# Supplementary Information

## A new approach to construct full-length glycosylphosphatidylinositols of parasitic protozoa and [4-deoxy-Man-III]-GPI analogues

Asif Ali[a], D. Channe Gowda[b] and Ram A. Vishwakarma*[a]

[a] *Bio-organic Chemistry Laboratory, National Institute of Immunology, JNU Complex, New Delhi, India Fax: 91-11-26162125; Tel: 91-11-26717178; E-mail: ram@nii.res.in*

[b] *Deparment of Biochemistry and Molecular Biology, Pennsylvania State University College of Medicine, Hershey, PA 17033, USA*

**General Experimental Procedures:**

Solvents were purified according to the standard procedures, and reagents used were of highest purity available. All reactions were performed in flame-dried glass apparatus under argon atmosphere unless mentioned otherwise. Anhydrous solvents like $CH_2Cl_2$, $Et_2O$, THF, $CH_3OH$, $CH_3CN$, DMF, pyridine, $Et_3N$ were freshly dried using standard methods. NMR measurements ($^1H$, $^{13}C$, $^{31}P$, 2D $^1H$-$^1H$ and $^1H$-$^{13}C$ COSY, HMQC) were recorded on a 300 MHz spectrometer (Bruker) fitted with pulse-field gradient probe, and trimethylsilane (TMS) or residual resonance of deuterated solvent were used as internal reference. For $^{31}P$ NMR spectra, phosphoric acid was used as external reference. $^{13}C$ NMR spectra were broadband $^1H$ decoupled or inverse HMQC experiments. Chemical shifts are expressed in ppm and coupling constants *J* in Hz. Mass-spectra (ESI) and high-resolution mass-spectra (HRMS) were obtained on quadrupole and LCT-TOF (time of flight) spectrometers respectively using acetonitrile-water (1:1) mobile phase. Optical rotations were measured on a digital Perkin-Elmer 241 polarimeter. Analytical TLC was performed on Merck Kieselgel 60 $F_{254}$ plates, and compounds visualized by ammonium-molybdate/ceric-sulfate developing reagent. Preparative TLC was conducted on Analtech Uniplate silica-gel plates (20 x 20 cm). Silica column chromatography was carried out with silica gel 60 (60-120 mesh) or flash silica gel (230-400 mesh). Analytical and semi-preparative HPLC purification were carried out on a Shimadzu system using RP-18 columns and a photodiode array detector system.

**2,3,4,5-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-(DL)-*myo*-inositol** (**7**). A solution of racemic 2,3:4,5-di-O-cyclohexylidene-*myo*-inositol (34 g, 100 mmol, prepared by a reported[1] method) and dibutyl tinoxide (24 g 93 mmol) in anhydrous $CH_3OH$ (200 mL) was heated to reflux for 4 h. Excess of solvent was removed and the residue was dried by repeated evaporation through toluene. The residue was dissolved in anhyd DMF (150 mL) followed by the addition of pre-dried CsF (20 g, 120 mmol), KI (20 g, 120 mmol) and PMBCl (25 mL, 184 mmol). The suspension was vigorously stirred for 24 h at rt. The solvent was removed under reduced pressure and the residue was purified by silica column chromatography (85:15 to 70:30 hexane/EtOAc) to provide two known[2] regio-isomers: 2,3:4,5-di-*O*-cyclohexylidene-6-*O*-(p-methoxybenzyl)-(DL)-*myo*-inositol (16 g, 38%, Rf = 0.43 in 20% EtOAc-hexane) and 2,3:4,5-di-*O*-cyclohexylidene-1-*O*-(p-methoxybenzyl)-(DL)-*myo*-inositol (18 g, 43%, Rf = 0.2 in 20% EtOAc-hexane). The desired more polar isomer (13.2 g, 28.6 mmol) was dissolved in anhyd DMF (250 mL) and solution was brought to 0 $^oC$ and then NaH (4.3 g) and allyl bromide (10 mL) were added. The reaction mixture was stirred for 3 h at room temperature and brine (500 mL) was added, and extracted with diethyl ether (250 mL x 4). The organic extract was dried over anhyd $Na_2SO_4$, concentrated and the residue was purified by a silica column to give 6-*O*-allyl-2,3,4,5-di-*O*-cyclohexylidene-1-*O*-(4-methoxybenzyl)-(DL)-*myo*-inositol (14 g, 99% yield). The above bis-ketal (14 g, 28 mmol) was dissolved in a mixture of $CH_3OH$-$CH_2Cl_2$ (1:1) followed by the addition of pTSA (1 g). The reaction was stirred for 24 h at room temperature, neutralized with triethylamine, concentrated and purified by a silica column (toluene/methanol, 3:1) to give 6-*O*-allyl-1-*O*-(4-methoxybenzyl)-(DL)-*myo*-inositol in (8.5 g, 90% yield). TLC (toluene/MeOH, 3:1): $R_f$ = 0.21; $^1$H NMR (300 MHz, $CD_3OD$): 3.19-3.34 (m, 3H), 3.60 (m, 2H), 3.71 (s, 3H, OMe), 4.08 (m, 1H), 4.29-4.34 (m, 2H, allyl), 4.52-4.65 (m, 2H, $CH_2Ph$), 5.07-5.29 (m, 2H, allyl), 5.94-6.04 (m, 1H, allyl), 6.83-6.92 (m, 2H, Ph), 7.30-7.35 (m, 2H, Ph); MS (positive ion ESMS, $M+Na^+$) calcd for $C_{17}H_{24}O_7Na$: 363.1420, found 363.1425. The above tetraol (7.5 g, 22 mmol) was dissolved in anhyd DMF (240 mL) and cooled to 0 $^oC$, followed by addition of benzyl bromide (16 mL) and NaH (4.2 g). The mixture was stirred for 4 h at room temp, cooled, quenched with $CH_3OH$ (3 mL), diluted with brine solution and extracted with EtOAc. The organic layer was concentrated, and the residue was purified by silica

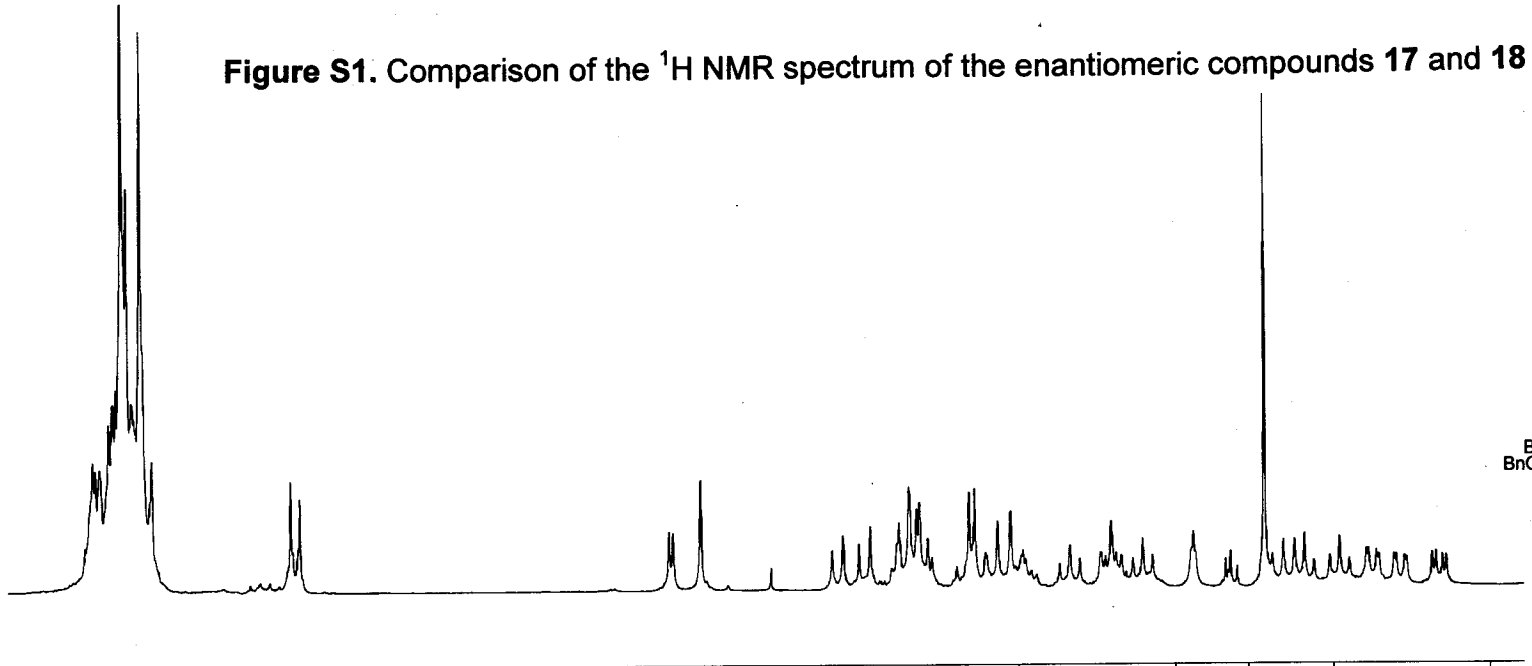
column (hexane/EtOAC, 7:1) to obtain the tetra-benzylated product, 6-*O*-allyl-2,3,4,5-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-(DL)-*myo*-inositol (14 g, 92%). TLC (toluene/ EtOAc, 3:1): $R_f$ = 0.55; $^1$H NMR (300 MHz, $CDCl_3$): 3.24 (dd, *J* = 2.2 and 9.7 Hz, 1H), 3.31 (dd, *J* = 2.2 and 9.7, 1H), 3.39 (dd, *J* = 9.1 Hz, 1H), 3.80 (s, 3H, OMe), 3.91 (m, 1H), 4.24-4.41 (m, 2H), 4.52-4.65 (m, 4H), 4.77-4.90 (m, 6H), 5.15 (m, 2H), 5.85-6.10 (m, 1H), 6.84-6.87 (m, 2H), 7.22-7.42 (m, 22H, Ph). MS (positive ion ESMS, M+$Na^+$) calcd for $C_{45}H_{48}O_7Na$ 723.3298, found 723.3303. The above intermediate (9 g, 12.8 mmol) was dissolved in anhyd DMSO (200 mL) and treated with potassium *tert*-butoxide (14 g). The reaction mixture was kept at 70 $^0$C for 2 h, after which it was poured onto ice-cold water, extracted with EtOAc. The organic layer was washed with brine and water, dried ($Na_2SO_4$) and concentrated. The residue was dissolved in a solution of 1 M HCl-acetone (1:9, 300 mL) and kept at 40 $^0$C for 30 min, neutralized with triethylamine and concentrated. The residue on silica column purification (hexane/EtOAc, 4:1) afforded 2,3,4,5-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-(DL)-*myo*-inositol (**7**, 7.6 g, 90%) as a colorless foam. TLC (hexane/EtOAc, 4:1): $R_f$ = 0.25. $^1$H NMR (300 MHz, $CDCl_3$): 2.59 (s, 1H, OH), 3.15 (dd, *J* = 1.8 and 9.8 Hz, 1H, 3-H), 3.35 (dd, *J* = 9.8 Hz, 1H, 5-H), 3.37 (dd, *J* = 2.0 and 9.6 Hz, 1H, 1-H), 3.79 (s, 3H, OMe), 4.10 (bs, 1H), 4.08 (dd, *J* = 9.8 Hz, 1H), 4.14 (m, 1H, 6-H), 4.42-4.92 (m, 10H, $CH_2Ph$), 6.84-6.88 (m, 2H, Ph), 7.20-7.40 (m, 22H, Ph); $^{13}$C NMR (75 MHz, $CDCl_3$): 55.23, 71.89, 72.80, 72.86, 73.66, 74.01, 75.28, 75.73, 76.49, 76.62, 77.04, 77.46, 79.74, 81.07, 81.38, 83.46, 113.87, 127.32, 127.45, 127.50, 127.57, 127.60, 127.69, 127.81, 127.99, 128.12, 128.25, 128.33, 128.35, 129.34, 129.97, 138.81, 138.86, 159.31; MS (positive ion ESMS, M+$Na^+$) calcd for $C_{42}H_{44}O_7Na$ 683.2985, found 683.2990.

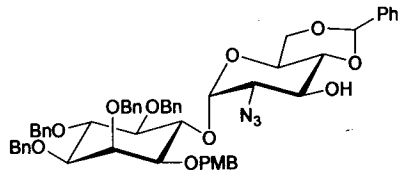
**(3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-**α**-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-(DL)-*myo*-inositol** (**15**). A mixture of 2,3,4,5-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-(DL)-*myo*-inositol acceptor **7** (7.8 g, 11.5 mmol) and 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranosyl-trichloroacetimidate (**6**, 10.5 g, 22 mmol, 1.6 equiv, prepared from tri-*O*-acetyl-D-glucal by a reported[3] azidonitration method), and freshly activated powdered 4A molecular sieves were dried by azeotropic removal of residual moisture through toluene. The mixture was dissolved in anhyd $CH_2Cl_2$ (70 mL),

stirred under argon at room temperature for 30 min, and then cooled to 0 $^{o}$C. To the above suspension was added a solution of TMSOTf (2 mL, 0.2 M solution in $CH_2Cl_2$) drop-wise and the mixture was stirred further for 40 min at 0 $^{o}$C. After completion, the reaction mixture was neutralized with triethyamine, filtered through celite and concentrated. The silica column chromatography (hexane/EtOAc, 3:1)) provided the product **15** (12 g, 90%, 1:1 diastereoisomeric mixture) as colorless solid. TLC (hexane/ EtOAc, 7:4): $R_f$ = 0.43. $^1$H NMR (300 MHz, $CDCl_3$): 1.83-2.07 (3x s, 9H, OAc), 3.11-3.15 (m, 1H), 3.39-3.42 (m, 2H), 3.44-3.46 (dd, *J* = 9.6 Hz, 1H), 3.47-3.50 (dd, *J* = 1.8 and 9.5 Hz, 1H), 3.60-3.63 (m, 2H), 3.82 (s, 3H, $OCH_3$), 4.06 (s, 1H), 4.13-4.14 (dd, *J* = 9.5 Hz, 1H), 4.20-4.33 (m, 2H), 4.40-5.18 (m, 10H, $CH_2Ph$), 4.92 (m, 1H), 5.40-5.43 (m, 1H), 5.64 (d, *J* = 3.6 Hz, 0.5H), 5.79 (d, *J* = 3.6 Hz, 0.5H), 6.84-6.87 (m, 2H, Ph), 7.22-7.43 (m, 22H, Ph); $^{13}$C NMR (75 MHz, $CDCl_3$): 20.54, 20.58, 20.63, 55.19, 60.89, 61.17, 66.73, 67.99, 68.99, 68.99, 70.57, 71.62, 71.66, 71.84, 72.77, 72.85, 73.61, 73.97, 75.04, 75.23, 75.69, 79.69, 80.74, 81.04, 81.33, 81.96, 83.41, 83.97, 97.35, 97.16, 113.83, 127.72-129.29 (multiple peaks), 138.09-138.81 (multiple peaks), 159.37, 169.48, 169.98, 170.64; HRMS (ESMS, M+$Na^+$) calcd for $C_{54}H_{59}O_{14}N_3Na$ 996.3895, found 996.3885.

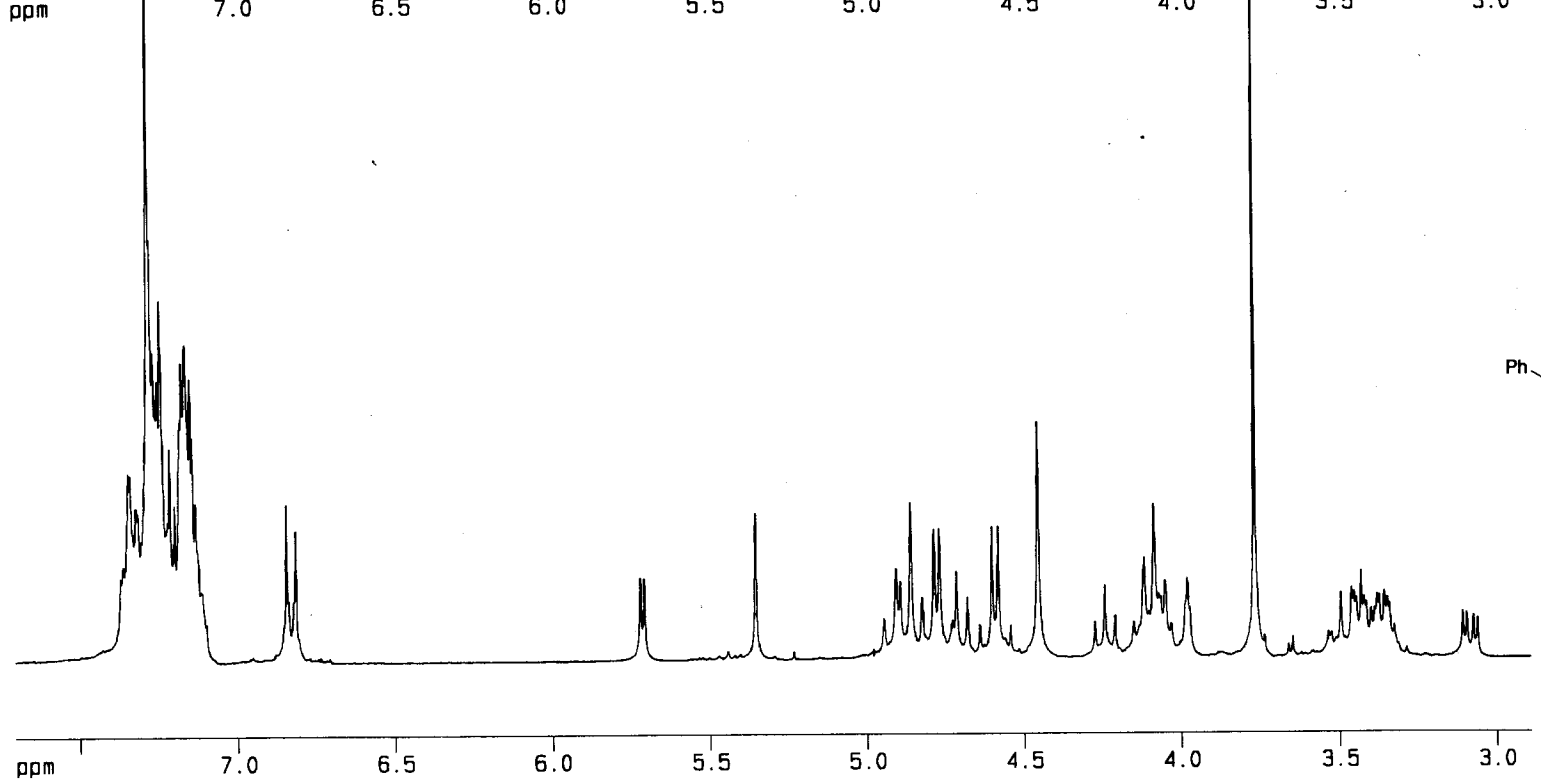
**(2-Azido-4,6-di-*O*-benzylidene-2-deoxy-**α**-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-D-*myo*-inositol (17) and other diastereoisomer (18).** The above pseudodisaccharide (**15**, 10.4 g, 10 mmol) dissolved in a solvent mixture of anhyd $CH_2Cl_2$ (24 mL) and $CH_3OH$ (96 mL) was treated with a saturated solution (1.6 mL) of sodium methoxide in $CH_3OH$ and the reaction mixture was stirred for 24 h at room temperature. After completion of reaction, it was neutralized with cation exchange resin (Amberlite IR 120$H^+$), filtered and concentrated to give 2-azido-2-deoxy-α-D-gluco pyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-(DL)-*myo*-inositol (**16**) in quantitative yield. This intermediate (8 g, 9.4 mmol) was dissolved in anhyd $CH_3CN$ (240 mL) followed by addition of benzaldehyde-dimethylacetal (12 mL, 6.88 mmol) and camphor-sulphonic acid (1.6 g, 6.88 mmol). The reaction mixture was stirred for 24 h at rt, neutralized with $Et_3N$ and concentrated. The residue was diluted with EtOAc, organic layer washed with saturated $NaHCO_3$ solution, brine and $H_2O$. Organic layer was dried ($Na_2SO_4$), concentrated and purified on a silica column (hexane-EtOAc, 85:15) provided

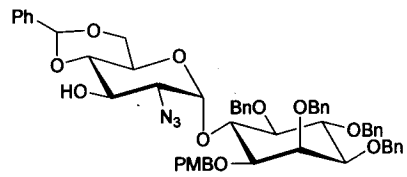
**Figure S1.** Comparison of the $^{1}H$ NMR spectrum of the enantiomeric compounds **17** and **18**




**18**




**17**

desired D-inositol isomer **17** (4.12 g, 47%) TLC (hexane/EtOAc, 7:3), $R_f$ = 0.35; $[\alpha]_D$ = +57 (*c* = 1.0, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$): 3.10 (dd, J = 3.9 and 10 Hz, 1H), 3.38 (dd, J = 2.2 and 9.8 Hz, 1H), 3.45 (m, 4H), 3.76 (s, 3H), 3.98 (bs, 1H), 4.05-4.11 (m, 4H), 4.24 (dd, J = 9.3 Hz, 1H), 4.45 (br s, 2H), 4.60-4.94 (m, 8H), 5.35 (s, 1H), 5.72 (d, J = 3.9 Hz, 1H), 6.81-6.84 (m, 2H), 7.14-7.27 (m, 27H); $^{13}C$ NMR (75 MHz, $CDCl_3$): 55.20, 61.92, 62.90, 68.53, 71.74, 72.73, 73.51, 74.20, 75.04, 75.35, 75.65, 80.79, 81.27, 81.84, 81.91, 97.70, 101.85, 113.81, 126.38, 127.12, 127.38, 127.58, 127.65, 127.87, 128.04, 128.14, 128.16, 128.28, 128.33, 129.04, 129.55, 129.66, 136.99, 138.16, 138.50, 138.80, 159.31; HRMS (ESMS, $M+Na^+$) calcd for $C_{55}H_{57}O_{11}N_3Na$ 958.3891, found 958.3885; and the L-inositol isomer **18** (4.2 g, 48%). TLC (hexane/EtOAc, 7:3), $R_f$ = 0.42; $[\alpha]_D$ = +43 (*c* = 1.0, $CHCl_3$) $^1H$ NMR (300 MHz, $CDCl_3$): 3.17-3.18 (dd, J = 3.9 and 9.8 Hz, 1H), 3.30 (dd, J = 1.8 and 9.8 Hz, 1H), 3.35-3.39 (dd, J = 2.1 and 9.6 Hz, 1H), 3.47 (t, J = 9.3 Hz, 1H), 3.59-3.65 (dd, J = 10 Hz, 2H), 3.71 (s, 3H), 3.82 (t, J = 5 Hz, 1H), 3.94 (br s, 1H), 4.10 (dd, J = 9.6 Hz, 2H), 4.17-4.23 (m, 2H), 4.33 (t, J = 9.6 Hz, 1H), 4.40-5.02 (m, 10H), 5.51 (s, 1H), 5.59 (d, J = 3.9 Hz, 1H), 6.78-6.81 (d, 2H), 7.28-7.38 (m, 27H); $^{13}C$ NMR (75 MHz, $CDCl_3$): 55.11, 61.65, 63.05, 68.73, 68.88, 72.10, 72.60, 74.36, 74.65, 75.01, 75.58, 77.77, 80.47, 81.78, 82.04, 84.29, 97.88, 101.88, 113.92, 126.29, 127.34, 127.38, 127.45, 127.56, 127.69, 127.81, 128.10, 128.21, 128.26, 128.29, 128.36, 129.11, 129.45, 129.75, 137.21-138.60 (multiple peaks), 159.28; HRMS (ESMS, $M+Na^+$) calcd for $C_{55}H_{57}O_{11}N_3Na$ 958.3891, found 958.3883

**(2-Azido-3,6-di-*O*-benzyl-2-deoxy-**a**-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benyl-1-*O*-(4-methoxybenzyl)-D-*myo*-inositol (5)**. Compound **17** (4 g, 4.24 mmol) was dissolved in anhyd DMF (60 mL) followed by the addition of benzyl bromide (2.0 mL, 16.8 mmol) and NaH (1.2 g, 52 mmol) at 0 $^0C$. After 30 min, the reaction was brought to room temperature and stirred for 4 h. After completion, the excess of NaH was destroyed by addition of a few drops of methanol. The mixture was diluted with excess of EtOAc, which was wash with saturated solution of $NaHCO_3$, water, dried over $NaSO_4$ and concentrated. Silica column chromatography (hexane/EtOAc, 9:1) afforded, 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-D-*myo*-inositol (4.28 g, 98%), as colorless syrup. TLC

(hexane/EtOAc, 8:2) $R_f$ = 0.50; $[\alpha]_D$ = +48 (*c* = 1.0, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): 3.24 (dd, *J* = 3.8 and 10.0 Hz, 1H, 2b-H), 3.38 (dd, *J* = 2.2 and 9.8, 1H, 1a-H or 3a-H), 3.45 (dd, *J* = 2.2 and 9.8, 1H, 1a-H or 3a-H), 3.46 (dd, *J* = 9.3 Hz, 1H), 3.52 (m, 2H), 3.80 (s, 3H, $OCH_3$), 3.96-4.04 (m, 2H, 2a-H, 3a-H), 4.06-4.29 (m, 4H), 4.48 (s, 2H, C*H*$_2$Ph), 4.57-4.96 (m, 10H, $CH_2$Ph), 5.47 (s, 1H), 5.72 (d, *J* = 3.8 Hz, 1H, 1b-H), 6.83-6.89 (m, 2H, Ph), 7.08-7.13 (m, 2H, Ph), 7.17-7.45 (m, 30H, Ph); $^{13}$C NMR (75 MHz, $CDCl_3$): 55.20, 62.83, 68.67, 71.77, 72.70, 73.50, 74.16, 74.72, 74.99, 75.49, 75.57, 77.36, 80.81, 81.13, 81.84, 82.92, 97.71, 101.14, 113.86, 126.03, 126.15, 127.60, 127.63, 127.80, 127.92, 128.13, 128.17, 128.20, 128.24, 128.31, 128.34, 129.60, 130.00, 137.48, 137.85, 137.97, 138.15, 138.59, 138.81, 159.30; HRMS (ESMS, M+$Na^+$) calcd for $C_{62}H_{63}O_{11}N_3Na$ 1048.4360, found 1048.4366. To a solution of above compound (4 g, 3.88 mmol), sodium cyanoborohydride (2.7 g, 40 mmol), freshly activated moleculer sieves (4A) in anhyd THF (140 mL), at 0 $^0$C under argon, was added drop-wise a saturated solution of HCl in diethyl-ether till pH 1 was reached. After stirring at 0 $^0$C for 30 min, the reaction mixture was neutralized with $Et_3N$, diluted with EtOAc and concentrated. The residue was purified on a silica column (hexane/EtOAc, 8:2) to provide desired compound **5** (3.3 g, 82%) and colorless solid. TLC (hexane/EtOAc, 5:2) $R_f$ = 0.46; $[\alpha]_D$ = +33.2 (*c* = 1.4, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): 1.92 (d, *J* = 3.7, 1H, OH), 3.17 (dd, *J* 3.8 and 9.9 Hz, 1H, 2b-H), 3.22 (m, 1H, 6b-H), 3.28 (dd, *J* = 3.8 and 10.5 Hz, 1H, 6'b-H), 3.38 (dd, *J* = 2.2 and 9.8 Hz, 1H, 3a-H), 3.44 (m, 1H, 5a-H), 3.47 (dd, *J* = 2.2 and 9.8 Hz, 1H, 1a-H), 3.68 (m, 1H, 4b-H), 3.76 (m, 1H, 3b-H), 3.80 (s, 3H, $OCH_3$), 3.95 (m, 1H, 5b-H), 4.01 (dd, *J* = 2.2 Hz, 1H, 2a-H), 4.11 (dd, *J* = 9.4 Hz, 1H, 4a-H), 4.25 (m, 1H, 6a-H), 4.23-5.04 (m, 14H, $CH_2$Ph), 5.72 (d, *J* = 3.7 Hz, 1H, 1b-H), 6.82-6.88 (m, 2H, Ph), 7.17-7.45 (m, 32H, Ph); $^{13}$C NMR (75 MHz, $CDCl_3$): 55.20, 62.66, 69.00, 69.30, 71.78, 72.18, 72.64, 73.32, 73.45, 74.16, 74.21, 74.68, 74.76, 75.49, 75.60, 79.27, 80.80, 81.54, 81.84, 81.90, 84.35, 97.30, 113,78, 127.49-129.96 (multiple peaks), 137.92, 138.17, 138.33, 138.43, 138.57, 138.83, 159.28; HRMS (ESMS, M+$Na^+$) calcd for $C_{62}H_{65}O_{11}N_3Na$ 1050.4517, found 1050.4521. The NMR spectral data and the optical rotation of **5** were identical to that reported[4] for this compound prepared by another route.

**(2-Azido-3,6-di-*O*-benzyl-2-deoxy-**a**-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benyl -1-*O*-(4-methoxybenzyl)-L-*myo*-inositol (19)**. An identical method, described above for compound **5,** was used for the preparation of diastereoisomeric compound **19.**

**2,3,4,6-Tetra-*O*-benzyl-**a**-D-mannopyranosyl trichloroacetimidate** (**11**). D-Mannose (20 g, 111 mmol) was heated at 80 $^0$C for 3 h in presence of $BF_3.Et_2O$ (1 ml, 7.7 mmol) in allyl alcohol (230 mL). After neutralization with $NEt_3$, the excess of allyl alcohol was evaporated, and the residue purified by silica column chromatography ($CH_2Cl_2$/MeOH; 9:1 to 8:2) which afforded an α/β-mixture of allyl-α-D-mannopyranoside (α/β ratio, 20:1) (20 g, 80%) as semisolid. TLC ($CH_2Cl_2$/MeOH): $R_f$ = 0.5. $^1$H NMR (300 MHz, $D_2O$): 3.42-4.11 (m, 11H), 4.72 (d, *J* = 2.0 Hz, 1H, 1-H), 5.06-5.21 (m, 2H, all), 5.69-5.83 (m, 1H, all); MS (ESMS, M+Na$^+$) calcd for $C_9H_{16}O_6Na$ 243.0845, found 243.0850. To a solution of above compound (7.5 g, 34 mmol) and benzyl bromide (24.5 mL, 180 mmol) in anhyd DMF (160 mL) was added, in portions, NaH (7 g, 175 mmol) at 0 $^0$C. After the mixture was stirred at 4 h, the excess of NaH was destroyed by addition of $CH_3OH$ drop wise. The solution was diluted with EtOAc, the organic layer washed with saturated solution of $NaHCO_3$, brine, water, and dried ($NaSO_4$) and concentrated. Silica column chromatography (hexanes/EtOAc, 7:1) afforded 2,3,4,6-tetra-*O*-benzyl-1-*O*-allyl-α-D-mannopyranoside (16.4 g, 83%) as colorless foam. TLC (hexane/EtOAc, 4:1): $R_f$ = 0.43; $^1$HNMR (300 MHz, $CDCl_3$); 3.71-3.74 (m, 4H), 3.91 (m, 2H), 4.46-4.86 (m, 8H), 4.86 (d J = 1.8 Hz, 1H, H-1), 5.17-5.23 (dd, 2H, allyl), 5.80 (m, 1H), 7.19-7.28 (m, 20H); MS (ESMS, M+Na$^+$) calcd for $C_{37}H_{40}O_6Na$ 603.2723, found 603.2723. For the removal of the anomeric allyl group, the above compound (16.4 g, 28 mmol) was dissolved in anyd DMSO (300 mL) and treated with potassium *tert*-butoxide (25 g). The reaction mixture was kept at 80 $^0$C for 2 h, after which it was poured onto ice-cold water, extracted with EtOAc. The organic layer was washed with brine and water, dried ($Na_2SO_4$) and concentrated. The residue was dissolved in a solution of 1 M HCl-acetone (1:9, 300 mL) and kept at 40 $^0$C for 30 min, neutralized with triethylamine and concentrated. The residue on silica column purification (hexane/EtOAc, 4:1) afforded 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranose (14 g, 95%). $^1$HNMR (300 MHz, $CDCl_3$): 3.68 (dd, 5.7 and 10.8 Hz, 1H), 3.80 (bs, 1H), 3.81 (dd, J = 9.3 Hz), 1H, 3.98 (m, 3H),

4.51 (d, J = 11 Hz, 2H), 4.57 (d, J = 5.7 Hz, 2H), 4.74 (d, J = 5.7 Hz, 2H), 4.89 (d, J = 10.8 Hz), 5.29 (d, J = 1.9 Hz, 1H), 7.19-7.28 (m, 20H); $^{13}$C NMR (75 MHz, $CDCl_3$): 69.55, 72.13, 72.65, 73.29, 74.80, 74.94, 75.12, 79.62, 83.00, 93.60, 127.48-128.42 (multiple peaks), 138.32-132.40 (4 signals); MS (ESMS, M+$Na^+$) calcd for $C_{34}H_{36}O_6Na$ 563.2410, found 563.2415. The above compound (5.0 g, 9.25 mmol) and $CCl_3CN$ (5.1 mL, 35 mmol) were dissolved in anhyd $CH_2Cl_2$ (18 mL). After addition of DBU (300 µL) and stirring at rt for 1 h, the solvent was removed and the residue was purified by silica column (hexane/EtOAc, 8:2) affording desired donor **11** (6.1 g, 98%) as a brown viscous compound. TLC (hexane/EtOac, 4:1): $R_f$ = 0.65; $^1$HNMR (300 MHz, $CDCl_3$): 3.75 (m, 1H), 3.88 (m, 2H), 3.99 (m, 2H), 4.16 (dd, J = 7.8 Hz, 1H), 4.55-4.88 (m, 8H), 6.37 (s, 1H), 7.19-7.41 (m, 20H), 8.53 (s, 1H, NH); MS (ESMS, M+$Na^+$) calcd for $C_{36}H_{36}O_6NCl_3Na$ 706.1506, found 706.1510.

**Allyl-3-*O*-benzyl-4,6-*O*-benzylidene-a-D-mannopyranoside** (**12**). A solution of allyl-α-D-mannopyranoside (15 g, 68 mmol), benzaldehyde-dimethylacetal (13 mL, 76 mmol) and camphor sulphonic acid (3.0 g, 13 mmol) in anhyd $CH_3CN$ (300 ml) was stirred at rt for 18 h. After neutralization with $NEt_3$ and the reaction mixture was concentrated, diluted with EtOAc and organic layer washed with saturated solution of $NaHCO_3$, brine and water. The organic layer dried ($Na_2SO_4$), concentrated and the residue was purified by silica column chromatography (hexane/EtOAc, 6:4) to provide compound allyl-4,6-*O*-benzylidene-α-D-mannopyranoside (15.6 g, 74%) as a colorless crystalline solid. TLC (hexane/EtOAc, 1:1): $R_f$ = 0.38; $^1$HNMR (300 MHz, $CDCl_3$): 3.78-3.90 (m, 2H, H-5 and H-6), 3.98 (m, 1H, H-3), 3.99 (m, 1H), 4.05-4.14 (m, 2H, H-2 and H-6), 4.19 (m, 1H), 4.24-4.28 (m, 1H, H-4), 4.92 (d, J = 1.3 Hz, 1H, H-1), 5.19-5.33 (m, 2H, allyl), 5.50 (s, 1H), 5.90 (m, 1H, allyl), 7.27-7.45 (m, 5H); $^{13}$C NMR (75 MHz, $CDCl_3$): 63.19, 68.01, 68.16, 68.52, 68.68, 78.79, 99.49, 102.13, 117.63, 126.22, 128.23, 129.1, 133.43, 137.17; MS (ESMS, M+$Na^+$) calcd for $C_{16}H_{20}O_6Na$ 331.1158, found 331.1165. To a solution of above compound (7.8 g, 25 mmol) in anhyd DMF (100 mL) was added benzyl bromide (3 mL, 22.5 mmol) and NaH (1.3 g, 32.5 mmol) at 0 $^0$C. The reaction mixture was stirred at rt for 4 h, excess of NaH destroyed by addition of $CH_3OH$, and diluted with EtOAc. The mixture was washed with saturated solution of $NaHCO_3$, brine and water, dried

($NaSO_4$) and concentrated. Silica column chromatography (hexane/EtOAc, 7:1) afforded pure compound allyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (6.6 g, 65%) as colorless syrup. TLC (hexane/EtOAc, 7:3): $R_f$ = 0.40; $^1$HNMR (300 MHz, $CDCl_3$): 3.78-3.80 (m, 2H, H-5 and H-6), 3.98 (m, 1H, H-3), 4.02-4.14 (m, 2H, H-2 and H-6), 4.24-4.28 (m, 1H, H-4), 4.78 (m, 2H, $CH_2$Ph), 4.84 (d, J = 1.3 Hz, 1H, H-1), 5.19-5.33 (m, 2H, allyl), 5.52 (s, 1H), 5.90 (ddt, 1H, allyl), 7.27-7.45 (m, 10H); $^{13}$C NMR (75 MHz, $CDCl_3$): 63.53, 68.03, 68.69, 73.59, 73.63, 73.70, 78.52, 79.46, 97.48, 101.37, 117.54, 125.99, 126.22, 127.89, 127.98, 128.17, 128.32, 128.38, 128.49, 128.99, 133.37, 137.31; MS (ESMS, M+$Na^+$) calcd for $C_{23}H_{26}O_6Na$ 421.1627, found 421.1633.

**3,4,6,-Tri-*O*-benzyl-b-D-mannopyranose-1,2-pen-4-enylorthobenzoate** (**13**). The penta-*O*-benzoyl-D-mannose (30 g, 42 mmol) was dissolved in $CH_2Cl_2$ (150 mL) and cooled to 0 $^0$C and treated with a solution of 30% HBr-AcOH (100 mL). The reaction mixture was stirred at rt for 12 h, diluted with $CH_2Cl_2$ (250 mL) and cold saturated $NaHCO_3$ solution (150 mL) and stirred for 30 min. The organic layer was washed with brine, dried ($Na_2SO_4$), concentrated, and puried by silica column (hexane/EtOAc, 4:1) to get the mannosyl bromide (23 g), TLC (hexane/EtOAc, 4:1): $R_f$ = 0.50, all of which (23 g, 48 mmol) was dissolved in $CH_2Cl_2$ (100 mL) and treated with 2,6-lutidine (14 mL, 142 mmol) and 4-penten-1-ol (7.05 ml, 68.5 mmol). After five days of stirring at rt, the reaction mixture was diluted with $CH_2Cl_2$, washed with saturated aqueous $NaHCO_3$ and brine, dried over $Na_2SO_4$ and concentrated. Silica chromatography (hexane/EtOAc, 3:1) afforded 3,4,6,-tri-*O*-benzoyl-β-D-mannopyranose-1,2-pen-4-enylorthobenzoate (23 g) as colorless solid. TLC (hexane/EtOAc, 4:1): $R_f$ = 0.30; $^1$H and $^{13}$C NMR data of this intermediate was identical to the previously reported.[5] The compound (9.0 g, 14. mmol) dissolved in $CH_2Cl_2$:$CH_3OH$ (72 mL, 8:1) was treated with sodium methoxide (400 mg, 7.4 mmol) and the reaction mixture stirred at room temperature for 2 h. After removal of solvent and column chromatography ($CH_3OH$:$CH_2Cl_2$, 95:5) provided fully debenzoylated derivative (4.2 g, 86%) colorless foam which (4.2 g, 12 mmol) was dissolved in anhyd DMF (50 mL) and benzyl bromide (7.4 ml, 54.36 mmol) and NaH (2.9 g, 72.5 mmol) were added at 0 $^0$C. After 1 h, the reaction was brought to rt and stirred for overnight. After completion of the reaction, the excess of NaH was destroyed

by addition methanol (5 mL) and concentrated. The residue was diluted with EtOAc, washed with saturated solution of $NaHCO_3$, brine and water respectively, dried over $NaSO_4$ and concentrated. Flash chromatography (hexane/EtOAc, 4:1) afforded compound **13** (7.0 g, 93%) as colorless syrup. TLC (hexane/EtOAc, 4:1): $R_f$ = 0.42; $^1$H NMR (300 MHz, $CDCl_3$): 1.71-1.82 (m, 2H), 2.18-2.26 (m, 2H), 3.40-3.69 (m, 4H), 3.80-3.94 (m, 2H), 4.85-5.13 (m, 6H), 5.52 (d, J = 3 Hz, 1H), 5.87 (m, 1H), 7.78-7.20 (m, 20H); $^{13}$C NMR (75 MHz, $CDCl_3$): 28.77, 30.19, 63.30, 69.09, 72.08, 73.14, 74.33, 74.95, 75.02, 76.13, 78.43, 97.72, 114.80, 122.10, 126.61, 127.27, 127.37, 127.86, 127.87, 127.95, 128.13, 128.27, 128.40, 137.84, 137.95; MS (ESMS, M+$Na^+$) calcd for $C_{39}H_{42}O_7Na$ 645.2828, found 645.2835.

**Allyl-2,3,4-tri-*O*-benzyl-**a**-D-mannopyranoside** (**14**). 1-*O*-Allyl-α-D-mannopyranose (24 g, 109 mmol) dissolved in anhyd pyridine (100 mL) was treated with trityl chloride (26 g, 93 mmol) and the reaction mixture was stirred over night at 80 $^0$C. The excess of pyridine was removed by distillation at reduced pressure and residue diluted with EtOAc, washed with saturated solution of $NaHCO_3$, brine and water, dried over $Na_2SO_4$ and concentrated. Silica column chromatography ($CH_2Cl_2$/MeOH, 95:5) afforded allyl-6-*O*-trityl-α-D-mannopyranoside (35 g, 70%) as pale yellow syrup which was dissolved in anhyd DMF (400 mL) followed by the addition of benzyl bromide (58 mL) and NaH (21 g) at 0 $^0$C. After 30 min, the reaction was brought to rt and stirred for 4 h. After completion, the excess of NaH was destroyed by addition of methanol and concentrated. The mixture was diluted with EtOAc, which was wash with saturated solution of $NaHCO_3$, water, dried over $NaSO_4$ and concentrated. Silica column chromatography (hexane/EtOAc, 3:1) afforded allyl-2,3,4-tri-*O*-benzyl-6-*O*-trityl-α-D-mannopyranoside (49 g, 89%). The above compound (49 g, 67 mmol) dissolved in a solvent mixture of $CH_2Cl_2$-$CH_3OH$ (720 mL, 1:3) was treated with p-toulene-sulponic acid (3.6 g) and stirred for 12 h at rt. After completion of the reaction, the reaction was neutralized with $Et_3N$ and concentrated. Silica column chromatography (hexane/EtOAc, 7:3) afforded allyl-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (30 g, 93%) as colorless foam. TLC (hexane/EtOAc, 7:3), $R_f$ = 0.25; $^1$HNMR (300 MHz, $CDCl_3$): 3.61 (m, 1H), 3.76 (m, 1H), 3.89, (m, 2H), 3.99 (m, 1H), 4.19 (dd, 1H), 4.05 (m, 1H), 4.58-4.80 (m, 6H), 4.80 (d, J =

1.3 Hz, 1H), 5.19-5.33 (m, 2H), 5.78 (m, 1H), 7.24-7.31 (m, 15H); $^{13}$C NMR (75 MHz, $CDCl_3$): 61.86, 67.65, 72.01, 72.61, 72.78, 74.76, 74.95, 80.10, 97.24, 117.00, 127.43, 127.49, 127.55, 127.73, 127.86, 128.14, 128.23, 133.74, 138.26, 138.48, 138.53; MS (ESMS, M+$Na^+$) calcd for $C_{30}H_{34}O_6Na$ 513.2253, found 513.2260.

**2,3,4,6-Tetra-*O*-benzyl-**a**-D-mannopyranosyl-(1®2)-3-*O*-benzyl-4,5-di-*O*-acetyl-**a**-D-mannopyranosyl trichloroacetimidate** (**9**).

(a) *Allyl (2,3,4,6-tetra-O-benzyl)-α-D-mannopyranosyl-(1®2)-3-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside*. The glycosyl donar (**11**, 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl trichloroacetimidate**,** 4.1 g, 6.0 mmol) and the acceptor (**12**, allyl-3-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside, 1.75 g, 4.39 mmol) were dried through anhyd toluene and then dissolved in anhyd diethyl-ether (100 mL) under argon. After addition of TMSOTf solution (2.95 mL, 0.1 N in anhyd diethyl-ether), the reaction mixture was stirred for 2 h at rt. This was followed by neutralization with $Et_3N$, concentration and silica column chromatography (hexane/EtOAc, 7:1) to obtain desired compound (4.4 g, 81%) as a colorless crystalline solid. TLC (hexane/EtOAc, 3:1): $R_f$ = 0.36; $^1$HNMR (300 MHz, $CDCl_3$): 3.70 (m, 2H), 3.75-4.00 (m, 6H), 4.10-4.25 (m, 3H), 4.30 (m, 1H), 4.40 (t, 1H), 4.45-5.00 (m, 11H), 5.15-5.30 (m, 2H), 5.41 (s, 1H), 5.58 (s, 1H), 5.80 (m, 1H), 7.09-7.50 (m, 30H); $^{13}$C NMR (75 MHz, $CDCl_3$): 64.05, 67.94, 68.03, 68.69, 68.79, 69.32, 71.60, 72.41, 73.23, 73.34, 73.42, 73.69, 74.07, 74.77, 74.81, 77.55, 78.51, 79.23, 79.50, 98.23, 98.69, 102.03, 117.47, 126.13, 127.20, 127.27, 127.33, 127.48, 127.52, 127.64, 127.68, 127.74, 127.87, 128.00, 128.12, 128.16, 128.19, 128.22, 128.27, 128.32, 128.39, 128.49, 129.12, 133.37, 137.54, 137.75, 138.11, 138.38, 138.41, 138.72; HRMS (ESMS, M+$Na^+$) calcd for $C_{57}H_{60}O_{11}Na$ 943.4033, found 943.4040.

(b) *2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl-(1®2)-3-O-benzyl-α-D-mannopyranoside*. The above mannobiose intermediate (2.0 g, 2.19 mmol) dissolved in DMSO (90 mL) was treated with potassium *t*-butaoxide (7 g, 62.5 mmol) and the reaction mixture was stirred at 80$^{\circ}$C for 3 h. After completion of the reaction, ice was added and the mixture extracted with EtOAc. The organic layer was dried with $Na_2SO_4$ and concentrated to

provide thick syrup. This was dissolved in a mixture of acetone:1M HCl (9:1, 79 mL) and heated at 55$^{\circ 0}$C for 2 h, the progress of reaction checked by TLC. The reaction mixture was cooled, neutralized with $NEt_3$ and concentrated. Flash chromatography (hexane/EtOAc, 1:1) provided desired compound (1.4 g, 82%) as colorless foam. TLC (hexane/EtOAc, 3:7): $R_f$ = 0.34; $^1$HNMR (300 MHz, $CDCl_3$): 3.58 (m, 2H), 3.75 (m, 5H), 3.85 (m, 3H), 4.00 (bs, 2H), 4.43-4.54 (m, 10H), 5.06 (bs, 1H), 5.34 (d, J = 1.9 Hz, 1H), 7.12-7.24 (m, 25H); $^{13}$C NMR (75 MHz, $CDCl_3$): 62.38, 62.84, 67.34, 67.70, 69.57, 69.73, 71.56, 72.12, 72.32, 72.43, 72.58, 72.67, 73.31, 74.53, 74.87, 75.12, 77.32, 77.65, 79.27, 92.37, 98.70, 127.44-128.31 (multiple peaks), 137.93-138.08 (5 peaks); HRMS (positive ion ESMS, M+Na$^+$) calcd for $C_{47}H_{52}O_{11}Na$ 815.3407, found 815.3412.

(c) Acetyl-(*2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)-(1®2)-3-O-benzyl-4,5-di-O-acetyl-α-D-mannopyranoside*. A solution of preceding deprotected intermediate (1.4 g, 1.78 mmol) in a mixture of pyridine and acetic anhydride (1:1, 6 equivalent) was stirred at 0$^{\circ 0}$C for 15 min and then kept at rt overnight. This was followed by addition of ice and stirring for 30 min, extraction with EtOAc. The organic layer was washed with saturated solution of $NaHCO_3$ and water, dried with $Na_2SO_4$ and concentrated. Flash chromatography (hexane/EtOAc, 3:1) afforded desired triacetylated compound (1.45 g, 93.35%) as colorless syrup. TLC (hexane/EtOac, 7:3) $R_f$ = 0.58; $^1$HNMR (300 MHz, $CDCl_3$): 1.84 (s, 3H), 1.96 (s, 3H), 2,03 (s, 3H), 3.75 (m, 1H), 4.10 (dd, J = 3 and 12 Hz, 1H), 4.15 (dd, J = 5Hz, 1H), 4.35 (m, 3H), 4.50-4.60 (m, 6H), 4.70 (t, J = 11 Hz, 1H), 4.96 (d, J = 2 Hz, 1H), 5.23 (s, 1H), 5.30 (t, J = 10 Hz, 1H), 6.13 (d J = 2 Hz, 1H), 7.25-7.53 (m, 25H); $^{13}$C NMR (75 MHz, $CDCl_3$): 20.54, 20.64, 20.71, 61.50, 62.47, 67.71, 69.63, 71.08, 71.93, 72.31, 72.40, 72.46, 72.69, 73.24, 74.01, 74.34, 75.04, 75.49, 75.80, 77.10, 79.49, 90.89, 100.60, 127.40-128.32 (multiple peaks), 138.12-138.38 (5 peaks), 167.99, 168.54, 170.70; HRMS (positive ion ESMS, M+Na$^+$) calcd for $C_{53}H_{58}O_{14}Na$ 941.3724, found 941.3730.

(d) *2,3,4,6-Tetra-O-benzyl-α-D-mannopyranosyl-(1®2)-3-O-benzyl-4,5-di-O-acetyl-α-D-mannopyranoside*. A solution of previous acetylated compound (1.0 g, 1.14 mmol) in a saturated solution of dimethylamine in $CH_3CN$ (55 mL) was stirred at –20$^{\circ 0}$C for 1 h. the

excess of solvent and reagent was carefully removed by evaporation under reduced pressure without heating. Flash chromatography (hexane/EtOAc, 3:1) provided compound **9** (0.9 g, 94%) as colorless foam. TLC (hexane/EtOAc, 7:3), $R_f$ = 0.34; $^1$HNMR (300 MHz, $CDCl_3$): 3.75 (m, 2H), 3.90 (m, 1H), 3.90-4.25 (m, 7H), 4.25-4.56 (m, 10H), 4.75 (t, 1H), 4.90 (d, J = 1.9 Hz, 1H), 5.08 (d, J = 1.9 Hz, 1H), 5.27 (t, 1H), 7.10-7.26 (m, 25H); $^{13}$C NMR (75 MHz, $CDCl_3$): 20.67, 20.71, 62.67, 62.90, 68.38, 68.71, 69.65, 72.18, 72.27, 72.55, 72.60, 72.67, 72.92, 72.97, 73.27, 74.35, 74.44, 74.03, 75.22, 77.21, 79.66, 92.45, 100.33, 127.37-128.29 (multiple peaks), 138.02-138.30 (5 peaks), 169.47, 170.77; HRMS (positive ion ESMS, M+$Na^+$) calcd for $C_{51}H_{56}O_{13}Na$ 899.3619, found 899.3625.

(e) *2,3,4,6-Tetra-O-benzyl-α-D-mannopyranosyl-(1®2)-3-O-benzyl-4,5-di-O-acetyl-α-D-mannopyranosyl trichloroacetimidate* (**9**). To a solution of compound **9** (800 mg, 0.69 mmol) in anhyd $CH_2Cl_2$ (10 mL) was added $Cl_3CCN$ (1.7 ml, 17 mmol) and DBU (90 µL) and the reaction mixture was stirred at rt for 1 h. The solvent was removed and the residue was purified by a silica column chromatography (hexane/EtOAc, 3:1) to afford compound **10** (890 mg, 96%) as colorless foam. TLC (hexane/EtOAc, 7:3): $R_f$ = 0.50; $^1$HNMR (300 MHz, $CDCl_3$): 3.76 (m, 2H), 3.93 (m, 1H), 3.95-4.25 (m, 7H), 4.26-4.56 (m, 10H), 4.75 (t, 1H), 5.08 (d, J = 1.9 Hz, 1H), 5.27 (t, 1H), 6.30 (bs, 1H), 7.10-7.26 (m, 25H), 8.60 (s, 1H, NH); HRMS (ESMS, M+$Na^+$) calcd for $C_{53}H_{56}O_{13}NCl_3Na$ 1042.2715, found 1042.2720.

**Allyl (3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranose** (**10**). The orthoester donor **13** (1.85 g, 3.11 mmol) and mannobiose acceptor **14** (1.55 g, 3.16 mmol) were dissolved in anhyd $CH_2Cl_2$ (15 mL) and freshly activated 4A° molecular sieves were added. The solution was stirred at rt for 30 min followed by addition of 0.1 N solution of TESOTf in $CH_2Cl_2$ (150 µL, 15 mmol) and N-iodosuccinimide (525 mg, 2.34 mmol). After 30 min stirring, the solution was neutralized with $Et_3N$, the solvent was evaporated and the residue purified by column chromatography (hexane/EtOAc, 85:15), which provided allyl (2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranose (2.31 g,

72%) as colorless syrup. TLC (hexane/EtOAc, 7:3) $R_f$ = 0.5; $^1$HNMR (300 MHz, $CDCl_3$): 3.50-4.00 (m, 7H), 4.12-4.25 (m, 4H), 4.50-5.10 (m, 11H), 5.19 (d, J = 1.9 Hz, 1H), 5.20 (t, 1H), 5.90 (m, 1H), 7.24-8.10 (m, 35H); $^{13}$C NMR (75 MHz, $CDCl_3$): 66.68, 67.78, 68.74, 69.00, 71.09, 71.65, 72.06, 72.70, 73.35, 74.23, 74.65, 74.76, 75.03, 75.11, 77.67, 80.30, 96.83, 98.07, 117.45, 127.51-128.35 (multiple peaks), 133.68, 138.49 (multiple peaks), 165.49; HRMS (positive ion ESMS, M+$Na^+$) calcd for $C_{64}H_{66}O_{12}Na$ 1049.4452, found 1049.4463. To a solution of above compound (2.3 g, 2.24 mmol) in a solvent mixture of $CH_3OH$-$CH_2Cl_2$ (20 mL, 7:1) was added sodium methoxide (350 mg, 6.48 mmol). The solution was stirred at rt for 3 h. After completion of the reaction, the solvent was evaporated and the residue was purified by silica column chromatography (hexane/EtOAc, 3:1) to get compound **10** (1.9 g, 92%) as colorless foam. TLC (hexane/EtOAc, 7:3) $R_f$ = 0.25; $^1$HNMR (300 MHz, $CDCl_3$): 3.50-3.60 (m, 2H), 3.62-3.70 (m, 2H), 3.75-3.80 (m, 4H), 4.0 (m, 4H), 4.35-4.75 (m, 12H), 5.0 (bs, 1H), 5.10-5.15 (m, 2H), 5.80 (m, 1H), 7.18-7.29 (m, 30H) ; $^{13}$C NMR (75 MHz, $CDCl_3$): 66.24, 67.76, 68.04, 68.87, 71.06, 71.44, 71.62, 72.08, 72.73, 73.32, 74.23, 74.63, 74.89, 75.01, 79.56, 80.20, 96.84, 99.59, 117.39, 127.62-128.29 (multiple peaks), 133.65, 138.46-138.50 (multiple peaks); HRMS (positive ion ESMS, M+$Na^+$) calcd for $C_{57}H_{62}O_{11}Na$ 945.4190, found 945.4197.

**(2,3,4,6-Tetra-*O*-benzyl-**α**-D-mannopyranosyl)-(1→2)-(4,6-di-*O*-acetyl-3-*O*-benzyl-**α**-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-**α**-D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzyl-**α**-D-mannopyranosyl)-trichloroacetimidate** (**8**).

(a) *Allyl (2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl)-(1→2)-(4,6-di-O-acetyl-3-O-benzyl-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1→6)-2,3,4-tri-O-benzyl-α-D-mannopyranose*. The mannobiosyl donor (2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3-*O*-benzyl-4,5-di-*O*-acetyl-α-D-mannopyranosyl trichloro acetimidate, **9**, 1.0 g, 1.08 mmol) and the acceptor (allyl (3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-mannopyranose, **10**, 650 mg, 0.63 mmol) were first dried through co-evaporation with anhyd toluene, further dried for 2 h under high vacuum, and then dissolved in anhyd $CH_2Cl_2$ (12 mL) and freshly activated

molecular sieves (4 Aº) were added and the suspension stirred under argon at rt for 30 min. The reaction mixture was cooled to 0 $^0$C and treated with 0.1 N TMSOTf solution (760 µL, 0.76 mmol) and stirred for 30 min. The reaction was neutralized with $Et_3N$ and solvent was evaporated. The residue was purified by column chromatography (hexane/EtOAc, 85:15) to provide target tetrasaccharide (1.05 g, 69%). TLC (hexane/EtOAc, 7:3) $R_f$ = 0.68. This glycosylation reaction required strictly anhydrous conditions; $^1$H NMR (300 MHz, $CDCl_3$); 1.80 (s, 3H), 2.01 (s, 3H), 3.52-4.32 (m, 22H), 4.35-500 (m, 26H), 5.05-5.40 (m, 5H), 5.29 (t, 1H), 5.77-5.87 (m, 1H), 7.16-7.29 (m, 55H); $^{13}$C NMR (75 MHz, $CDCl_3$): 20.57, 20.64, 62.87, 66.53, 67.69, 68.47, 68.86, 69.01, 69.13, 71.34, 71.41, 71.74, 72.01, 72.20, 72.24, 72.44, 72.59, 72.99, 73.18, 74.48, 74.61, 74.70, 74.88, 75.37, 75.76, 77.13, 79.03, 79.89, 80.27, 96.87, 99.05, 99.51, 99.81, 117.34, 127.30-128.24 (multiple peaks), 133.57, 137.98-138.76 (multiple peaks), 169.44, 170.69; HRMS (positive ion ESMS, M+$Na^+$) calcd for $C_{108}H_{116}O_{23}Na$ 1803.7805, found 1803.7811.

(b) *2,3,4,6-tetra-O-benzyl-α-D-mannopyranosyl-(1®2)-4,6-di-O-acetyl-3-O-benzyl-α-D-mannopyranosyl-(1®2)-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1®6)-2,3,4-tri-O-benzyl-α-D-mannopyranose*. To a solution of protected above tetrasaccharide (425 mg, 0.238 mmol) in AcOH-$H_2O$ (11 ml, 19:1) was added $PdCl_2$ (400 mg, 2.25 mmol) and anhyd NaOAc (400 mg, 4.87 mmol). The reaction mixture was stirred at rt for 16 h under argon atmoshphere. After completion of the reaction, it was diluted with EtOAc, organic layer washed with saturated $NaHCO_3$ solution and water, dried ($Na_2SO_4$) and evaporated. The residue was purified by silica chromatography (hexane/EtOAc, 7:3) to provide anomeric-deprotected tetrasaccharide (380 mg, 91%) as colorless foam. TLC (hexane/EtOAc, 6:4) $R_f$ = 0.3; $^1$HNMR (300 MHz, $CDCl_3$) 1.79 (s, 3H), 2.00 (s, 3H), 3.30-4.25 (m, 22H), 4.30-4.90 (m, 24H), 4.96 (d, 1H), 5.05 (d, 1H), 5.09 (d, 1H), 5.16 (d, 1H), 5.28 (t, 1H), 7.08-7.29 (m, 55H); $^{13}$C NMR (75 MHz, $CDCl_3$): 20.62, 20.76, 62.99, 68.12, 68.65, 68.87, 69.04, 69.17, 69.50, 71.34, 71.50, 71.55, 71.71, 72.01, 72.24, 72.37, 72.46, 72.62, 73.11, 73.20, 73.37, 74.02, 74.26, 74.52, 74.64, 74.78, 74.82, 74.90, 75.00, 75.09, 75.86, 75.99, 77.13, 78.59, 78.98, 79.86, 92.46, 99.09, 99.28, 99.89, 127.53-

128.27 (multiple peaks), 138.24-138.41 (multiple peaks), 169.51, 170.96; HRMS (positive ion ESMS, $M+Na^+$) calcd for $C_{105}H_{112}O_{23}Na$ 1763.7492, found 1763.7503.

(c) *2,3,4,6-Tetra-O-benzyl-α-D-mannopyranosyl)-(1→2)-(4,6-di-O-acetyl-3-O-benzyl -α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1→6)-(2,3,4-tri-O-benzyl-α-D-mannopyranosyl)-trichloroacetimidate* (**8**). The above tetrasaccharide (300 mg, 0.172 mmol) was dissolved in anhyd $CH_2Cl_2$ (5 mL) followed by addition of $CCl_3CN$ (0.51 mL, 5.1 mmol) and DBU (150 μL) and the reaction was stirred at rt for 1.5 h. After completion of the reaction, the solvent was removed under reduced pressure and the residue was purified on a silica column (hexane/EtOAc, 3:1) to give desired tetrasaccharide trichloroacetimidate donor (**21**, 320 mg, 98%) as colorless foam. TLC (hexane/EtOAc, 3:1): $R_f$=0.53; $^1$HNMR (300 MHz, $CDCl_3$): 1.79 (s, 3H), 2.00 (s, 3H), 3.30-4.25 (m, 22H), 4.30-4.90 (m, 24H), 5.06 (d, 2H), 5.16 (d, 1H), 5.28 (t, 1H), 6.32 (bs, 1H), 7.08-7.29 (m, 55H), 8.61 (s, 1H, NH); MS (ESMS, $M-C_2NCl_3+H^+$) calcd for $C_{105}H_{112}O_{23}$ 1740.7594, found 1740.7599.

**2,3,4,6-Tetra-*O*-benzyl-**α**-D-mannopyranosyl)-(1→2)-(4,6-di-O-acetyl-3-*O*-benzyl-**α**-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-**α**-D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzyl-**α**-D-mannopyranosyl)-(1→4)-(2-azido-3,6-di-*O*-benzyl-2-deoxy-**α**-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-D-myo-inositol** (**3a**). The above tetramannose-trichoroacetimidate donor (2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-(4,6-di-*O*-acetyl-3-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2,3,4-tri-O-benzyl-α-D-mannopyranosyl)-trichloroacetimidate, **8**, 250 mg, 0.114 mmol) and the glucosamine-inositol acceptor (2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benzyl-1-O-(4-methoxybenzyl)-D-*myo*-inositol, **5**, 150 mg, 0.15 mmol) were dried by evaporation through anhyd toluene and then dissolved in anhyd diethyl-ether (10 mL) under argon and cooled to 0 $^0$C. To this was added a solution of 0.1 N TMSOTf (320 μL, 0.36 mmol) and reaction mixture was stirred for 30 min. After completion of reaction the reaction was neutralized with $Et_3N$ and solvent evaporated, and residue purified by a silica column

(hexane/EtOAc, 8:2) to provide desired pseudohexasaccharide **3a** (220 mg, 60%) as viscous substance. TLC (hexane/EtOAc, 3:1) $R_f$ = 0.25; $^1$HNMR (300 MHz, $CDCl_3$): 1.80 (s, 3H), 1.93 (s, 3H), 3.25-4.01 (m, 38H), 3.83 (s, 3H), 4.33-5.08 (m, 34H), 5.26 (bs, 1H), 5.28 (bs, 1H), 5.37 (bs, 1H), 5.38 (bs, 1H), 5.80 (d, J = 3.8 Hz, 1H), 6.89 (d, 2H), 7.07-7.39 (m, 87H); $^{13}$C NMR (75 MHz, $CDCl_3$): 20.61, 22.59, 55.20, 62.03, 62.77, 62.97, 65.73, 66.51, 68.09, 68.51, 68.63, 68.86, 69.01, 69.18, 69.62, 69.69, 71.48, 71.71, 71.96, 72.05, 72.10, 72.21, 72.47, 72.66, 73.01, 73.12, 73.19, 74.16, 74.50, 74.61, 74.78, 74.94, 75.07, 76.20, 77.17, 79.03, 79.94, 80.04, 80.85, 81.52, 81.82, 81.87, 97.28, 99.23, 99.35, 99.80, 100.29, 113.92, 127.19-128.23 (multiple peaks), 129.44, 138.04-138.85 (multiple peaks), 159.31, 169.41, 170.67; HRMS (positive ion ESMS, M+$Na^+$) calcd for $C_{167}H_{175}O_{33}N_3Na$ 2773.2006, found 2773.2010.

**(2,3,4,6-Tetra-*O*-benzyl-**a**-D-mannopyranosyl)-(1→2)-(3-*O*-benzyl-6-*O*-tert-butyldi phenylsilyl-**a**-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-**a**-D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzyl-**a**-D-mannopyranosyl)-(1→4)-(2-azido-3,6-di-*O*-benzyl-2-deoxy-**a**-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-D-myo-inositol** (**3c**). The above pseudohexasaccharide **3a** (85 mg, 0.03 mmol) was dissolved in a solvent mixture of $CH_3OH$-$CH_2Cl_2$ (3:1, 6 mL) followed by addition of sodium methoxide (90 mg, 1.66 mmol). The reaction was stirred at rt for 1h, solvent was evaporated under reduced pressure and the residue purified by a silica column (hexane/EtOAc, 65:35) to obtain desired deacetylated pseudohexasaccharide **3b** (80 mg, 97%) as colorless solid which was dissolved in anhyd THF (1 mL) followed by addition of imidazole (25 mg, 0.36 mmol) and *tert*-butyldiphenylsilyl chloride (TBDPSCl, 60 µL, 0.23 mmol). The reaction mixture was stirred for 5 h, diluted with EtOAc, organic layer washed with saturated aq solution of $NaHCO_3$ and $H_2O$, dried over $Na_2SO_4$ and concentrated. The residue was purified through a small silica column to provide selectively silylated compound **3c** (82 mg, 94%). TLC (hexane/EtOAc, 7:3) $R_f$ = 0.40; $^1$HNMR (300 MHz, $CDCl_3$): 1.15 (s, 9H, TBDPS), 3.07-4.05 (m, 36H), 3.73 (s, 3H), 4.10-4.95 (m, 36H), 4.97 (bs, 1H), 5.17 (bs, 1H), 5.29 (bs, 1H), 5.42 (bs, 1H), 5.72 (d, J = 3.6 Hz, 1H), 6.80-6.82 (d, 2H), 7.04-7.26 (m, 93H), 7.61-7.77 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$): 19.14, 29.24, 55.17, 62.01, 62.89, 64.95, 68.61, 68.83, 69.11, 69.53,

71.55, 71.66, 71.78, 71.90, 72.05, 72.20, 72.65, 72.98, 73.05, 73.20, 74.13, 74.60, 74.75, 74.86, 75.01, 75.62, 76.18, 77.11, 77.81, 79.81, 79.53, 79.68, 79.91, 80.83, 81.52, 81.79, 81.89, 97.20, 98.29, 99.00, 99.17, 100.25, 113.89, 127.15-128.21 (multiple peaks), 133.02, 135.55, 135.47, 137.75-138.89 (multiple peaks), 159.26. HRMS (positive ion ESMS, $M+Na^+$) calcd for $C_{179}H_{189}O_{31}N_3SiNa$ 2927.2972, found 2927.2981.

**(2,3,4,6-Tetra-*O*-benzyl-**a**-D-mannopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-**a**-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-**a**-D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzyl-**a**-D-mannopyranosyl)-(1→4)-(2-azido-3,6-di-O-benzyl-2-deoxy-**a**-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-O-benzyl-1-*O*-(4-methoxybenzyl)-D-myo-inositol** (**3d**). The TBDPS protected pseudohexasaccharide (80 mg, 0.25 mmol) was dissolved in anhyd DMF (2 mL) followed by addition of benzyl bromide (90 µL, 0.66 mmol) and sodium methoxide (10 mg, 0.25 mmol). The reaction mixture was stirred at 0 $^0$C for 1 h, quenched with methanol, diluted with EtOAc, organic layer washed with brine and $H_2O$, dried over $Na_2SO_4$ and concentrated. The residue was dissolved in 1.2 mL of a 1M solution of tetrabutylammonium fluoride (TBAF) in anhydrous THF and stirred at room temperature for 48 h. After completion of reaction, solvent was quickly removed under vacuum and the viscous yellow mass was purified through a small silica column (hexane-EtOAc, 70:30) to provide desired compound (87 mg, 90%) as colorless solid. TLC (hexane/EtOAc, 70:30) $R_f$ = 0.25; $^1$HNMR (300 MHz, $CDCl_3$): 3.15-3.85 (m, 36H), 3.96-4.88 (m, 38H), 3.73 (s, 3H), 4.94 (s, 1H), 5.17 (s, 2H), 5.29 (s, 1H), 5.71 (d, J = 3.6 Hz, 1H), 6.80 (d, 2H), 7.05-7.26 (m, 92H); $^{13}$C NMR (75 MHz, $CDCl_3$): 63.00, 65.96, 68.44, 68.33, 69.01, 69.25, 69.64, 70.25, 70.45, 71.57, 71.65, 71.73, 71.94, 72.00, 72.08, 72.54, 72.64, 73.07, 73.18, 74.11, 74.58, 74.65, 74.80, 74.91, 75.43, 77.10, 77.32, 77.71, 79.14, 79.62, 79.89, 80.80, 81.48, 81.78, 81.86, 97.27, 99.30, 99.31, 99.86, 100.43, 113.87, 127.21-128.17 (multiple peaks), 129.44, 138.32-138.35 (multiple peaks), 159.24; HRMS (positive ion ESMS, $M+Na^+$) calcd for $C_{170}H_{177}O_{31}N_3Na$ 2779.2264, found 2779.2273.

**(2,3,4,6-Tetra-*O*-benzyl-**a**-D-mannopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-6-*O*-(benzyl-2-(N-benzyloxycarbonyl)-aminoethyl-phosphonato)-**a**-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-**a**-D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzyl-**a**-D-mannopyr**

**anosyl)-(1→4)-(2-azido-3,6-di-*O*-benzyl-2-deoxy-**a**-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benzyl-1-*O*-(4-methoxybenzyl)-D-*myo*-inositol**. Above pseudohexasaccharide **3d** (40 mg, 0.014 mmol), dried thoroughly first with co-evaporation with anhydrous toluene (three times) and then under high-vacuum for two hours, was dissolved in anhydrous $CH_2Cl_2$ (1 mL) and to this solution was added freshly prepared[6] $CbzNH(CH_2)_2OPOBnNiPr_2$ (12 mg, 0.027 mmol) and 1H-tetrazole (2 mg, 0.027 mmol). The reaction mixture was stirred under argon at room temperature for 3 h. The reaction mixture was brought to –40 $^0$C and treated with mCPBA (4 mg), stirred at –40 $^0$C for 30 min and at room temp for 1 h. The reaction was now quenched with saturated aqueous $NaHCO_3$ solution, diluted with $CH_2Cl_2$, the organic phase was dried ($Na_2SO_4$), concentrated and the residue was purified on a small silica column (EtOAc:Hexane:$Et_3N$; 1:3:0.1) to give desired phosphorylated product (27 mg, 60%) as a diastereoisomeric mixture. TLC (hexane/EtOAc, 60:40) $R_f$ = 0.35/0.37; $^1$HNMR (300 MHz, $CDCl_3$): 3.18-5.15 (m, 90H), 5.52 (d, 1H), 6.80 (d, 2H), 7.09-7.40 (m, 102H, ArH); $^{13}$C NMR (75 MHz, $CDCl_3$): 65.19, 66.54, 66.79, 68.83, 69.69, 71.96, 72.19, 72.81, 73.01, 74.15, 74.48, 74.87, 75.21, 76.45, 77.35, 78.59, 79.58, 79.99, 80.91, 95.13, 98.89, 99.12, 100.07, 113.87, 127.04-128.37 (multiple peaks), 129.44, 137.59-138.67 (multiple peaks), 156.33, 159.24; $^{31}$P NMR (125 MHz): -0.61, 0.84; HRMS (positive ion ESMS, M+$Na^+$) calcd for $C_{187}H_{195}O_{36}N_4PNa$ 3126.3186, found 3126.3192.

**(2,3,4,6-Tetra-*O*-benzyl-**a**-D-mannopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-6-*O*-(benzyl-2-(N-benzyloxycarbonyl)-aminoethyl-phosphonato)-**a**-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-**a**-D-mannopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzyl-**a**-D-mannopyranosyl)-(1→4)-(2-azido-3,6-di-*O*-benzyl-2-deoxy-**a**-D-glucopyranosyl)-(1→6)-2,3,4,5-tetra-*O*-benzyl-1-*O*-(2-hexadecanoyl-1-*O*-octadecyl-*sn*-glyceryl-phosphonato)-D-*myo*-inositol** (**Fully-protected GPI anchor**). The above compound (27 mg, 8.7 μmol) dissolved in a solution of $CH_3CN$/ toluene/water (1 mL, 91:5:4) was treated with CAN (25 mg, 45 μmol) was at 0 $^0$C, and the solution was stirred at for 30 min at the same temp and at room temperature for 1 h. the reaction mixture was diluted with $CH_2Cl_2$, washed with saturated $NAHCO_3$ solution and the combined organic layer was dried over $Na_2SO_4$. Silica column (toluene/acetone, 1:1) afforded PMB deprotected phosphohexasaccahride

(20 mg, 77%). The above compound (17 mg, 5.7 μmol), and freshly prepared 2-*O*-octadecanoyl-1-*O*-octadecyl-*sn*-glyceryl-*H*-phosphonate (**2**, 30 mg, 44 μmol) were dried by evaporation with anhyd pyridine three times, and dissolved in anhyd pyridine (0.4 mL). This was followed by addition of pivaloyl chloride (9.6 μL, 80 μmol). After stirring at room temperature for 30 min, the reaction was treated with an iodine solution (2 equiv, 20 mg iodine in pyridine-water, 2.45:0.05) and the mixture was further stirred for 25 min. The reaction was diluted with $CHCl_3$ and organic layer washed with 5% sodium bisulfite solution. The organic layer was dried over $Na_2SO_4$, concentrated and purified on a silica column using 5% MeOH-$CH_2Cl_2$ (with 1% triethylamine) solvent system, providing the desired phospholipidated fully protected GPI-anchor (12 mg, 55%). $^1$H NMR (300 MHz, $CDCl_3$): 0. 87 (t, 6H), 1.24 (m, 58H), 1.43 (m, 2H), 1.51-1.65 (m, 4H), 2.80-5.85 (m, 89H), 7.0-7.80 (m, 100H); HRMS (ESMS, M+$Na^+$) calcd for $C_{218}H_{264}O_{41}N_4P_2Na$ 3678.8069, found 3678.8021.

a **-D-mannopyranosyl)-(1→2)-(6-*O*-(aminoethylphosphonato)-**a **-D-mannopyranosyl)-(1→2)-**a **-D-mannopyranosyl)-(1→6)-**a **-D-mannopyranosyl)-(1→4)-(2-amino-2-deoxy-**a **-D-glucopyranosyl)-(1→6)-1-*O*-(2-hexadecanoyl-1-*O*-octadecyl-*sn*-glyceryl-phosphonato)-D-*myo*-inositol** (**1**). The protected GPI-anchor (12 mg, 3.2 μmol) and the catalyst 20% $Pd(OH)_2$ (25 mg) were dissolved in a solvent mixture of MeOH (1 mL), $CH_2Cl_2$ (1 mL) and $H_2O$ (0.05 mL). The residual and dissolved air from the flask was removed by repeated evacuations by suction. The reaction mixture was then stirred under positive hydrogen atmosphere for 48 h. After completion of reaction, the mixture was filtered through a small celite pad, which was washed several times with the solvent mixture, and concentrated under reduced pressure to provide desired GPI-anchor **1** (4.2 mg, 73%). $^1$H NMR (300 MHz, $CD_3OD$-$CDCl_3$-$D_2O$) 0.87-1.00 (m, 6H), 1.16-2.35 (m, 66H), 2.63-4.28 (m, 45H), 4.76 (1H), 5.10 (br s, 2H), 5.18 (br s, 1H), 5.40 (br s, 1H); MS (ESMS, M+H+Na) calcd for $C_{77}H_{147}O_{39}N_2P_2Na$ 1808.8954, found 1808.8990.

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