.0, 69.9, 69.8, 69.04, 69.00, 67.5, 66.6, 54.6, 47.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.3, -2.8; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{62}H_{63}NO_{13}P]^+$, 1060.4032; found, 1060.4029.

2.3. Procedure (C) for donor synthesis and characterization



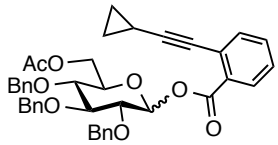
General procedure (C) for the synthesis of glycosyl *ortho*-alkynylbenzoate: to a solution of protected glycose (1.0 mmol) in CH_2Cl_2 (10 mL) was added *ortho*-alkynyl benzoic acid (279 mg, 1.5 mmol), DMAP (24 mg, 0.2 mmol) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCl) (344 mg, 1.8 mmol), respectively. After stirred for 4 h, the reaction mixture was diluted with EtOAc, washed with H_2O, saturated $NaHCO_3$ and brine, dried over Na_2SO_4. After filtration, the filtrate was concentrated to give a residue. The residue was purified via flash silica gel chromatography (Hexanes/EtOAc, 20/1 → 10/1) to afford the α/β mixed donors.

2,3,4-tri-*O*-benzyl-*α/β*-D-xylopyranosyl *ortho*-cyclopropylethynylbenzoate (1b)



1b, prepared via procedure (B), R_f = 0.2 (Hexanes/EtOAc, 12/1), colorless oil, 553 mg, 93% yield, α/β = 1/2. α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.20 (m, 19H, Ar*H*), 6.52 (d, *J* = 3.6 Hz, 1H), 4.95-4.62 (m, 6H, 3 x CH_2Ph), 4.05-3.99 (m, 2H, H-4, H-5), 3.85-3.65 (m, 1H, H-2), 3.55-3.44 (m, 2H, H-3, H-5')1.55-1.47 (m, 1H, CH_2CHCH_2), 0.87-0.77 (m, CH_2CHCH_2); β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.20 (m, 19H, Ar*H*), 5.87 (d, *J* = 7.3 Hz, 1H), 4.95-4.62 (m, 6H, 3 x CH_2Ph), 3.85-3.65 (m, 4H, H-2, H-3, H-4, H-5), 1.55-1.47 (m, 1H, CH_2CHCH_2), 0.87-0.77 (m, CH_2CHCH_2); mixture of α and β anomers ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.8, 164.2, 138.9, 138.6, 138.2, 138.1, 138.0, 137.9, 134.7, 134.5, 132.2, 132.1, 131.1, 130.9, 130.6, 130.5, 128.61, 128.57, 128.52, 128.50, 128.47, 128.4, 128.2, 128.1, 128.04, 128.01, 127.97, 127.9, 127.8, 127.7, 127.14, 127.06, 125.5, 125.2, 100.2, 100.0, 95.2, 91.0, 83.5, 81.4, 80.3, 78.9, 77.59, 77.56, 75.8, 75.6, 75.0, 74.9, 74.6, 73.8, 73.4, 73.3, 64.6, 62.7, 9.1, 9.03, 9.01, 0.9; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{38}H_{36}NaO_6]^+$, 611.2404; found, 611.2400.

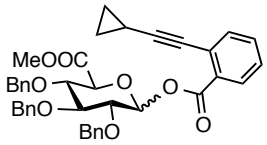
6-*O*-acetyl-2,3,4-tri-*O*-benzyl-*α/β*-D-glucopyranosyl *ortho*-cyclopropylethynylbenzoate (1c)



1c, prepared via procedure (B), R_f = 0.2 (Hexanes/EtOAc, 8/1), colorless oil, 614 mg, 93% yield, α/β = 1/1.3. α anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.21 (m, 19H, Ar*H*), 6.64 (d, *J* = 3.6 Hz, 1H), 5.02-4.56 (m, 6H, 6 x C*H*Ph), 4.37-4.25 (m, 2H, H-6, H-6'), 4.19-4.12 (m, 1H, H-3), 3.86-3.61 (m, 3H, H-2, H-4, H-5), 2.03 (s, 3H, CH_3), 1.57-1.49 (m, 1H, CH_2CHCH_2), 0.85-0.76 (m, 4H, CH_2CHCH_2); β anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.21 (m, 19H, Ar*H*), 5.92 (d, *J* = 7.9 Hz, 1H), 5.02-4.56 (m, 6H, 6 x C*H*Ph), 4.37-4.25 (m, 2H, H-6, H-6'), 4.19-4.12 (m, 1H, H-3), 3.86-3.61 (m, 3H, H-2, H-4, H-5), 2.03 (s, 3H, CH_3), 1.57-1.49 (m, 1H, CH_2CHCH_2), 0.85-0.76 (m, 4H, CH_2CHCH_2); mixture of α and β anomers: ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.8, 164.6, 164.0, 138.7, 138.4, 137.89, 137.85, 137.77, 137.74, 134.8, 134.5, 132.3, 132.2, 131.02, 130.96, 130.8, 130.5, 128.7, 128.60, 128.57, 128.50, 128.30, 128.26, 128.16,

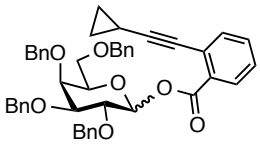
128.14, 128.08, 128.04, 128.02, 127.9, 127.8, 127.2, 127.1, 125.6, 125.2, 100.3, 100.1, 94.5, 90.7, 85.0, 81.9, 75.9, 75.4, 75.1, 75.0, 74.6, 73.9, 73.2, 71.7, 63.0, 62.8, 21.0, 9.16, 9.12, 9.05, 9.02, 0.90, 0.87; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{41}H_{40}NaO_8]^+$, 683.2615; found, 683.2611.

methyl-2,3,4-tri-*O*-benzyl-*α/β*-D-glucopyranuronatosyl *ortho*cyclopropylethynylbenzoate (1d)



1d, prepared via procedure (B), R_f= 0.2 (Hexanes/EtOAc, 8/1), colorless oil, 595 mg, 92% yield, α/β = 1/2. α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.24 (m, 19H, Ar*H*), 6.65 (d, *J* = 3.6 Hz, 1H), 4.98-4.60 (m, 6H, 6 x C*H*Ph), 4.17-3.78 (m, 4H, H-2, H-3, H-4, H-5), 3.71 (s, 3H, OMe), 1.61-1.49 (m, 1H, CH_2CHCH_2), 0.90-0.89 (m, 4H, CH_2CHCH_2); β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.24 (m, 19H, Ar*H*), 5.96 (d, *J* = 7.2 Hz, 1H), 4.98-4.60 (m, 6H, 6 x C*H*Ph), 4.17-3.78 (m, 4H, H-2, H-3, H-4, H-5), 3.68 (s, 3H, OMe), 1.61-1.49 (m, 1H, CH_2CHCH_2), 0.90-0.89 (m, 4H, CH_2CHCH_2); α and β anomers: ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.7, 168.2, 163.5, 162.9, 137.7, 137.4, 137.02, 136.96, 136.90, 136.7, 134.0, 133.7, 131.5, 131.4, 130.2, 130.0, 129.8, 129.3, 127.73, 127.70, 127.67, 127.6, 127.4, 127.34, 127.27, 127.23, 127.20, 127.18, 127.10, 127.07, 126.99, 126.3, 126.2, 124.9, 124.5, 99.6, 93.6, 89.9, 83.1, 80.4, 79.9, 78.39, 78.37, 77.8, 75.1, 75.0, 74.7, 74.4, 74.22, 74.18, 73.7, 72.5, 72.0, 51.8, 8.35, 8.29, 8.23, 8.20, 0.1, -0.0; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{40}H_{38}NaO_8]^+$, 669.2459; found, 669.2458.

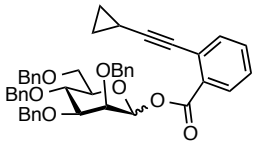
2,3,4,6-tetra-*O*-benzyl-*α/β*-D-galactopyranosyl *ortho*-cyclopropylethynylbenzoate (1e)



1e, prepared via procedure (B), the α/β mixture can be separated by gel silica chromatography, 701 mg, 99% yield, α/β = 1/3. α-anomer: R_f= 0.3 (Hexanes/EtOAc, 10/1), $[\alpha]_D^{25}$ = 57.7 (*c* 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.23 (m, 20H, Ar*H*), 6.67 (d, *J* = 3.6 Hz, 1H, H-1), 4.99 (d, *J* = 11.3 Hz, 1H, C*H*Ph), 4.85 (d, *J* = 11.9 Hz, 1H, C*H*Ph), 4.81-4.74 (m, 2H, 2 x C*H*Ph), 4.70 (d, *J* = 11.6 Hz, 1H), 4.61 (d, *J* = 11.3 Hz, 1H, C*H*Ph), 4.50-4.37 (m, 2H, 2 x C*H*Ph), 4.31-4.23 (m, 2H, H-2, H-5), 4.15-

4.03 (m, 2H, H-3, H-4), 3.63 (t, *J* = 8.5 Hz, 1H, H-6), 3.56 (dd, *J* = 9.0, 5.4 Hz, 1H, H-6'), 1.45-1.38 (m, 1H, CH_2CHCH_2), 0.87-0.74 (m, 4H, CH_2CH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.7, 138.8, 138.7, 138.3, 138.0, 134.7, 131.9, 131.5, 130.9, 128.52, 128.47, 128.40, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.62, 127.58, 127.2, 125.1, 99.5, 91.8, 78.7, 75.8, 75.09, 75.85, 74.9, 73.7, 73.2, 73.1, 72.3, 68.4, 9.1, 9.1, 0.8; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{46}H_{44}NaO_7]^+$, 731.2979; found, 731.2977. β-anomer: R_f = 0.2 (Hexanes/EtOAc, 10/1), $[\alpha]_D^{25}$ = -10.9 (*c* 2.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.19 (m, 20H, Ar*H*), 5.84 (d, *J* = 8.1 Hz, 1H, H-1), 4.96 (d, *J* = 11.3 Hz, 1H, C*H*Ph), 4.83-4.75 (m, 4H, 4 x C*H*Ph), 4.63 (d, *J* = 11.4 Hz, 1H, C*H*Ph), 4.50-4.38 (m, 2H, 2 x C*H*Ph), 4.10 (dd, *J* = 9.8, 8.0 Hz, 1H, H-2), 4.03 (d, *J* = 2.8 Hz, 1H, H-4), 3.79 (dd, *J* = 7.9, 5.4 Hz, 1H, H-5), 3.73-3.65 (m, 2H, H-3, H-6), 3.62 (dt, *J* = 9.0, 3.7 Hz, 1H, H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.9, 138.4, 138.1, 138.0, 137.6, 134.0, 131.8, 130.7, 130.3, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4, 126.7, 125.3, 82.3, 78.0, 75.1, 74.7, 74.4, 74.0, 73.3, 73.2, 72.7, 67.7, 8.7, 8.7, 0.5; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{46}H_{44}NaO_7]^+$, 731.2979; found, 731.3002.

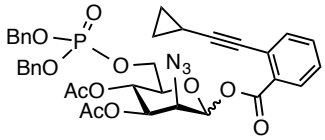
2,3,4,6-tetra-*O*-benzyl-*α/β*-D-mannopyranosyl *ortho*-cyclopropylethynylbenzoate (1f)



1f, prepared via procedure (B), R_f = 0.2 (Hexanes/EtOAc, 10/1), colorless oil, 638 mg, 90% yield, α/β = 2/1. α anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.13 (m, 20H, Ar*H*), 6.53 (d, *J* = 2.0 Hz, 1H, H-1), 4.94-4.53 (m, 8H, CH_2Ph x 4), 4.19 (t, *J* = 9.7 Hz, 1H, H-4), 4.09 (dd, *J* = 9.5, 3.0 Hz, 1H, H-3), 4.07-4.03 (m, 1H, H-5), 3.90 (dd, *J* = 3.1, 2.1 Hz, 1H, H-2), 3.85 (dd, *J* = 11.1, 4.2 Hz, 1H, H-6), 3.75 (dd, *J* = 11.2, 1.9 Hz, 1H, H-6'), 1.57-1.47 (m, 1H, CH_2CHCH_2), 0.81-0.76 (m, 4H, CH_2CHCH_2); β anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-7.12 (m, 24H, Ar*H*), 5.90 (d, *J* = 1.0 Hz, 1H), 4.93-4.53 (m, 8H, 8 x C*H*Ph), 4.22-4.03 (m, 2H, H-3, H-4), 3.90-3.65 (m, 4H, H-2, H-5, H-6, H-6'); mixture of α and β anomers: ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.4, 164.0, 161.9, 138.6, 138.5, 138.44, 138.41, 138.36, 138.29, 138.17, 138.06, 134.7, 134.5, 134.4, 133.0, 132.21, 132.17, 131.7, 130.92, 130.88, 130.8, 130.3, 128.6, 128.5, 128.42, 128.38, 128.31, 128.2, 128.13, 128.11, 128.06, 128.02, 127.9, 127.83, 127.76, 127.74, 127.63, 127.61, 127.2, 127.1, 127.0, 126.1, 125.6, 125.0, 101.2, 100.3, 100.2, 94.0, 92.9, 82.2, 79.4, 76.7, 75.4, 75.2, 75.01, 75.96, 74.5, 74.33, 74.29, 74.1, 73.8, 73.6, 73.5, 72.6,

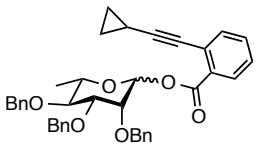
72.3, 72.25, 69.2, 69.0, 9.13, 9.08, 9.03, 8.99, 0.8, 0.7; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{46}H_{44}NaO_7]^+$, 731.2979; found, 731.3002.

3,4-di-*O*-acetyl-2-azido-6-*O*-dibenzyloxyphosphoryl-2-deoxy-*α/β*-D-mannopyranosyl *ortho*-cyclopropylethynylbenzoate (3g)



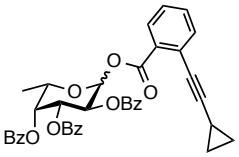
1g, prepared via procedure (B), the α/β mixture can be separated by gel silica chromatography, 631 mg, 99% yield, α/β = 4/1. α-anomer: R_f = 0.3 (Hexanes/EtOAc, 3/2), $[\alpha]_D^{25}$ = -35.6 (*c* 1.1 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.31 (m, 14H, Ar*H*), 6.36 (d, *J* = 1.8 Hz, 1H, H-1), 5.56 (dd, *J* = 9.9, 3.7 Hz, 1H, H-3), 5.48 (t, *J* = 9.9 Hz, 1H, H-4), 5.14-4.93 (m, 4H, 2 x C*H*$_2$Ph), 4.32-4.19 (m, 2H, H-2, H-5), 4.17-4.09 (m, 2H, H-6, H-6'), 2.11 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 1.57-1.51 (m, 1H, CH_2CHCH_2), 0.89-0.86 (m, 4H, CH_2CHCH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 169.3, 168.6, 162.9, 135.1, 134.3, 131.9, 130.1, 129.1, 127.9, 127.80, 127.77, 127.4, 127.3, 126.7, 124.5, 99.7, 91.6, 73.9, 71.1 (d, *J* = 7.9 Hz), 70.1, 68.9 (d, 2^{13}C, *J* = 5.9 Hz), 64.9, 64.7 (d, *J* = 4.9 Hz), 60.2, 19.95, 19.86, 0.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -1.5; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{36}H_{37}N_3O_{11}P]^+$, 718.2160; found, 718.2158. β-anomer: R_f = 0.2 (Hexanes/EtOAc, 3/2), $[\alpha]_D^{25}$ = 53.4 (*c* 4.2 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.22 (m, 14H, Ar*H*), 6.09 (d, *J* = 1.4 Hz, 1H, H-1), 5.33 (t, *J* = 9.8 Hz, 1H, H-4), 5.12 (dd, *J* = 9.8, 3.6 Hz, 1H, H-3), 5.08-4.94 (m, 4H, 2 x C*H*$_2$Ph), 4.27 (dd, *J* = 3.7, 1.4 Hz, 1H, H-2), 4.19-4.02 (m, 2H, H-6, H-6'), 3.83-3.72 (m, 1H, H-5), 2.13 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 1.54-1.43 (m, 1H, CH_2CHCH_2), 0.93-0.79 (m, 4H, C*H*$_2$CHC*H*$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 169.4, 168.7, 162.4, 135.2, 135.14, 135.10, 133.8, 132.0, 130.2, 128.6, 127.9, 127.86, 127.79, 127.35, 127.31, 126.4, 125.2, 100.0, 90.9, 73.5, 73.2 (d, *J* = 7.8 Hz), 71.2, 68.9 (d, *J* = 5.9 Hz), 68.8 (d, *J* = 5.9 Hz), 64.7 (d, *J* = 5.2 Hz), 64.5, 60.7, 20.0, 19.97, 19.94, 0.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -1.6; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{36}H_{37}N_3O_{11}P]^+$, 718.2160; found, 718.2161.

2,3,4-tri-*O*-benzyl-*α/β*-D-rhamnopyranosyl *ortho*-cyclopropylethynylbenzoate (1h)



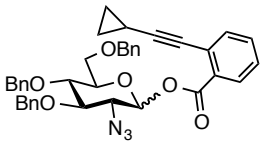
1h, prepared via procedure (B), R_f = 0.2 (Hexanes/EtOAc, 10/1), colorless oil, 597 mg, 99% yield, α/β = 2/1. α anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08-7.20 (m, 15H, Ar*H*), 6.41 (d, *J* = 1.9 Hz, 1H, H-1), 4.98 (d, *J* = 10.7 Hz, 1H, C*H*Ph), 4.87-4.74 (m, 2H, CH_2Ph), 4.66 (d, *J* = 10.6 Hz, 1H, C*H*Ph), 4.61-4.56 (m, 2H, CH_2Ph), 4.04 (dd, *J* = 9.6, 3.3 Hz, 1H, H-4), 4.01-3.97 (m, 1H, H-5), 3.89 (dd, *J* = 3.2, 2.0 Hz, 1H, H-2), 3.75 (d, *J* = 9.5 Hz, 1H, H-3), 1.57-1.50 (m, 1H, CH_2CHCH_2), 1.39 (d, *J* = 6.2 Hz, 3H, CH_3), 0.81-.073 (m, 4H, CH_2CHCH_2); β anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.20 (m, 19H, Ar*H*), 5.85 (s, 1H, H-1), 4.99-4.58 (m, 6H, 6 x C*H*Ph), 4.09-3.53 (m, 4H, H-2, H-3, H-4, H-5), 1.42-1.33 (m, 1H, CH_2CHCH_2), 0.90-0.73 (m, 4H, CH_2CHCH_2); mixture of α and β anomers: ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.5, 164.0, 161.9, 138.6, 138.4, 138.3, 138.2, 138.0, 134.7, 134.6, 134.4, 133.0, 132.25, 132.16, 131.7, 130.9, 130.8, 130.3, 128.6, 128.54, 128.49, 128.46, 128.3, 128.24, 128.19, 128.13, 127.92, 127.90, 127.86, 127.82, 127.78, 127.76, 127.71, 127.3, 127.2, 127.0, 126.1, 125.6, 125.0, 101.2, 100.3, 100.1, 93.9, 92.8, 82.4, 80.0, 79.9, 79.4, 75.7, 75.6, 74.9, 74.5, 74.3, 74.0, 73.1, 72.7, 72.3, 72.2, 71.1, 18.2, 18.1, 9.15, 9.12, 9.09, 9.0; HR ESI-MS: $[M+Na^+]^+$calcd for $[C_{39}H_{38}NaO_6]^-$, 625.2561; found, 625.2564.

2,3,4-tri-*O*-benzoyl-*α/β*-D-fucopyranosyl *ortho*-cyclopropylethynylbenzoate (1i)



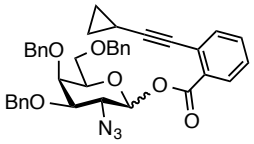
1i, prepared via procedure (B), R_f = 0.2 (Hexanes/EtOAc, 4/1), colorless oil, 554 mg, 86% yield, α/β = 1/1. Mixture of α and β anomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15-7.24 (m, 30H, ArH^{α}, ArH^{β}), 6.92 (d, *J* = 3.6 Hz, 1H, H-1$^{\alpha}$), 6.25 (d, *J* = 8.3 Hz, 1H, H-1$^{\beta}$), 6.11 (dd, *J* = 10.7, 3.3 Hz, 1H, H-3$^{\beta}$), 6.06-5.97 (m, 2H, H-1$^{\alpha}$, H-1$^{\beta}$), 5.91 (dd, *J* = 3.3, 1.3 Hz, 1H, H-4$^{\beta}$), 5.80 (dd, *J* = 3.5, 1.1 Hz, 1H, H-4$^{\alpha}$), 5.69 (dd, *J* = 10.4, 3.5 Hz, 1H, H-3$^{\alpha}$), 4.92-4.72 (m, 1H, H-5$^{\beta}$), 4.43-4.23 (m, 1H, H-5$^{\alpha}$), 1.61-1.50 (m, 2H, $CH_2CHCH_2^{\alpha}$, $CH_2CHCH_2^{\beta}$), 1.39 (d, *J* = 6.4 Hz, 3H, H-6$^{\alpha}$), 1.34 (d, *J* = 6.5 Hz, 3H, H-6$^{\beta}$), 0.91-0.83 (m, 8H, CH_2CHCH_2^{α}, CH_2CHCH_2^{β}); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.2, 165.0, 164.9, 164.7, 163.7, 162.9, 134.3, 133.6, 132.82, 132.78, 132.6, 132.54, 132.49, 131.6, 131.5, 130.2, 130.1, 129.3, 129.2, 129.1, 129.08, 129.05, 129.01, 128.8, 128.5, 128.4, 128.3, 128.2, 128.1, 127.94, 127.87, 127.7, 127.64, 127.58, 126.6, 126.3, 125.0, 124.3, 99.7, 99.2, 92.1, 90.4, 74.1, 73.6, 71.4, 70.8, 70.3, 70.2, 68.5, 68.1, 67.5, 66.9, 15.55, 15.49, 8.3, 8.2, 0.0, -0.1; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{39}H_{32}NaO_9]^+$, 667.1939; found, 667.1936.

2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-*α/β*-D-glucopyranosyl *ortho*-cyclopropylethynylbenzoate (1j)



1j, prepared via procedure (B), R_f = 0.2 (Hexanes/EtOAc, 8/1), colorless oil, 611 mg, 95% yield, α/β = 1/3. β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.12 (m, 15H, Ar*H*), 5.72 (d, *J* = 8.5 Hz, 1H), 4.93-4.47 (m, 6H, C*H*$_2$Ph x 3), 3.83 (t, *J* = 9.3 Hz, 1H, H-4), 3.79-3.69 (m, 3H, H-2, H-6, H-6'), 3.65 -3.56 (m, 2H, H-3, H-5), 1.55-1.47 (m, 1H, C*H*), 0.89-0.83 (m, 4H, C*H*$_2$C*H*$_2$); α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.12 (m, 15H, Ar*H*), 6.56 (d, *J* = 3.6 Hz, 1H, H-1), 4.20-4.06 (m, 2H, H-3, H-5), 3.91 (t, *J* = 9.6 Hz, 1H, H-4), 3.81-3.58 (m, 3H, H-2, H-6, H-6'); mixture of α and β anomers: ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.3, 163.8, 138.00, 137.93, 137.90, 134.9, 134.6, 132.5, 132.3, 131.0, 130.9, 130.1, 128.63, 128.59, 128.55, 128.50, 128.24, 128.18, 128.09, 128.07, 128.02, 127.96, 127.90, 127.8, 127.2, 127.1, 125.8, 125.2, 100.4, 100.3, 93.5, 91.7, 83.5, 80.9, 76.0, 75.8, 75.7, 75.3, 75.2, 74.6, 73.8, 73.74, 73.69, 68.1, 68.0, 65.6, 63.3, 9.1, 0.85; HR ESI-MS: $[M+Na^+]^+$calcd for $[C_{39}H_{37}N_3NaO_6]^+$, 666.2575; found, 666.2574.

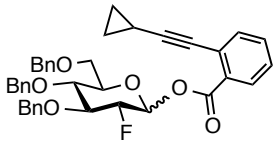
2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-*α/β*-D-galactopyranosyl *ortho*-cyclopropylethynylbenzoate (1k)



1k, prepared via procedure (B), R_f = 0.2 (Hexanes/EtOAc, 8/1), colorless oil, 618 mg, 96% yield, α/β = 1/3. α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.25 (m, 19H, Ar*H*), 6.50 (d, *J* = 3.4 Hz, 1H, H-1), 4.94-4.40 (m, 6H, 6 x C*H*Ph), 4.26-4.08 (m, 4H, H-2, H-3, H-4, H-5), 3.76-3.49 (m, 2H, H-6, H-6'), 1.49-1.42 (m, 1H, CH_2CHCH_2), 0.86-0.76 (m, 4H, C*H*$_2$CHC*H*$_2$); β anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.25 (m, 19H, Ar*H*), 4.94-4.40 (m, 6H, 6 x C*H*Ph), 5.65 (d, *J* = 8.5 Hz, 1H, H-1), 4.13-4.09 (m, 2H, H-3), 4.01 (d, *J* = 2.7 Hz, 1H, H-4), 3.76-3.49 (m, 4H, H-2, H-5, H-6, H-6'), 1.49-1.42 (m, 1H, CH_2CHCH_2), 0.86-0.76 (m, 4H, C*H*$_2$CHC*H*$_2$); mixture of α and β anomer: ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.3, 164.0, 138.4, 137.81, 137.78, 137.5, 134.9, 134.4, 132.4, 132.2, 131.1, 130.8, 130.1, 128.7, 128.68, 128.60, 128.56, 128.40, 128.35, 128.18, 128.16, 128.10, 128.08, 128.04, 127.99, 127.91, 127.86, 127.2, 127.1,

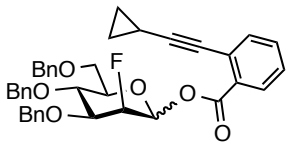
125.7, 125.1, 100.3, 99.8, 93.7, 92.0, 81.1, 78.0, 75.1, 75.0, 74.6, 74.4, 73.73, 73.70, 73.0, 72.7, 72.2, 72.1, 68.0, 67.8, 62.3, 59.6, 9.0, 0.8; HR ESI-MS: $[M+Na^+]^+$calcd for $[C_{39}H_{37}N_3NaO_6]^+$, 666.2575; found, 666.2575.

3,4,6-tri-*O*-benzyl-2-fluoro-2-deoxy-*α/β*-D-glucopyranosyl *ortho*-cyclopropylethynylbenzoate (1l)



1l, prepared via procedure (B), R_f= 0.2 (Hexanes/EtOAc, 10/1), colorless oil, 558 mg, 90% yield, α/β = 1/2.3. α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.11 (m, 19H, Ar*H*), 6.67 (d, *J* = 3.8 Hz, 1H), 4.96-4.46 (m, 7H, 3 x C*H*$_2$Ph, H-2), 4.26 (dt, *J* = 12.2, 9.2 Hz, 1H, H-3), 4.15-4.04 (m, 1H, H-5), 3.94-3.67 (m, 3H, H-4, H-6, H-6'), 1.57-1.48 (m, 1H, CH_2CHCH_2), 0.89-0.73 (m, 4H, C*H*$_2$CHC*H*$_2$); β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.11 (m, 19H, Ar*H*), 5.96 (dd, *J* = 8.1, 3.1 Hz, 1H), 4.96-4.46 (m, 7H, 3 x C*H*$_2$Ph, H-2), 3.94-3.67 (m, 5H, H-3, H-4, H-5, H-6, H-6'), 1.57-1.48 (m, 1H, CH_2CHCH_2), 0.89-0.73 (m, 4H, C*H*$_2$CHC*H*$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.3, 138.3, 138.1, 138.05, 137.96, 137.92, 134.8, 134.5, 132.4, 132.3, 131.05, 131.02, 130.3, 128.6, 128.5, 128.2, 128.12, 128.08, 128.04, 128.00, 127.97, 127.93, 127.90, 127.8, 127.2, 127.1, 125.6, 125.2, 100.31, 100.25, 92.4, 92.2, 91.4, 91.3, 90.4, 90.2, 89.5, 83.4, 80.9, 76.6, 76.3, 75.9, 75.5, 75.33, 75.26, 75.1, 74.9, 74.5, 73.73, 73.65, 73.2, 68.1, 68.0, 9.1, 9.0, 0.9, 0.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ = -196.5, -199.0. HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{39}H_{38}FO_6]^+$, 621.2647; found, 621.2650.

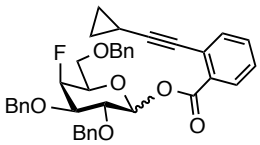
3,4,6-tri-*O*-benzyl-2-fluoro-2-deoxy-*α/β*-D-mannopyranosyl *ortho*-cyclopropylethynylbenzoate (1m)



1m, prepared via procedure (B), R_f= 0.2 (Hexanes/EtOAc, 10/1), colorless oil, 576 mg, 93% yield, α/β = 3.2/1. α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.63 (m, 19H, Ar*H*), 6.54 (dd, *J* = 6.2, 2.2 Hz, 1H, H-1$^\alpha$), 4.89-4.51 (m, 7H, H-2$^\alpha$, 3 x CH_2Ph), 4.14-4.01 (m, 2H, H-3$^\alpha$, H-4$^\alpha$, H-5$^\alpha$), 3.85-3.64 (m, 2H, H-6$^\alpha$, H-6'$^\alpha$), 1.57-1.49 (m, 1H, CH_2CHCH_2), 0.89-0.71 (m, 4H, C*H*$_2$CHC*H*$_2$); β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.63 (m, 19H, Ar*H*), 5.90 (d, *J* = 19.3 Hz, 1H, H-1$^\beta$), 4.89-4.51 (m, 7H, H-2$^\beta$, 3 x CH_2Ph), 4.14-4.01 (m, 2H, H-3$^\beta$, H-4$^\beta$, H-5$^\beta$), 3.85-3.64 (m, 2H, H-6$^\beta$, H-6' $^\beta$), 1.57-

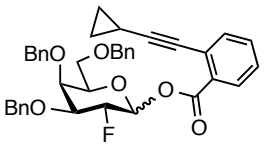
1.49 (m, 1H, CH_2CHCH_2), 0.89-0.71 (m, 4H, CH_2CHCH_2); mixture of α and β anomer: ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.0, 163.9, 138.3, 138.2, 138.1, 137.8, 137.5, 134.8, 134.5, 132.5, 132.4, 131.2, 130.9, 130.3, 130.0, 128.7, 128.6, 128.53, 128.47, 128.4, 128.2, 128.13, 128.09, 128.03, 127.95, 127.9, 127.73, 127.71, 127.2, 127.1, 125.6, 125.1, 100.43, 100.35, 92.1 (d, *J* = 19 Hz)), 92.0 (d, *J* = 31 Hz), 86.4 (d, *J* = 190 Hz), 86.0 (d, *J* = 180 Hz), 80.3 (d, *J* = 17.6 Hz), 78.2 (d, *J* = 17.5 Hz), 76.5, 75.55, 75.46, 74.9, 74.7, 74.4, 74.0, 73.9, 73.7, 73.6, 72.5, 72.2, 68.6, 68.5, 9.2, 9.0, 0.82, 0.78; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -203; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{39}H_{38}FO_6]^+$, 621.2647; found, 621.2649.

2,3,6-tri-*O*-benzyl-4-fluoro-4-deoxy-*α/β*-D-galactopyranosyl *ortho*-cyclopropylethynylbenzoate (1n)



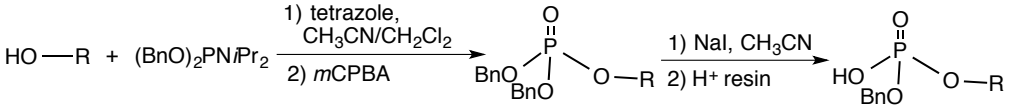
1n, prepared via procedure (B), the α/β mixture can be separated by gel silica chromatography, colorless oil, 576mg, 93% yield, α/β = 1.5/1. α-anomer: R_f = 0.25 (Hexanes/EtOAc, 10/1), $[\alpha]_D^{25}$ = 43 (*c* 1.7 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.25 (m, 19H, Ar*H*), 6.63 (d, *J* = 3.2 Hz, 1H, H-1), 5.01 (dd, *J* = 50.0, 2.3 Hz, 1H, H-4), 4.85-4.66 (m, 4H, 2 x CH_2Ph), 4.53 (s, 2H, CH_2Ph), 4.32-4.21 (m, 1H, H-5), 4.14-4.00 (m, 2H, H-2, H-3), 3.70 (t, *J* = 8.7 Hz, 1H, H-6), 3.63 (ddd, *J* = 9.2, 5.6, 1.6 Hz, 1H, H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.9, 137.4, 137.2, 137.1, 134.1, 131.3, 130.4, 130.3, 130.2, 128.2, 127.79, 127.77, 127.74, 127.3, 127.18, 127.16, 127.1, 126.5, 124.3, 98.8, 90.7, 86.4 (d, *J* = 184 Hz), 74.9 (d, *J* = 20.0 Hz), 74.35, 74.38, 73.1, 72.8, 72.0, 70.2 (d, *J* = 18.5 Hz), 66.7 (d, *J* = 6.0 Hz), 8.33, 8.28, 0.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -218.8; HR ESI-MS: $[M+Na^+]^-$ calcd for $[C_{39}H_{37}FNaO_6]^+$, 643.2466; found, 643.2467. β-anomer: R_f = 0.2 (Hexanes/EtOAc, 10/1), $[\alpha]_D^{25}$ = -31 (*c* 2.9 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.19 (m, 19H, Ar*H*), 5.86 (d, *J* = 8.1 Hz, 1H, H-1), 4.93 (dd, *J* = 49.7, 2.6 Hz, 1H, H-4), 4.84-4.68 (m, 4H, 2 x CH_2Ph), 4.55 (s, 2H, CH_2Ph), 4.00 (dd, *J* = 9.6, 8.1 Hz, 1H, H-2), 3.88-3.57 (m, 4H, H-3, H-5, H-6, H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.3, 137.2, 137.0, 133.6, 131.5, 130.1, 129.6, 127.80, 127.78, 127.6, 127.4, 127.24, 127.18, 127.0, 126.3, 124.8, 99.5, 93.7, 84.8 (d, *J* = 184 Hz), 78.9, 78.7, 76.9, 74.8, 73.8, 73.0, 72.3, 72.1, 71.7, 66.4 (d, *J* = 5.5 Hz), 8.2, 8.2, -0.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ = -217.5; HR ESI-MS: $[M+Na^+]^-$ calcd for $[C_{39}H_{37}FNaO_6]^+$, 643.2466; found, 643.2463.

3,4,6-tri-*O*-benzyl-2-fluoro-2-deoxy-*α/β*-D-galactopyranosyl *ortho*-cyclopropylethynylbenzoate (1o)



1o, prepared via procedure (B), R_f= 0.2 (Hexanes/EtOAc, 10/1), colorless oil, 613 mg, 99%, α/β = 1/3. α-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-7.24 (m, 19H, Ar*H*), 6.66 (d, *J* = 3.8 Hz, 1H, H-1), 5.19 (ddd, *J* = 49.6, 9.7, 3.9 Hz, 1H, H-2), 4.96-4.40 (m, 6H, 6 x C*H*Ph), 4.28-4.17 (m, 2H, H-3, H-5), 4.17-4.10 (m, 1H, H-4), 3.81-3.56 (m, 2H, H-6, H-6'), 1.49-1.34 (m, 1H, CH_2CHCH_2), 0.86-0.73 (m, 4H, CH_2CHCH_2); β-anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-7.24 (m, 19H, Ar*H*), 5.92 (dd, *J* = 7.9, 4.6 Hz, 1H, H-1), 5.07-4.38 (m, 7H, H-2, 6 x C*H*Ph), 4.04 (t, *J* = 3.3 Hz, 1H, H-4), 3.84-3.79 (m, 1H, H-5), 3.75 (ddd, *J* = 12.5, 9.4, 3.1 Hz, 1H, H-3), 3.68-3.54 (m, 2H, H-6, H-6'), 1.49-1.34 (m, 1H, CH_2CHCH_2), 0.86-0.73 (m, 4H, CH_2CHCH_2); mixture of α and β anomers: ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.5, 164.4, 138.4, 138.2, 138.0, 137.83, 137.79, 134.8, 134.5, 134.3, 133.0, 132.3, 132.2, 131.7, 131.1, 131.0, 130.8, 130.31, 130.28, 128.60, 128.58, 128.53, 128.44, 128.40, 128.36, 128.3, 128.1, 128.02, 128.00, 127.97, 127.94 127.86, 127.81, 127.7, 127.25, 127.21, 127.0, 125.5, 125.1, 101.2, 100.2, 99.8, 92.7 (d, *J* = 25.4 Hz), 91.7, 90.8 (d, *J* = 23.1 Hz), 89.9, 89.5, 87.6, 80.2, 75.3, 75.2, 75.0, 74.5, 74.32, 74.27, 73.7, 73.0, 72.2, 67.9, 67.7, 9.08, 9.06, 8.98, 0.8, 0.73, 0.71; mixture of α and β anomers: ^{19}F NMR (376 MHz, $CDCl_3$) δ = -206, -207; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{39}H_{37}FNaO_6]^+$, 643.2466; found, 643.2464.

2.4 Procedure (D) for acceptor synthesis and characterization

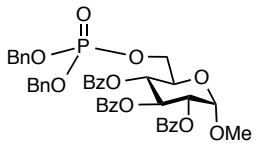


General procedure (D) for the synthesis of phosphoric acid acceptor. To a solution of alcohol (1.0 equiv.) in CH_3CN and CH_2Cl_2 (1/4, 0.2 M) was added $(BnO)_2PN^iPr_2$ (1.5 equiv.) and tetrazole (1.8 equiv.), and the mixture was stirred for 2 h at room temperature, after which the alcohol disappeared on TLC plate. Then, *m*CPBA (4.0 equiv.) was added into the mixture, and the reaction was stirred for 2 h, after which the reaction was quenched with $Na_2S_2O_3$ solution. The mixture was diluted with EtOAc, washed with H_2O, saturated $NaHCO_3$, brine and dried over Na_2SO_4. After filtration, the

filtrate was concentrated to give a residue, which was purified via flash silica gel chromatography to give the desired product phosphotriester (**S1**-**S6**).

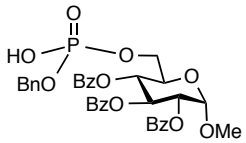
General procedure (E): To a solution of phosphotriester in CH_3CN (0.2 M) was added NaI (4.0 equiv.), then the mixture was stirred at 60 °C for 3 h. After cooling down, the solvent was removed and the mixture was acidified with aqueous HCl (1.0 M, 3.0 mL), extracted with EtOAc (4 x 20 mL), dried over Na_2SO_4. After filtration, the filtrate was concentrated to give a residue, which was loaded to silica gel column which was neutralized by using Hexanes/Et3N (100/1) and purified by eluting with solvents (Hexanes/EtOAc, 1/1→CH_2Cl_2/MeOH, 50/1→10/1) to give the product in the form of phosphate salt. Then, a solution of the salt in mixed solvent of CH_2Cl_2/MeOH (3 mL/3 mL) was added H^+ resin (Dowex 50WX8, 400 mg) to acidify, and after filtration through cotton, phosphoric acid glycosyl benzyl ester (**2b**-**2g**) was obtained.

Methyl 6-*O*-dibenzyloxyphosphoryl-2,3,4-tri-*O*-benzoyl-*α*-D-glucopyranoside (S1)



S1, prepared via procedure (D), purified via flash silica gel chromatography (Hexanes/EtOAc, 3/1 to 2/1), R_f= 0.2 (Hexanes/EtOAc, 3/2), white foam, 400 mg, 90% yield. $[\alpha]_D^{25}$ = 45.6 (*c* 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.27 (m, 25H, Ar*H*), 6.12 (t, *J* = 9.4 Hz, 1H, H-3), 5.52 (t, *J* = 9.7 Hz, 1H, H-4), 5.22-5.18 (m, 2H, H-1, H-2), 5.09-5.01 (m, 4H, C*H*$_2$Ph x 2), 4.23-4.16 (m, 3H, H-5, H-6, H-6'), 3.41 (s, 3H, C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.91, 165.89, 165.3, 136.0, 135.96, 135.92, 135.89, 135.86, 133.6, 133.5, 133.2, 130.1, 130.0, 129.8, 129.3, 129.2, 129.0, 128.8, 128.69, 128.65, 128.59, 128.55, 128.4, 128.2, 128.1, 128.0, 97.1, 72.1, 70.5, 69.55 (d, J = 5.7 Hz), 69.53 (d, J = 5.7 Hz), 69.1, 68.4 (d, *J* = 8.0 Hz), 66.0 (d, *J* = 5.3 Hz), 55.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -1.2; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{42}H_{40}O_{12}P]^+$, 767.2252; found, 767.2250.

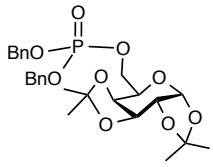
methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(benzyloxy-hydroxy-phosphoryl)-*α*-D-glucopyranoside (2b)



2b, prepared via procedure (E), R_f= 0.2 (CH_2Cl_2/MeOH, 10/1), white foam, 300 mg, 84% yield. $[\alpha]_D^{25}$ = 65.7 (*c* 1.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (bs, 1H,

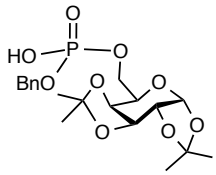
O*H*), 7.98-7.28 (m, 20H, Ar*H*), 6.13 (t, *J* = 9.6 Hz, 1H, H-3), 5.50 (t, *J* = 9.7 Hz, 1H, H-4), 5.24-5.20 (m, 2H, H-1, H-2), 5.08-4.99 (m, 2H, C*H*$_2$Ph), 4.33-4.05 (m, 3H, H-5, H-6, H-6'), 3.41 (s, 3H, C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.9, 165.8, 165.5, 133.52, 133.45, 133.2, 130.1, 130.0, 129.8, 129.4, 129.2, 129.0, 128.6, 128.5, 128.44, 128.39, 127.9, 97.0, 72.1, 70.6, 69.3, 69.2, 68.5 (d, *J* = 7.9 Hz), 66.0, 55.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ = 0.7; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{35}H_{34}O_{12}P]^+$, 677.1782; found, 677.1781.

6-*O*-dibenzyloxyphosphoryl-1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose (S2)



S2, prepared via procedure (D), purified by silica gel chromatography (Hexanes/EtOAc, 2/1 to 3/2), R_f = 0.2 (Hexanes/EtOAc, 3/2), white foam, 570 mg, 95% yield. $[\alpha]_D^{25}$ = -37.5 (*c* 3.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.32 (m, 10H, Ar*H*), 5.53 (d, *J* = 4.9 Hz, 1H, H-1), 5.15 – 5.02 (m, 4H, C*H*$_2$Ph x 2), 4.59 (dd, *J* = 7.9, 2.5 Hz, 1H, H-3), 4.32 (dd, *J* = 5.0, 2.5 Hz, 1H, H-2), 4.21-4.12 (m, 3H, H-4, H-6, H-6'), 4.12-4.04 (m, 1H, H-5), 1.49 (s, 3H, C*H*$_3$), 1.41 (s, 3H, C*H*$_3$), 1.31 (s, 3H, C*H*$_3$), 1.30 (s, 3H, C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 136.04, 135.96, 128.8, 128.6, 128.5, 128.14, 128.07, 128.0, 109.7, 108.9, 96.4, 70.74, 70.68, 70.56, 69.4 (d, *J* =5.7 Hz, 2C), 67.4, 67.38, 66.9 (d, *J* = 7.1 Hz), 66.4 (d, *J* = 5.6 Hz), 26.1, 26.0, 25.1, 24.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ -1.08; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{26}H_{34}O_9P]^+$, 521.1935; found, 521.1933.

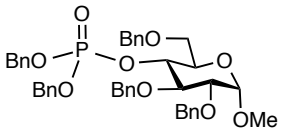
6-*O*-(benzyloxy-hydroxy-phosphoryl)-1,2:3,4-di-*O*-isopropylidene-*α*-D-galactopyranose (2c)



2c, prepared via procedure (E), R_f = 0.2 (CH_2Cl_2/MeOH, 9/1), white solid, 230 mg (72% yield); $[\alpha]_D^{25}$ = -33.3 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 5H, Ar*H*), 5.50 (d, *J* = 5.0 Hz, 1H, H-1), 5.05 (d, *J* = 6.7 Hz, 2H, C*H*$_2$Ph), 4.54 (dd, *J* = 7.8, 2.4 Hz, 1H, H-3), 4.28 (dd, *J* = 5.0, 2.4 Hz, 1H, H-2), 4.20-4.07 (m, 3H, H-4, H-6, H-6'), 4.01 (t, *J* = 6.3 Hz, 1H, H-5), 1.48 (s, 3H, C*H*$_3$), 1.38 (s, 3H, C*H*$_3$), 1.29 (s, 3H, C*H*$_3$), 1.27 (s, 3H, C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 136.5, 136.4, 128.6, 128.2,

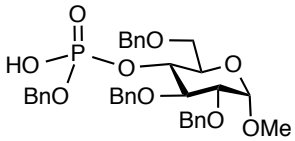
128.0, 109.7, 109.0, 96.3, 70.7, 70.6, 70.6, 69.0 (d, *J* = 4.5 Hz), 67.0 (d, *J* = 7.8 Hz), 66.0 (bs), 26.1, 26.1, 25.0, 24.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -1.0; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{19}H_{28}O_9P]^+$, 431.14465; found, 431.1464.

methyl 2,3,6-tri-*O*-benzyl-4-*O*-dibenzyloxyphosphoryl-*α*-D-glucopyranoside (S3)



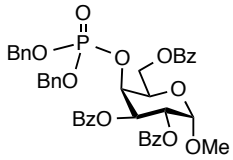
S3, prepared via procedure (D), purified by silica gel chromatography (Hexanes/EtOAc, 3/1 to 2/1), R_f = 0.2 (Hexanes/EtOAc, 2/1), colorless oil, 298 mg, 96% yield. $[\alpha]_D^{25}$ = 10.5 (*c* 1.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.10 (m, 25H, Ar*H*), 4.97-4.73 (m, 7H, 7 x C*H*Ph), 4.61-4.58 (m, 2H, C*H*Ph, H-1), 4.53-4.46 (m, 2H, C*H*Ph, H-4), 4.41 (d, *J* = 11.9 Hz, 1H, C*H*Ph), 3.96 (t, *J* = 9.3 Hz, 1H, H-3), 3.83 (ddd, *J* = 10.1, 4.7, 2.0 Hz, 1H, H-5), 3.75-3.66 (m, 2H, H-6, H-6'), 3.56 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2), 3.38 (s, 3H, OMe); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.8, 138.3, 138.0, 136.04, 136.96, 128.6, 128.53, 128.48, 128.40, 128.36, 128.3, 128.1, 127.94, 127.91, 127.81, 127.77, 127.6, 127.4, 98.0, 79.9 (d, *J* = 2.9 Hz), 79.7, 75.9 (d, *J* = 7.1 Hz), 75.4, 73.6, 73.5, 69.5, 69.4 (d, 2^{13}C, *J* = 5.5 Hz), 68.6, 55.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -0.6; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{42}H_{46}O_9P]^+$, 725.2874; found, 725.2873.

methyl 2,3,6-tri-*O*-benzyl-4-*O*-(benzyloxy-hydroxy-phosphoryl)-*α*-D-glucopyranoside (2d)



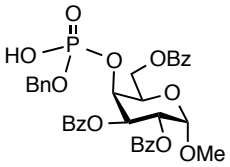
2d, prepared via procedure (E), R_f = 0.2 (CH_2Cl_2/MeOH, 10/1), white foam, 200 mg, 88% yield. $[\alpha]_D^{25}$ = 3.1 (*c* 3.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.14 (m, 20H, Ar*H*), 4.92-4.81 (m, 4H, CH_2Ph x 2), 4.70 (d, *J* = 12.1 Hz, 1H, C*H*Ph), 4.55-4.50 (m, 3H, CH_2Ph, H-1), 4.44-4.37 (m, 2H, C*H*Ph, H-4), 3.92 (t, *J* = 9.3 Hz, 1H, H-3), 3.77-3.65 (m, 3H, H-5, H-6, H-6'), 3.44 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2), 3.34 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.5, 138.2, 138.1, 128.5, 128.5, 128.5, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 127.5, 98.0, 80.1, 79.5, 76.0 (d, *J* = 7.6 Hz), 75.9, 69.3 (bs), 68.3, 55.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -0.5; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{35}H_{40}O_9P]^+$, 635.2404; found, 635.2405.

methyl 2,3,6-tri-*O*-benzoyl-4-*O*-dibenzyloxyphosphoryl-*α*-D-galactopyranoside (S4)



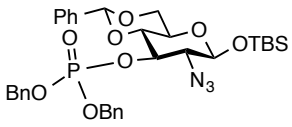
S4, prepared via procedure (D), purified by silica gel chromatography (Hexanes/EtOAc, 3/1 to 2/1), R_f = 0.2 (Hexanes/EtOAc, 3/1), colorless oil, 567 mg, 94% yield. $[\alpha]_D^{25}$ = 81.9 (*c* 4.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.07-7.12 (m, 25H, Ar*H*), 5.78 (ddd, *J* = 10.8, 3.0, 1.4 Hz, 1H, H-3), 5.68 (dd, *J* = 10.8, 3.6 Hz, 1H, H-2), 5.31 (dd, *J* = 9.4, 3.0 Hz, 1H, H-4), 5.21 (d, *J* = 3.6 Hz, 1H, H-1), 4.99-4.85 (m, 4H, C*H*$_2$Ph x 2), 4.68-4.62 (m, 1H, H-6), 4.50-4.43 (m, 2H, H-5, H-6'), 3.44 (s, 3H, C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.1, 166.08, 166.0, 135.7, 135.6, 133.5, 133.31, 133.25, 130.0, 129.9, 129.8, 129.5, 129.4, 128.63, 128.59, 128.55, 128.52, 128.4, 128.0, 127.97, 97.7, 74.5 (d, *J* = 5.4 Hz), 69.74 (d, *J* = 5.9 Hz), 69.70 (d, *J* = 5.4 Hz), 69.1 (d, *J* = 2.2 Hz), 68.6, 67.2 (d, *J* = 4.2 Hz), 62.8, 55.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -0.9; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{42}H_{40}O_{12}P]^+$, 767.2252; found, 767.2250.

methyl 2,3,6-tri-*O*-benzoyl-4-*O*-(benzyloxy-hydroxy-phosphoryl)-*α*-D-galactopyranoside (2e)



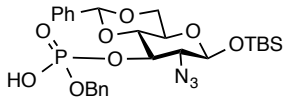
2e, prepared via procedure (E), R_f = 0.35 (CH_2Cl_2/MeOH, 10/1), white foam, 440 mg, 88% yield. $[\alpha]_D^{25}$ = 114 (*c* 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98-7,13 (m, 20H, Ar*H*), 6.64 (br, 1H, O*H*), 5.69 (d, *J* = 10.7 Hz, 1H, H-3), 5.55 (dd, *J* = 10.7, 3.5 Hz, 1H, H-2), 5.10 (s, 1H, H-1), 5.00 (d, *J* = 9.3 Hz, 1H, H-4), 4.93-4.81 (m, 2H, C*H*$_2$Ph), 4.60 (dd, *J* = 11.7, 8.3 Hz, 1H, H-6), 4.47 (d, *J* = 11.3 Hz, 1H, H-6'), 4.23 (s, 1H, H-5), 3.36 (s, 3H, C*H*$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.4, 166.1, 166.0, 133.3, 133.1, 133.0, 130.03, 130.01, 129.9, 129.63, 129.59, 128.5, 128.4, 128.3, 127.8, 97.3, 74.1, 69.2, 69.0, 67.5, 55.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ = 0.2; HR ESI-MS: $[M-H^+]^-$ calcd for $[C_{35}H_{32}O_{12}P]^-$, 675.1637; found, 675.1641.

***tert*-butyldimethylsilyl 2-azido-4,6-*O*-benzylidene-3-*O*-dibenzyloxyphosphoryl-2-deoxy-*β*-D-glucopyranoside (S5)**



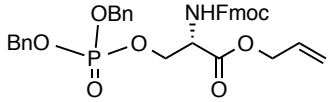
S5, prepared via procedure (D), purified by silica gel chromatography (Hexanes/EtOAc, 6/1→4/1), R_f= 0.2 (Hexanes/EtOAc, 4/1), colorless oil, 340 mg, 85% yield. $[\alpha]_D^{25}$ = -51.4 (*c* 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.01 (m, 15H, Ar*H*), 5.47 (s, 1H, PhC*H*), 5.13-5.04 (m, 2H, CH_2Ph), 4.94 (dd, *J* = 12.1, 6.6 Hz, 1H, C*H*HPh), 4.87 (dd, *J* = 12.1, 7.5 Hz, 1H, C*H*HPh), 4.69 (d, *J* = 7.6 Hz, 1H, H-1), 4.49 (dd, *J* = 9.6 Hz, *J* = 9.6 Hz, 1H, H-3), 4.30 (dd, *J* = 10.6, 5.0 Hz, 1H, H-6), 3.78 (t, *J* = 10.3 Hz, 1H, H-6'), 3.71 (t, *J* = 9.4 Hz, 1H, H-4), 3.48-3.42 (m, 2H, H-2, H-5), 0.94 (s, 9H, C$(CH_3)_3$), 0.18 (s, 3H, CH_3), 0.16 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 136.8, 136.1, 135.97, 135.9, 129.4, 128.6, 128.5, 128.4, 128.2, 127.9, 127.4, 126.5, 102.1, 97.8, 79.4 (d, *J* = 2.9 Hz), 77.20 (d, *J* = 32 Hz), 69.6 (d, *J* = 5.6 Hz), 69.3 (d, *J* = 5.2 Hz), 68.6 (d, *J* = 3.0 Hz), 68.3, 66.3, 25.7, -4.3, -5.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -1.9; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{33}H_{43}N_3O_8PSi]^+$, 668.2552; found, 668.2547.

***tert*-butyldimethylsilyl 2-azido-4,6-*O*-benzylidene-3-*O*-(benzyloxy-hydroxy-phosphoryl)-2-deoxy-*β*-D-glucopyranoside (2f)**



2f, prepared via procedure (E), R_f= 0.45 (CH_2Cl_2/MeOH, 10/1), colorless oil, 118 mg, 75% yield. $[\alpha]_D^{25}$ = -40.9 (*c* 1.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (bs, 1H, OH), 7.31-6.98 (m, 10H, Ar*H*), 5.33 (s, 1H, C*H*Ph), 4.85-4.76 (m, CH_2Ph), 4.43 (d, *J* = 7.6 Hz, 1H, H-1), 4.22-4.11 (m, 2H, H-4, H-6), 3.61 (t, *J* = 10.3 Hz, 1H, H-6'), 3.52 (t, *J* = 9.4 Hz, 1H, H-4), 3.27 (dd, *J* = 9.7, 7.6 Hz, 1H, H-2), 3.20 (td, *J* = 9.7, 5.0 Hz, 1H, H-5), 0.79 (s, 9H, ^{t}Bu), 0.01 (s, 3H, CH_3), 0.00 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 136.8, 136.1, 136.0, 129.2, 128.43, 128.39, 128.1, 127.4, 126.3, 101.6, 97.6, 79.3 (d, *J* = 3.3 Hz), 69.1 (d, *J* = 5.3 Hz), 68.5 (d, *J* = 2.7 Hz), 68.4, 66.1, 25.6, 18.0, -4.2, -5.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -0.4; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{26}H_{37}N_3O_8PSi]^+$, 578.2082; found, 578.2087.

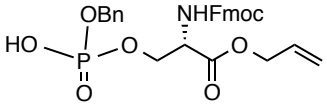
3-*O*-dibenzyloxyphosphoryl-*N*-(9-fluorenylmethoxycarbonyl)-L-serine allyl ester (S6)



S6, prepared via procedure (D), purified by silica gel chromatography (Hexanes/EtOAc, 2/1 to 3/2), R_f = 0.2 (Hexanes/EtOAc, 2/1), colorless oil, 183 mg, 99% yield. $[\alpha]_D^{25}$ = 7.0 (*c* 1.4 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.28 (m, 18H, Ar*H*), 5.91-5.79 (m, 2H, NH, C*H*=CH_2), 5.35-5.26 (m, 1H, CH*H*=CH), 5.22 (dd, *J* = 10.4, 1.4 Hz, 1H,

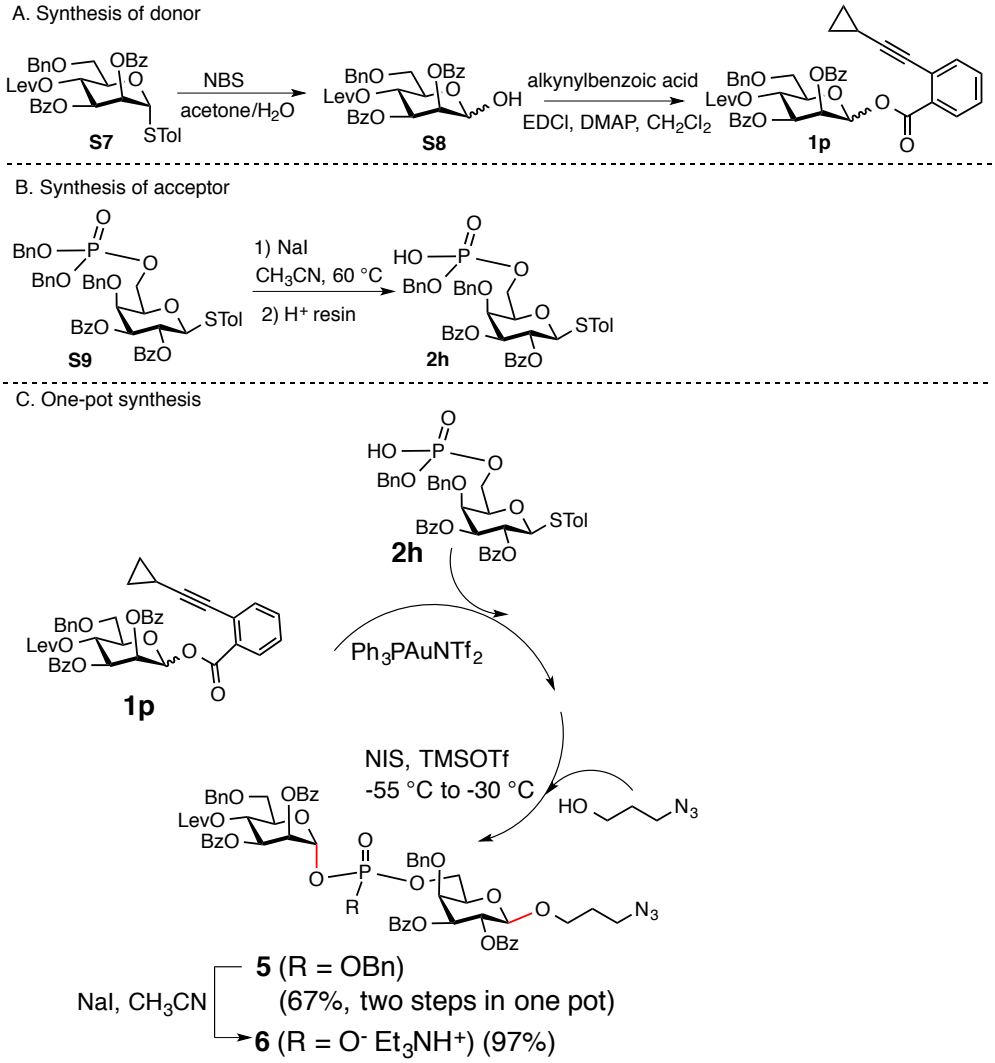
C*H*H=CH), 5.07-4.91 (m, 4H, 2 x CH_2Ph), 4.64-4.55 (m, 3H, C*H*NH, CH_2CH=CH_2), 4.46-4.40 (m, 2H, CH_2OP), 4.33-4.19 (m, 3H, CH(Fmoc), CH_2(Fmoc)); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.7, 156.0, 143.9, 143.8, 141.4, 135.64, 135.57, 131.4, 128.9, 128.8, 128.1, 127.9, 127.3, 125.31, 125.25, 120.1, 119.2, 69.9 (d, *J* = 5.7 Hz), 69.8 (d, *J* = 5.7 Hz), 67.5, 67.4 (d, *J* = 5.7 Hz), 66.7, 54.6 (d, *J* = 7.3 Hz), 47.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -0.9; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{35}H_{35}NO_8P]^+$, 628.2095; found, 628.2099.

3-*O*-(benzyloxy-hydroxy-phosphoryl)-*N*-(9-fluorenylmethoxycarbonyl)-L-serine allyl ester (2g)

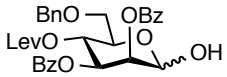


2g, prepared via procedure (E), R_f = 0.2 (CH_2Cl_2/MeOH, 10/1), white solid, 130 mg, 76% yield. $[\alpha]_D^{25}$ = 14 (*c* 0.3 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.28 (m, 13H, Ar*H*), 5.91-5.81 (m, C*H*=CH_2), 5.30 (dd, *J* = 17.1, 1.7 Hz, 1H, CH=C*H*H), 5.24-5.17 (m, 1H, CH=CH*H*), 5.02 (d, *J* = 7.9 Hz, 2H, CH_2Ph), 4.69-4.56 (m, 3H, C*H*NH, CH_2CH=CH_2), 4.47-4.18 (m, 6H, CH(Fmoc), CH_2(Fmoc), CH_2OP, OH); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.8, 156.1, 143.9, 141.4, 131.4, 128.81, 128.77, 128.0, 127.9, 127.3, 125.4, 120.1, 119.3, 69.7 (bs), 67.6, 67.4 (bs), 66.8, 54.6 (d, *J* = 7.1 Hz), 47.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ = 0.5; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{28}H_{29}NO_8P]^+$, 538.1625; found, 538.1624.

2.5. One-pot synthesis and characterization



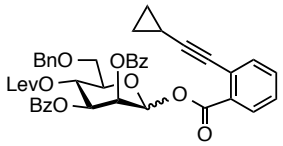
6-*O*-benzyl-2,3-di-*O*-benzoyl-4-*O*-levulinyl-*α/β*-D-mannopyranose (S8)



To a solution of **S7** (1.3 g, 1.9 mmol) in mixed acetone and H_2O (10 mL/2 mL) was added *N*-bromosuccinimide (NBS) (1.1 g, 3.0 equiv.) at room temperature. After stirred for 2 h, the mixture was quenched with aqueous $Na_2S_2O_3$, diluted with EtOAc, washed with H_2O, saturated $NaHCO_3$, brine and dried over Na_2SO_4. After filtration, the filtrate was concentrated to give a residue, which was purified via flash silica gel chromatography (Hexanes/EtOAc, 4/1→2/1) to give product **S8** (0.98 g, 89% yield). R_f= 0.2 (Hexanes/EtOAc, 2/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.29 (m, 15H, Ar*H*), 5.77 (dd, *J* = 10.1, 3.3 Hz, 1H, H-3), 5.67 (t, *J* = 10.0 Hz, 1H, H-4), 5.61 (dd, *J* = 3.3, 1.9 Hz, 1H, H-2), 5.41 (dd, *J* = 3.8, 1.9 Hz, 1H, H-1), 4.60 (q, *J* = 11.7 Hz, 2H, CH_2Ph), 4.37 (ddd, *J* = 10.0, 5.2, 3.1 Hz, 1H, H-5), 3.97 (bs, 1H, O*H*), 3.76-3.67 (m, 2H, H-6,

H-6'), 2.03 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 206.1, 171.9, 165.7, 165.6, 138.0, 133.5, 133.3, 130.0, 129.9, 129.51, 129.45, 128.6, 128.5, 128.2, 127.8, 92.3, 73.9, 71.0, 70.0, 69.9, 69.3, 67.2, 38.0, 29.7, 28.1; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{32}H_{33}O_{10}]^+$, 577.2068; found, 577.2068.

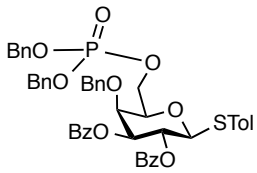
6-*O*-benzyl-2,3-di-*O*-benzoyl-4-*O*-levulinyl-*α/β*-D-mannopyranosyl *ortho*-cyclopropylethynylbenzoate (1p)



To a solution of **S8** (576 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) was added *ortho*-cyclopropylethynylalkynyl benzoic acid (279 mg, 1.5 mmol), DMAP (24 mg, 0.2 mmol) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCl) (344 mg, 1.8 mmol), respectively. After stirring for 4 h at room temperature, the reaction mixture was diluted with EtOAc, washed with H_2O, saturated $NaHCO_3$ and brine, dried over Na_2SO_4. After filtration, the filtrate was concentrated to give a residue. The residue was purified via flash silica gel chromatography (Hexanes/EtOAc, 6/1 → 3/1) to afford the donors (707 mg, 95% yield, α/β = 4.5/1). α-anomer: R_f = 0.25 (Hexanes/EtOAc, 2/1). $[\alpha]_D^{25}$ = -17.5 (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-7.28 (m, 19H, Ar*H*), 6.59 (d, *J* = 2.0 Hz, 1H, H-1), 5.97 (t, *J* = 9.9 Hz, 1H, H-4), 5.91 (dd, *J* = 10.2, 3.2 Hz, 1H, H-3), 5.82 (dd, *J* = 3.1, 2.0 Hz, 1H, H-2), 4.73-4.54 (m, 2H, CH_2Ph), 4.39 (dt, *J* = 9.7, 3.3 Hz, 1H, H-5), 3.88-3.73 (m, 2H, H-6, H-6'), 2.63-2.29 (m, 4H, CH_2CH_2COCH$_3$), 2.00 (s, 3H, CH_3), 1.59-1.56 (m, 1H, CH$_2$C*H*CH$_2$), 0.92-0.86 (m, 4H, CH_2CHCH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 206.0, 171.7, 165.6, 165.3, 163.8, 138.3, 134.9, 133.6, 133.4, 132.5, 131.0, 130.4, 130.1, 130.0, 129.3, 129.2, 128.7, 128.5, 128.4, 128.0, 127.6, 127.4, 125.3, 100.4, 91.7, 74.7, 73.8, 72.7, 70.2, 69.5, 68.7, 66.6, 37.9, 29.7, 28.0, 9.2, 9.2, 0.9; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{44}H_{40}NaO_{11}]^+$, 767.2463; found, 767.2461. β-anomer: R_f = 0.2 (Hexanes/EtOAc, 2/1). $[\alpha]_D^{25}$ = -100 (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.30 (d, *J* = 1.1 Hz, 1H, H-1), 5.99 (dd, *J* = 3.2, 1.1 Hz, 1H, H-2), 5.83 (t, *J* = 9.9 Hz, 1H, H-4), 5.56 (dd, *J* = 10.0, 3.2 Hz, 1H, H-3), 4.74-4.49 (m, 2H, CH_2Ph), 4.03 (ddd, *J* = 9.8, 4.3, 2.9 Hz, 1H, H-5), 3.85 (dd, *J* = 11.1, 2.9 Hz, 1H, H-6), 3.79 (dd, *J* = 11.1, 4.4 Hz, 1H, H-6'), 2.62-2.33 (m, 4H, CH_2CH_2COCH$_3$), 2.01 (s, 3H, CH_3), 1.50-1.43 (m, 1H, CH$_2$C*H*CH$_2$), 0.86-0.82 (m, 4H, CH_2CHCH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 206.0, 171.7, 165.7, 165.6, 163.2, 138.2, 134.3, 133.49, 133.47, 132.3, 130.8, 130.2, 130.0, 129.9, 129.5, 129.1, 128.6, 128.5,

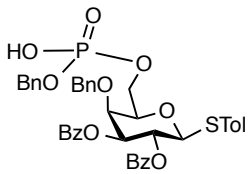
128.4, 128.0, 127.7, 127.0, 125.8, 100.5, 91.4, 74.9, 74.3, 73.8, 71.9, 69.5, 68.8, 66.6, 37.9, 29.6, 28.1, 9.1, 0.8; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{44}H_{40}NaO_{11}]^+$, 767.2463; found, 767.2461.

***p*-tolyl 4-*O*-benzyl-2,3-di-*O*-benzoyl-6-*O*-dibenzyloxyphosphoryl-1-thio-*β*-D-galactopyranoside (S9)**



S9 was prepared via procedure (D), purified via flash column on silica gel (Hexanes/EtOAc, 3/1 to 3/2), R_f= 0.2 (Hexanes/EtOAc, 3/2), white foam, 500 mg, 97% yield; $[\alpha]_D^{25}$ = 45.7 (*c* 2.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96-7.01 (m, 30H, Ar*H*), 5.77 (t, *J* = 9.9 Hz, 1H, H-2), 5.33-5.25 (m, 1H, H-3), 5.09-4.97 (m, 4H, 2x CH_2Ph), 4.77 (d, *J* = 10.0 Hz, 1H, H-1), 4.63 (d, *J* = 11.4 Hz, 1H, C*H*Ph), 4.42 (d, *J* = 11.4 Hz, 1H, C*H*Ph), 4.21 (ddd, *J* = 10.4, 8.2, 6.4 Hz, 1H), 4.03 (dd, *J* = 13.0, 4.9 Hz, 2H, H-4), 3.73 (t, *J* = 6.5 Hz, 1H, H-5), 2.29 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.9, 165.3, 138.3, 137.6, 135.9, 135.8, 133.6, 133.3, 130.0, 129.9, 129.7, 129.1, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 128.2, 127.9, 127.8, 127.8, 127.1, 86.9, 76.7, 75.7, 75.0, 73.8, 69.7 (2C, d, *J* =5.3 Hz), 68.4, 65.3 (d, *J* = 5.3 Hz), 21.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -1.0; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{48}H_{46}O_{10}PS]^+$, 845.2544; found, 845.2539.

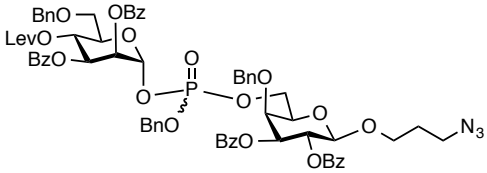
***p*-tolyl 4-*O*-benzyl-2,3-di-*O*-benzoyl-6-*O*-(benzyloxy-hydroxy-phosphoryl)-1-thio-*β*-D-galactopyranoside (2h)**



2h was prepared via the general procedure (E), R_f = 0.25 (CH_2Cl_2/MeOH, 10/1), white solid, 200 mg, 86% yield; $[\alpha]_D^{25}$ = 66.4 (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.01 (m, 35H, Ar*H*), 5.78 (t, *J* = 10.0 Hz, 1H, H-2), 5.32 (dd, *J* = 10.0, 2.9 Hz, 1H, H-3), 5.07-4.99 (m, 2H, CH_2Ph), 4.80 (d, *J* = 9.9 Hz, 1H, H-1), 4.62 (d, *J* = 11.3 Hz, 1H, C*H*Ph), 4.46 (d, *J* = 11.3 Hz, 1H, C*H*Ph), 4.24 (dt, *J* = 10.2, 6.6 Hz, 1H, H-6), 4.12-4.07 (m, 2H, H-4, H-6'), 3.84 (t, *J* = 6.5 Hz, 1H, H-5), 2.28 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.9, 165.3, 138.3, 137.7, 133.5, 133.3, 133.2, 130.0, 129.9, 129.8, 129.7, 129.1, 128.8, 128.7, 128.6, 128.6, 128.4, 128.4, 128.1, 128.0, 127.8, 86.7,

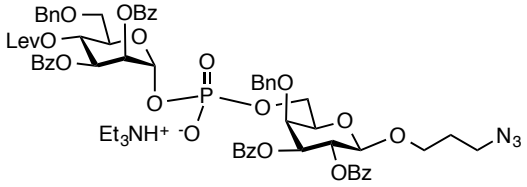
76.6, 75.8, 75.0, 73.7, 69.5 (d, J = 4.9 Hz), 68.4, 65.1 (d, J = 5.1 Hz), 21.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ = 0.4; HR ESI-MS: $[M\text{-}H^+]^-$ calcd for $[C_{41}H_{38}O_{10}PS]^-$, 753.1929; found, 753.1928.

3-azidopropanyl 6-*O*-benzyl-2,3-di-*O*-benzoyl-4-*O*-levulinyl-*α*-D-mannopyranosyl benzyloxyphosphoryl-(→6)-4-*O*-benzyl-2,3-di-*O*-benzoyl-*β*-D-galactopyranoside (5)



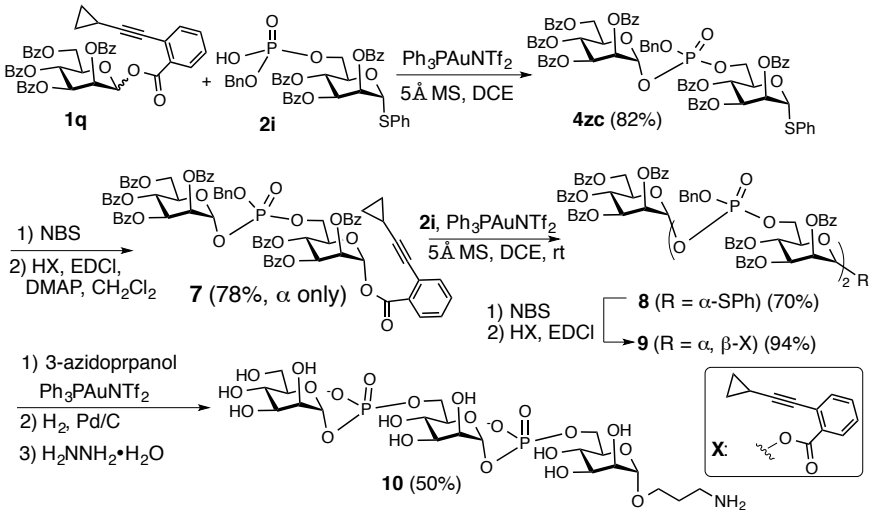
To a solution of donor **1p** (55.9 mg, 0.075 mmol) and acceptor **2h** (37.7 mg, 0.05 mmol) in $ClCH_2CH_2Cl$ (1.0 mL) was added $Ph_3PAuNTf_2$ (3.7 mg, 0.005 mmol) at 0 °C. After stirring for 0.5 h, the reaction was stirred at room temperature for 2 h. Then, the reaction mixture was cooled to -55 °C, and NIS (22 mg, 0.1 mmol) and TMSOTf (0.9 μL, 0.005 mmol) was subsequently added to the mixture at -55 °C. After warming up to -30 °C in one hour, the reaction was quenched with Et_3N (1.0 mL) and aqueous $Na_2S_2O_3$. After filtration, the filtrate was concentrated to give a residue, which was loaded to a silica gel column which was neutralized prior to use by using Hexanes/Et_3N (100/1), and purified (eluting solvent: Hexanes/EtOAc/Et_3N, 3/2/0.01) to give desired product **5** (43.2 mg, 67% yield). R_f= 0.2 (Hexanes/EtOAc, 3/2). mixture of *R* and *S* anomers (R_P : S_P = 1/1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91-5.64 (m, 5H, H-2^A, H-3^A, H-1^B, H-2^B, H-4^B), 5.40-5.34 (m, 1H, H-3^B), 5.21-5.14 (m, 2H, CH_2Ph), 4.73-4.49 (m, 5H, 2 x CH_2Ph, H-1^A), 4.39-4.26 (m, 2H, H-6^A, H-5^B), 4.23-4.10 (m, 2H, H-6'^{A}, H-4^A), 4.00-3.88 (m, 2H, OCH(H)CH_2, H-5^A), 3.77-3.65 (m, 2H, H-6^B, H-6'^{B}), 3.57-3.50 (m, 1H, OCH(H)CH_2), 3.20-3.11 (m, 2H, CH_2N_3), 2.67-2.34 (m, 2H, CH_2CH_2COCH_3), 2.02 (s, 3H, CH_3), 1.77-1.58 (m, 2H, CH_2CHCH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 205.82, 205.79, 171.6, 165.8, 165.7, 165.5, 165.4, 165.2, 165.1, 138.2, 138.1, 137.43, 137.39, 135.5, 135.32, 135.25, 133.64, 133.59, 133.41, 133.38, 133.3, 133.2, 130.0, 129.92, 129.88, 129.7, 129.6, 129.2, 129.09, 129.06, 129.0, 128.9, 128.84, 128.80, 128.65, 128.61, 128.52, 128.50, 128.45, 128.42, 128.37, 128.24, 128.19, 127.91, 127.87, 127.6, 101.42, 101.39, 95.5, 95.4, 75.1, 74.2, 73.7, 73.65, 73.61, 73.4, 73.1, 73.0, 72.1, 72.0, 70.3, 70.2, 70.1, 69.8, 69.7, 69.42, 69.36, 68.4, 68.3, 66.5, 66.3, 65.9, 48.0, 37.9, 29.5, 29.0, 27.94, 27.92; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -3.1, -3.3; HR ESI-MS: $[M+Na^+]^+$ calcd for $[C_{69}H_{68}N_3NaO_{20}P]^+$, 1312.4026; found, 1312.4031.

3-azidopropanyl 6-*O*-benzyl-2,3-di-*O*-benzoyl-4-*O*-levulinyl-*α*-D-mannopyranosyl phosphoryl-(→6)-4-*O*-benzyl-2,3-di-*O*-benzoyl-*β*-D-galactopyranosyl phosphate triethylammonium salt (6)

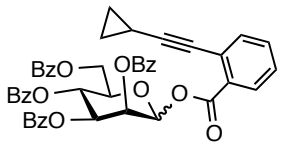


6 was prepared via procedure (E) and converted to triethylammonium salt by washing with triethylammonium bicarbonate buffer (1.0 M), R_f = 0.2 (CH_2Cl_2/MeOH, 8/1), colorless oil, 42.3 mg, 97% yield; $[\alpha]_D^{25}$ = -9.2 (*c* 4.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.11 (m, 30H, Ar*H*), 5.87 (t, *J* = 9.9 Hz, 1H, H-2^A), 5.82-5.754 (m, 4H, H-1^B, H-2^B, H-4^B, H-3^A), 5.40 (dd, *J* = 10.5, 3.1 Hz, 1H, H-3^B), 4.75-4.67 (m, 3H, C*H*$_2$Ph, H-1^A), 4.61 (d, *J* = 11.7 Hz, 1H, C*H*Ph), 4.51 (d, *J* = 11.7 Hz, 1H, C*H*Ph), 4.45 (dt, *J* = 9.8, 3.3 Hz, 1H, H-5^B), 4.39-4.33 (m, 2H, H-4^A, H-6^A), 4.27-4.20 (m, 1H, H-6'^{A}), 4.14 (t, *J* = 6.7 Hz, 1H, H-5^A), 3.96 (dt, *J* = 10.5, 5.4 Hz, 1H, OC*H*(H)CH$_2$), 3.73 (d, *J* = 3.3 Hz, 2H, H-6^B, H-6'^{B}), 3.57 (ddd, *J* = 9.9, 8.0, 4.6 Hz, 1H, OC*H*(H)CH$_2$), 3.17 (td, *J* = 6.8, 2.3 Hz, 2H, C*H*$_2$N$_3$), 2.60-2.35 (m, 4H, C*H*$_2$C*H*$_2$COCH$_3$), 2.01 (s, 3H, C*H*$_3$), 1.79-1.63 (m, 2H, OCH$_2$C*H*$_2$CH$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 206.0, 171.7, 165.8, 165.7, 165.52, 165.47, 138.4, 138.2, 133.3, 133.21, 133.16, 133.1, 130.0, 129.93, 129.87, 129.7, 129.54, 129.51, 129.3, 128.6, 128.44, 128.41, 128.39, 128.36, 128.2, 128.1, 128.0, 127.53, 127.49, 101.4, 93.9 (d, *J* = 4.6 Hz), 75.3, 74.5, 74.4, 73.8 (d, *J* = 6.6 Hz), 73.6, 70.9, 70.7 (d, *J* = 7.2 Hz), 70.5, 70.4, 69.0, 66.6, 66.3, 63.7 (d, *J* = 5.2 Hz), 48.1, 38.0, 29.6, 29.0, 28.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.9; HR ESI-MS: [M-Et$_3$NH$^+$]$^-$ calcd for [$C_{62}H_{61}N_3O_{20}P$]$^-$, 1198.3592; found, 1198.3586.

2.6. Synthesis of trisaccharide and characterization

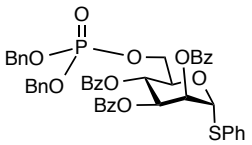


2,3,4,6-tetra-*O*-benzoyl-*α/β*-D-mannopyranosyl *ortho*-cyclopropylethynylbenzoate (1q)



1q, prepared via procedure (C), purified via silica gel chromatography (Hexanes/EtOAc, 3/1), R_f= 0.2 (Hexanes/EtOAc, 3/1), white foam, 860 mg, 90 % yield, α/β = 3/1. α anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-7.25 (m, 24H, Ar*H*), 6.65 (d, *J* = 2.2 Hz, 1H), 6.28 (t, *J* = 9.9 Hz, 1H, H-4), 6.12 (dd, *J* = 10.3, 3.1 Hz, 1H, H-3), 5.94 (bs, 1H, H-2), 4.75-4.50 (m, 3H, H-5, H-6, H-6'), 1.62-1.43 (m, 1H, CH_2CHCH_2), 0.92-0.83 (m, 4H, CH_2CHCH_2); β anomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-7.25 (m, 24H, Ar*H*), 6.44 (s, 1H), 6.28-6.11 (m, 2H, H-3, H-4), 5.80 (dd, *J* = 10.0, 3.2 Hz, 1H, H-2), 4.78-4.51 (m, H-6, H-6'), 4.42-4.29 (m, 1H, H-5), 1.62-1.43 (m, 1H, CH_2CHCH_2), 0.92-0.83 (m, 4H, CH_2CHCH_2); mixture of α and β anomers: ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.25, 166.21, 165.7, 165.61, 165.59, 165.46, 165.42, 165.3, 163.9, 163.2, 134.8, 134.3, 133.8, 133.7, 133.62, 133.58, 133.50, 133.4, 133.2, 132.6, 132.4, 130.91, 130.87, 130.4, 130.13, 130.08, 129.97, 129.94, 129.91, 128.87, 129.84, 129.6, 129.2, 129.0, 128.93, 128.87, 128.79, 128.73, 128.61, 128.57, 128.49, 127.5, 127.0, 125.8, 125.3, 100.6, 100.4, 91.8, 91.4, 74.7, 73.5, 71.8, 71.4, 70.1, 69.7, 69.6, 66.6, 62.9, 62.5, 9.2, 9.1, 0.9, 0.8; HR ESI-MS: $[M+Na^+]^+$calcd for $[C_{46}H_{36}NaO_{11}]^+$, 787.2150; found, 787.2148.

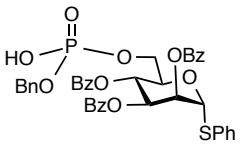
phenyl 2,3,4-tri-*O*-benzoyl-6-*O*-dibenzyloxyphosphoryl-1-thio-*α*-D-mannopyranoside (S10)



S10, prepared via procedure (D), purified via silica gel chromatography (Hexanes/EtOAc, 2/1→3/2), R_f= 0.2 (Hexanes/EtOAc, 3/2), 600 mg, 95% yield. $[\alpha]_D^{25}$ = -6.0 (*c* 2.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-7.19 (m, 30H, Ar*H*), 5.99 (t, *J* = 10.0 Hz, 1H, H-4), 5.93 (dd, *J* = 3.2, 1.6 Hz, 1H, H-2), 5.81 (dd, *J* = 10.0, 3.2 Hz, 1H, H-3), 5.68 (d, *J* = 1.6 Hz, 1H, H-1), 4.99-4.86 (m, 4H, 2 x CH_2Ph), 4.87-4.81 (m, 1H, H-5), 4.31-4.22 (m, 2H, H-6, H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.54, 165.50, 165.47, 135.9, 135.8, 135.7, 133.7, 133.5, 132.8, 132.6, 130.0, 129.9, 129.4, 129.3, 129.0, 128.9, 128.8, 128.7, 128.62, 128.57, 128.52, 128.49, 128.4, 128.1, 127.9,

86.2, 72.1, 70.7 (d, J = 8.4 Hz), 70.5, 69.5 (d, J = 2.4 Hz), 69.4 (d, J = 2.4 Hz), 66.8, 66.0 (d, J = 5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ = -1.4; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{47}H_{42}O_{11}PS]^-$, 845.2180; found, 845.2178.

phenyl 2,3,4-tri-*O*-benzoyl-6-*O*-(benzyloxy-hydroxy-phosphoryl)-1-thio-*α*-D-mannopyranoside (2f)



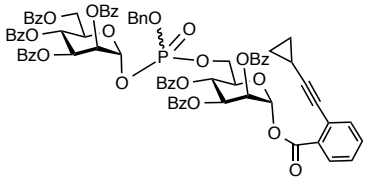
2f, prepared via procedure (E), R_f = 0.2 (CH_2Cl_2/MeOH, 10/1), white solid, 189 mg, 75% yield. $[\alpha]_D^{25}$ = -10.1 (*c* 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-7.16 (m, 25H, Ar*H*), 6.01-5.88 (m, 2H, H-2, H-4), 5.84-5.74 (m, 4H, H-3, OH), 5.63 (s, 1H, H-1), 4.87 (dd, J = 7.1, 2.0 Hz, 2H, CH_2Ph), 4.81 (d, J = 6.7 Hz, 1H, H-5), 4.27-4.17 (m, 2H, H-6, H-6'); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.6, 165.5, 135.8, 135.7, 133.72, 133.65, 133.4, 132.73, 132.69, 130.1, 130.0, 129.9, 129.5, 129.3, 129.01, 128.97, 128.8, 128.6, 128.52, 128.48, 128.4, 127.8, 86.2, 71.9, 70.7 (d, J = 8.7 Hz), 70.6, 69.2 (d, J = 5.4 Hz), 66.9, 66.0 (d, J = 4.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ = 0.49; HR ESI-MS: $[M+H^+]^+$ calcd for $[C_{40}H_{36}O_{11}PS]^+$, 755.1710; found, 755.1709.

phenyl 2,3,4,6-tetra-*O*-benzoyl-*α*-D-mannopyranosyl-benzyloxyphosphoryl-(→6)-2,3,4-tri-*O*-benzoyl-1-thio-*α*-D-mannopyranoside (4zc)

4zc, prepared via procedure (A), R_f = 0.2 (Hexanes/EtOAc, 3/2), colorless oil, 350 mg, 82% yield. The hydrogenated form of **4zc** via procedure (B) is here characterized instead of **4zc**. **4zc-H2**: $[\alpha]_D^{25}$ = -21.1 (*c* 2.3 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.04 (m, 35H, Ar*H*), 6.05 (t, J = 10.1 Hz, 1H, H-4^B), 5.92-5.88 (m, 3H, H-2^B, H-3^B, H-4^A), 5.79-5.72 (m, 3H, H-1^B, H-2^A, H-3^A), 5.65 (s, 1H, H-1^A), 4.97-4.87 (m, 1H, H-5^A), 4.60-4.50 (m, 2H, H-5^B, H-6^B), 4.33-4.23 (m, 2H, H-6^A, H-6'^{A}), 4.12 (d, J = 11.9 Hz, 1H, H-6'^{B}); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.1, 165.7, 165.6, 165.4, 165.2, 133.4, 133.3, 133.2, 133.1, 133.0, 132.9, 130.2, 130.1, 130.0, 129.94, 129.89, 129.84, 129.7, 129.5, 129.43, 129.35, 129.3, 129.25, 129.21, 128.62, 128.57, 128.5, 128.4, 128.3, 128.2, 94.0 (d, J = 4.5 Hz), 86.2, 72.1, 71.8 (d, J = 8.8 Hz), 71.0, 70.8 (d, J = 8.6 Hz), 70.3, 69.5, 67.4, 66.6, 65.1 (d, J = 4.9 Hz), 62.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ =

-3.2; HR ESI-MS: [M-Et_3NH^++Na^++H^+]$^+$calcd for [$C_{67}H_{55}NaO_{20}PS$]$^+$, 1265.2637; found, 1265.2644.

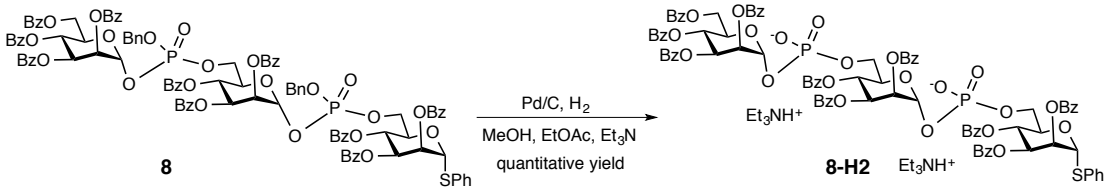
2,3,4,6-tetra-*O*-benzoyl-*α*-D-mannopyranosyl-benzyloxyphosphoryl-(→6)-2,3,4-tri-*O*-benzoyl-*α*-D-mannopyranosyl *ortho*-cyclopropylethynylbenzoate (7)



To a solution of compound **4zc** (300 mg, 0.22 mmol) in acetone/H_2O (10 mL/2 mL), *N*-bromosuccinimide (NBS) (313 mg, 1.76 mmol) was added at room temperature. After stirring for 0.5 h, the reaction was quenched with aqueous saturated $Na_2S_2O_3$ and $NaHCO_3$, and diluted with EtOAc, washed with H_2O, brine and dried over Na_2SO_4. After filtration, the filtrate was concentrated *in vacuo* to give a yellow residue. The resulting residue was loaded to silica gel column which was neutralized with solvent (Hexanes/Et_3N, 100/1), and purified with solvent (Hexanes/EtOAc/Et_3N, 4/1/0.01→ Hexanes/EtOAc/acetone/Et_3N 2/1/1/0.01) to give product (256 mg, 92%). The above product was next installed *ortho*alkynyl benzoate to form glycsoysl donor. To a solution of disaccharide (256 mg, 0.21 mmol) in CH_2Cl_2 (2 mL) was added *ortho*-alkynyl benzoic acid (57 mg, 0.32 mmol), DMAP (5 mg, 0.04 mmol) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCl) (71 mg, 0.37 mmol), respectively. After stirred for 2 h, the reaction mixture was diluted with EtOAc, washed with H_2O, saturated $NaHCO_3$ and brine, dried over Na_2SO_4. After filtration, the filtrate was concentrated to give a residue. The residue was loaded to silica gel column which was neutralized prior to use by using solvent (Hexanes/Et_3N, 100/1), and purified by eluting with solvent (Hexanes/EtOAc/Et_3N, 3/1/0.01 to 2/1/0.01) to afford the α/β mixed donors **7** (247 mg, 78% over two steps). R_f= 0.2 (Hexanes/EtOAc, 2/1). $[\alpha]_D^{25}$ = -32 (*c* 0.17 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15-8.72 (m, 78H, Ar*H*), 6.72 (s, 1H, H-1), 6.64 (s, 1H, H-1^{epimer}), 6.22-5.76 (m, 14H, H-1^B, H-1^{Bepimer}, H-2^A, H-3^A, H-4^A, H-2^B, H-3^B, H-4^B, H-2^{Aepimer}, H-3^{Aepimer}, H-4^{Aepimer}, H-2^{Bepimer}, H-3^{Bepimer}, H-4^{Bepimer}), 5.31-5.18 (m, 4H, 4 x C*H*Ph), 4.71-4.28 (m, 12H, H-6^A, H-6'^{A}, H-6^{Aepimer}, H-6'^{Aepimer}, H-6^B, H-6'^{B}, H-6^{Bepimer}, H-6'^{Bepimer}, H-5^A, H-5^B, H-5^{Aepimer}, H-5^{Bepimer},), 1.64-1.55 (2H, 2 x CH_2CHCH_2), 0.91-0.80 (m, 8H, 2 x CH_2CHCH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.0, 165.49, 165.45, 165.4, 165.33, 165.29, 164.95, 164.91, 163.8, 135.6, 135.5, 135.3, 135.2, 134.79, 134.76, 133.73, 133.68, 133.65, 133.58, 133.51, 133.4, 133.2,

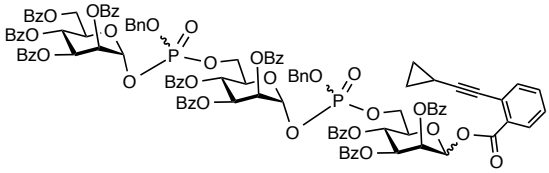
133.0, 132.5, 132.4, 131.0, 130.9, 130.3, 130.1, 130.03, 129.96, 129.90, 129.87, 129.83, 129.2, 129.1, 129.04, 129.00, 128.96, 128.79, 128.76, 128.72, 128.66, 128.55, 128.50, 128.46, 128.42, 128.35, 128.30, 128.2, 127.4, 127.3, 125.2, 100.4, 100.3, 95.6, 95.5, 91.70, 91.67, 74.8, 74.7, 72.0, 71.9, 70.7, 70.6, 70.42, 70.36, 70.0, 69.9, 69.8, 69.7, 69.5, 69.44, 69.37, 66.52, 66.45, 66.38, 66.0, 62.14, 62.08, 9.2, 9.1, 0.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -3.1, -3.44; HR ESI-MS: $[M+Na^+]^+$calcd for $[C_{80}H_{65}NaO_{22}P]^+$, 1431.3597; found, 1431.3597.

phenyl 2,3,4,6-tetra-*O*-benzoyl-*α*-D-mannopyranosyl-benzyloxyphosphoryl-(→6)-2,3,4-tri-*O*-benzoyl-*α*-D-mannopyranosyl-benzyloxyphosphoryl-(→6)-2,3,4-tri-*O*-benzoyl-1-thio-*α*-D-mannopyranoside (8)



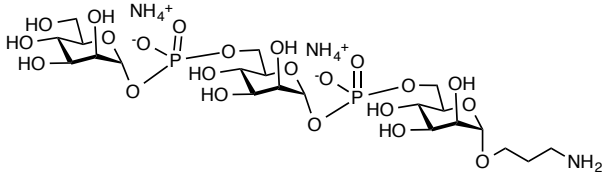
8, prepared via procedure (A) and (B), R_f= 0.3 (Hexanes/EtOAc, 3/2), white foam, 177 mg, 70% yield. Because there are four unseparated diastereomers which causing difficulty in characterization, benzyl groups of compound **8** were removed quantitatively via hydrogenolysis with Pd/C in mixed solvent of MeOH/EtOAc/Et_3N to afford a single stereomer (**8-H2**). **8-H2** is characterized as follows: $[\alpha]_D^{25}$ = -40.9 (*c* 2.2 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.02 (m, 45H, Ar*H*), 6.08-5.65 (m, 12H, H-1^A, H-2^A, H-3^A, H-4^A, H-1^B, H-2^B, H-3^B, H-4^B, H-1^C, H-2^C, H-3^C, H-4^C), 4.94-4.54 (m, 3H, H-5^A, H-5^B, H-5^C), 4.49-4.14 (m, 6H, H-6^A, H-6'^{A}, H-6^B, H-6'^{B}, H-6^C, H-6'^{C}); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.1, 165.72, 165.67, 165.59, 165.57, 165.45, 165.3, 165.23, 165.18, 165.08, 133.40, 133.36, 133.24, 133.18, 133.08, 133.01, 132.97, 132.8, 130.3, 130.15, 130.12, 130.0, 129.93, 129.90, 129.82, 129.78, 129.68, 129.58, 129.47, 129.41, 129.29, 129.25, 129.21, 128.7, 128.60, 128.56, 128.50, 128.44, 128.37, 128.32, 128.2, 93.9, 93.87, 93.79, 93.74, 86.1, 72.1, 71.75, 71.67, 71.1, 70.9, 70.2, 69.5, 67.6, 67.5, 66.7, 65.4, 65.0, 62.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -3.3, -3.7; HR ESI-MS: $[M-2Et_3NH^+]^{2-}$ calcd for $[C_{94}H_{76}O_{31}P_2S]^{2-}$, 897.1789; found, 897.1787.

2,3,4,6-tetra-*O*-benzoyl-*α*-D-mannopyranosyl-benzyloxyphosphoryl-(→6)-2,3,4-tri-*O*-benzoyl-*α*-D-mannopyranosyl-benzyloxyphosphoryl-(→6)-2,3,4-tri-*O*-benzoyl-*α/β*-D-mannopyranosyl *ortho*-cyclopropylethynylbenzoate (9)



9, was prepared by using a similar procedure as that for compound **7**, and purified via silica gel column which was neutralized by Hexanes/Et_3N (100/1) (eluting solvent: Hexanes/EtOAc/Et_3N, 3/1/0.01 to 2/1/0.01), R_f = 0.2 (Hexanes/EtOAc, 3/2), white foam, 107 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-7.14 (m, 64H, Ar*H*), 6.69-6.45 (m, 1H, H-1^A), 6.2-5.7 (m, 11H, H-2^A, H-3^A, H-4^A, H-1^B, H-2^B, H-3^B, H-4^B, H-1^C, H-2^C, H-3^C, H-4^C), 5.28-5.06 (m, 4H, 2 x C*H*$_2$Ph), 4.70-4.20 (m, 9H, H-5^A, H-6^A, H-6'^{A}, H-5^B, H-6^B, H-6'^{B}, H-5^C, H-6^C, H-6'^{C}); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.01, 165.81, 165.55, 165.44, 165.37, 165.3, 164.9, 135.6, 135.4, 135.3, 134.8, 134.3, 133.8, 133.7, 133.6, 133.5, 133.4, 133.3, 133.24, 133.21, 133.08, 132.4, 131.04, 130.95, 130.42, 130.37, 130.2, 130.14, 130.7, 130.00, 129.93, 129.88, 129.3, 129.22, 129.17, 129.10, 129.06, 129.0, 128.9, 128.84, 128.79, 128.73, 128.70, 128.65, 128.62, 128.55, 128.51, 128.45, 128.40, 128.36, 128.31, 128.29, 128.25, 127.43, 127.38, 125.3, 100.4, 100.3, 95.6, 91.8, 74.8, 72.0, 71.2, 70.7, 70.61, 70.56, 70.4, 70.3, 70.1, 69.7, 69.6, 69.4, 66.4, 66.3, 66.1, 65.8, 62.0, 9.2, 0.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -2.9, -3.0, -3.1, -3.2, -3.3, -3.3, -3.4, -3.5; HR ESI-MS: $[M+H^+]^+$calcd for $[C_{114}H_{95}O_{33}P_2]^+$, 2053.5225; found, 2053.2539.

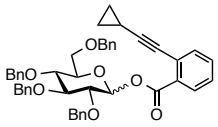
3-aminopropanyl *α*-D-mannopyranosyl-phosphoryl-(→6)-*α*-D-mannopyranosyl-phosphoryl-(→6)-*α*-D-mannopyranoside bis-ammonium salt (10)



Glycosylation reaction. To a solution of donor **9** (67 mmol, 0.033 mmol) and 3-azido-propanol (6.6 mg, 0.066 mmol) in $ClCH_2CH_2Cl$ (0.6 mL) was added $Ph_3PAuNTf_2$ (2.4 mg, 0.0033 mmol) at 0 °C. After stirring for 0.5 h, the reaction was stirred at room temperature for 2 h. Then, the mixture was filtrated, and the filtrate was concentrated to give a residue, which was loaded to a silica gel column which was neutralized prior to use by using Hexanes/Et_3N (100/1), and purified (eluting solvent: Hexanes/EtOAc/Et_3N, 3/1/0.01→Hexanes/EtOAc/acetone/Et_3N, 2/1/0.5/0.01) to give the desired product of linker-tethered trisaccharide (45 mg, 70% yield).

Deprotection. To a solution of protected trisaccharide (20 mg) in THF/^{t}BuOH (1.0 mL/2.0 mL) was added $HCOONH_4$ (14 mg), HCOOH (30 μL) and Pd/C (60 mg). Then, the mixture was stirred under an atmosphere of H_2 at room temperature for 5 h. After filtration through syringe filter, the filtrate was concentrated to give a residue. The resulting residue was dissolved in MeOH/NH_2NH_2•H_2O (1.0 mL/0.4 mL), and the resulting mixture was stirred for 12 h at room temperature, after which the solvent was removed via evaporation to provide the crude product. Afterwards, the product was purified via P2 polyacrylamide gel column (45x0.7 cm, eluent: 10 mM aqueous NH_4HCO_3) to give deprotected amino-tethered trisaccharide **10** (5.2 mg, 71%). $[\alpha]_D^{25}$ = -306 (*c* 0.26 $CHCl_3$); ^{1}H NMR (800 MHz, D_2O) δ 5.44-5.21 (m, 2H), 4.78 (s, 1H), 4.19-4.11 (m, 1H), 4.06 (dd, *J* = 5.5, 3.1 Hz, 2H), 3.97-3.90 (m, 3H), 3.86 (dd, *J* = 3.4, 1.7 Hz, 1H), 3.84-3.76 (m, 5H), 3.75-3.67 (m, 5H), 3.60 (t, *J* = 9.8 Hz, 1H), 3.57-3.54 (m, 2H), 3.13-2.99 (m, 2H), 1.93 (p, *J* = 6.7 Hz, 2H); ^{13}C NMR (201 MHz, D_2O) δ = 99.9, 96.2, 96.2, 73.7, 72.6, 71.9, 70.5, 70.46, 70.45, 70.41, 69.9, 69.8, 69.7, 66.5, 66.3, 65.8, 65.2, 65.1, 64.5, 60.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ = -1.8, -2.0; HR ESI-MS: $[M-2NH_4^+ + H^+]^-$calcd for $[C_{21}H_{40}NO_{22}P_2]^-$, 720.1523; found, 720.1521.

3. The reported compounds and related references



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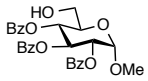

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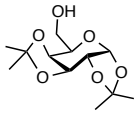

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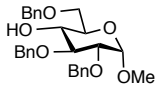

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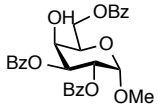

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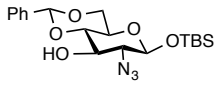

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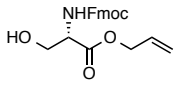

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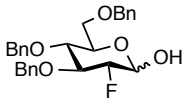

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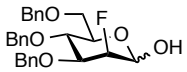

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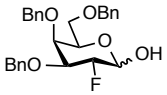

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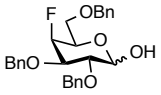

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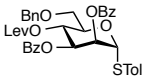

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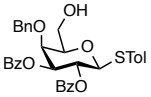

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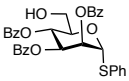

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