Supplementary Information for:

A VERSATILE, THREE-COMPONENT-REACTION ROUTE TO N-GLYCOSYLAMINES[1]

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1-N-(acetyl)-[N-(benzyloxycarbonyl)-L-leucine]-2-deoxy-2-tetrachloro- phthalimido-3,4-di-O-benzoyl-6-O-*tert*- butyl dimethyl silyl-β-D-glucopyranosyl amine.

To a solution of pentenyl glycoside (270 mg, 0.32 mmol) and N-(benzyloxy carbonyl)-L-leucine (93 mg, 0.35 mmol) in acetonitrile (8 mL) was added NBS (125 mg, 0.704 mmol). The solution was protected from light and stirred at RT under argon atmosphere for 3hrs. The reaction was quenched by adding 10% sodium thiosulfate solution (7 mL) and saturated $NaHCO_3$ solution (7 mL) and then extracted with CH_2Cl_2. The organic layer was dried, concentrated and the residue on flash column chromatography (10% EtOAc-Hexane) afforded the product (232 mg, 0.218mmol, 69%) as a colorless amorphous solid.

^{1}H NMR ($CDCl_3$,400 MHz): δ 7.89 - 7.86 (d, 2H, ArH), 7.74 - 7.71 (d, 2H, ArH), 7.46 - 7.42 (t, 1H, ArH), 7.40 - 7.36 (t, 1H, ArH), 7.33 - 7.21 (m, 5H, ArH), 6.33 - 6.28 (dd, J_1, J_2=9.6, 10.0 Hz, 1H), 6.18 - 6.09 (m, 2H), 5.60 - 5.57 (t, 1H, J=9.6 Hz), 5.10 - 4.94 (m, 3H), 4.35 - 4.30 (t, J=9.6Hz, 1H), 4.01 - 3.97 (m, 1H), 3.88 - 3.74 (m, 2H), 2.41 (s, 3H, -$NCOCH_3$), 1.88 - 1.78 (m, 1H), 1.49 - 1.40 (m, 1H), 1.28 - 1.25 (m, 1H), 0.82 (bs, 9H), 0.80 - 0.70 (t, 6H), 0.10 (d, 6H).

^{13}C NMR ($CDCl_3$,100 MHz): δ 172.82, 169.71, 165.68, 164.94, 163.35, 162.77, 153.78, 140.45, 139.91, 133.85, 133.30, 133.18, 129.79, 129.68, 129.19, 129.04, 128.71, 128.44, 128.29, 127.90, 127.10, 126.96, 75.79, 71.34, 69.85, 69.29, 62.42, 56.16, 55.67, 37.21, 34.60, 31.51, 26.52, 25.81, 25.14, 22.79, 22.58, 21.77, 18.33, 14.05, -5.43, -5.51.

FAB-MS, m/z: 1058 (MH^+)

Anal. cald. for $C_{50}H_{53}Cl_4N_3O_{12}Si$: C, 56.77; H, 5.05; N, 3.97, Cl, 13.41. Found: C, 56.41; H, 5.04; N, 3.60; Cl, 13.78.

1-N-(acetyl)-[N-(benzyloxy carbonyl)-L-leucine]-2-deoxy-2-tetrachlorophthali-mido-3-O-benzoyl-6-O-*tert*-butyl dimethyl silyl-β-D-glucopyranosyl amine.

To a solution of pentenyl glycoside (86 mg, 0.1 mmol) and N-(benzyloxy carbonyl)-L-leucine (26 mg, 0.1 mmol) in dry CH_3CN(2 mL), NBS (40 mg, 0.225 mmol) was added. The reaction mixture was stirred in darkness at RT under argon atmosphere for 4hrs. The reaction was quenched by adding 10% sodium thiosulfate solution (3 mL) and saturated $NaHCO_3$ solution (3 mL) and extracted with CH_2Cl_2. The organic layer was evaporated off and the crude residue on column chromatography (10% EtOAc-Hexane) afforded the product (95 mg, 95%) as a colorless amorphous solid.

^{1}H NMR ($CDCl_3$,400 MHz): δ 7.89 - 7.82 (m, 2H, ArH), 7.51 - 7.44 (m, 1H, ArH), 7.37 - 7.20 (m, 7H, ArH), 6.22 - 6.17 (dd, 1H, J_1, J_2=8.8, 11.2 Hz), 6.11 - 6.09 (d, 1H, 9.6 Hz), 6.05 - 5.97 (m, 1H), 5.73 - 5.68 (m, 1H), 5.05 - 4.92 (m, 2H), 4.87 - 4.83 (m, 1H), 4.02 - 3.64 (m, 4H), 3.53 - 3.50 (d, 1H), 2.49 (s, 3H), 1.88 - 1.74 (m, 1H), 1.46 - 1.37 (m, 1H), 1.46 - 1.37 (m, 1H), 0.88 (bs, 9H), 0.71 - 0.68 (t, 6H), 0.09 - 0.05 (m, 6H).

^{13}C NMR ($CDCl_3$,100 MHz): δ 172.82, 171.53, 167.20, 165.99, 154.025, 140.53, 133.47 129.89, 128.72, 128.60, 128.41, 128.00, 127.90,127.01, 92.16, 75.95, 75.69, 74.72, 73.84, 73.33, 72.35, 72.11, 70.62, 70.20, 69.16, 68.93, 64.69, 64.37, 56.56, 56.30, 55.02, 51.92, 37.66, 37.22, 26.84, 26.48, 25.84, 25.35, 25.13, 23.24, 22.83, 21.77, 21.63, 18.31, -5.43.

FAB-MS, m/z: 954 (MH^+)

1-N-(acetyl)-[N-(benzyloxycarbonyl)-L-leucine]-2-deoxy-2-tetrachlorophthalimido-3,6-di-O-benzoyl-β-D-glucopyranosyl amine.

To a solution of pentenyl glycoside (156 mg, 0.22 mmol) and N-(benzyloxy carbonyl)-L-leucine (53 mg, 0.2 mmol) was added NBS (80 mg, 0.45 mmol). The solution was protected from light and stirred at RT under argon atmosphere for 4hrs. The reaction was quenched by adding 10% sodium thiosulfate (7 mL) and saturated $NaHCO_3$ solution (7 mL) and then extracted with CH_2Cl_2. The organic layer was dried, concentrated and the residue on flash column chromatography (15% EtOAc-Hexane) afforded (104 mg, 0.10 mmol, 55%) as a colorless viscous liquid. [Some product with the benzoyl gp migrated sugar was also observed].

^1H NMR ($CDCl_3$,400 MHz): δ 8.11 - 8.08 (d, 2H, ArH), 7.88 - 7.85 (d, 2H, ArH), 7.62 - 7.21 (m, 11H, ArH), 6.16 - 6.07 (m, 2H), 5.07 - 4.95 (m, 3H), 4.86 - 4.82 (dd, J_1, J_2=3.6, 12 Hz, 1H), 4.33 - 4.29 (t, J=9.6 Hz, 1H), 4.61 - 4.58 (dd, 1H), 4.06 - 3.99 (m, 1H), 3.84 - 3.80 (m, 1H), 3.58 (bs, 1H), 2.42 (s, 3H) 1.84 - 1.81 (m, 1H), 1.50 - 1.43 (m, 1H), 0.93 - 0.84 (m, 1H), 0.74 - 0.70 (dd, J_1, J_2=6.8, 10.4 Hz, 6H).

FAB-MS, m/z: 944 (MH^+)

1-N-(acetyl)-[N-(benzyloxycarbonyl)-L-leucine]-2-deoxy-2-tetrachlorophthali-mido-3,4,6-tri-O-benzoyl-β-D-glucopyranosyl amine.

To a solution of pentenyl glycoside (82 mg, 0.1 mmol) and N-(benzyloxy carbonyl)-L-leucine (31 mg, 0.12 mmol) in CH_3CN (2 mL) was added NBS (40 mg, .125 mmol). The solution was protected from light and stirred at RT under argon atmosphere for 3hrs. The reaction was quenched by adding 10% sodium thiosulfate solution (7 mL)

and saturated $NaHCO_3$ solution (7 mL) and then extracted with CH_2Cl_2. The organic layer was dried, concentrated and the residue on flash column chromatography afforded the product (55 mg, 53%) as a colorless paste.

^1H NMR ($CDCl_3$, 400 MHz): δ 8.03 - 8.01 (d, 2H, ArH), 7.86 - 7.82 (d, 2H, ArH), 7.76 - 7.70 (d, 2H, ArH), 7.54 - 7.19 (m, 14H, ArH), 6.38 - 6.32 (t, J=9.3, 10.2 Hz, 1H), 6.23 - 6.19 (d, J=9 Hz, 1H), 5.73 - 5.67 (t, J=9.6 Hz, 1H), 5.07 - 4.95 (m, 2H), 4.60 - 4.32 (m, 3H), 4.15 - 4.00 (m, 1H), 2.38 (s, 3H), 1.83 - 1.43 (m, 2H), 0.93 - 0.79 (m, 1H), 0.712 - 0.690 (d, 6H).

FAB-MS, m/z: 1047 (M^+)

1-N-(acetyl)-[N-(-9-fluorenylmethoxycarbonyl)-L-isoleucine]-2-deoxy-2-tetrachloro-phthalimido-3,4-di-O-benzoyl-6-O-*tert*- butyl dimethyl silyl-β-D-glucopyranosyl amine.

To a solution of pentenyl glycoside (135 mg, 0.16 mmol) and N-FMoc-isoleucine (56 mg, 0.16 mmol) in CH_3CN (2 mL) was added NBS (67 mg, 0.375 mmol). The solution was protected from light and stirred at RT under argon atmosphere for 3hrs. The reaction was quenched by adding 10% sodium thiosulfate solution (7 mL) and saturated $NaHCO_3$ solution (7 mL) and then extracted with CH_2Cl_2. The organic layer was dried, concentrated and the residue on flash column chromatography afforded the product (98 mg, 54%) as a colorless paste.

^1H NMR ($CDCl_3$,400 MHz): δ 7.85-7.83 (m, 2H, ArH), 7.71-7.68 (m, 3H. ArH), 7.40-7.18(m, 13H, ArH), 7.71-7.68(m, 3H, ArH), 7.40-7.18(m, 13H, ArH), 6.24-6.19 (t, J=9.2 Hz, 1H), 6.12-6.07 (t, J=9.2 Hz,1H), 6.04-6.03 (m, 2H), 5.58-5.54 (t, J=10Hz, 1H), 5.53-5.49 (t, J=9.2Hz, 1H), 4.65-4.64(d, 1H), 4.38-4.37 (t, J=2Hz, 1H), 3.95-3.72(m, 3H), 1.95 (s, 3H), 1.24-1.16(m, 9H), 0.82-0,77(m, 9H), -0.68(d, 6H).

FAB-MS m/z :1146(MH^+)

1- N- (acetyl) - [N-(4-chloromethyl)-benzoyl]-2-deoxy-2-tetrachlorophthalimido-4, 6- O-benzylidine-β-D-glucopyranosyl amine.

To a solution of pentenyl glycoside (59 mg, 0.1 mmol) and 4-chloromethyl benzoic acid (20 mg, 0.12 mmol) in CH_3CN (4 mL) was added NBS (40 mg, 0.225 mmol).

The solution was protected from light and stirred at RT under argon atmosphere for 1hr. The reaction was quenched by adding 10% sodium thiosulfate solution (7 mL) and saturated $NaHCO_3$ solution(7 mL) and then extracted with CH_2Cl_2. The organic layer was concentrated and the residue on flash column chromatography (20% EtoAc-Hexane) afforded the product (40 mg, 55%).

^1H NMR ($CDCl_3$, 300 MHz): δ 7.72 - 7.69 (d, 2H, ArH). 7.45 - 7.42 (m, 3H, ArH), 7.39 - 7.34 (m, 4H, ArH), 6.10 - 6.07 (d, J=9.6Hz, 1H), 5.56 (s, 1H), 5.24 -5.17 (t, J - 9.6 Hz, 1H), 4.64 -4. 57 (m, 3H), 4.41 -4.30 (m, 1H), 3.88 - 3.81 (t, J=9.6Hz, 1H), 3.72 - 3.62 (m, 2H), 2.79 (bs, 1H), 2.08 (S, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.73, 171.68, 163.74, 162.63, 143.39, 140.53,136.65, 133.93, 130.09, 129.88,129.43, 128.88, 128.62, 128.37, 127.99, 126.79, 126.17, 101.89, 81.85, 81.27, 69.02, 68.29, 54.31, 44.93, 29.71, 25.67.

FAB-MS, m/z : 818.99 (M^+), 816.96 (M-2)$^+$

<u>1-N-(acetyl)-[N-(4-chloromethyl)-benzoyl]-2-deoxy-2-tetrachlorophthalimido-3-benzyl, 4,6-O-benzylidine-β-D-glucopyranosyl amine.</u>

A solution of pentenyl glycoside (69 mg, 0.1 mmol) and 4-chloromethyl benzoic acid (20 mg, 0.12 mmol) were treated with NBS (40 mg, 0.225 mmol) in CH_3CN (4mL) at RT under argon atmosphere for 2hrs. The reaction was quenched with 10% sodium thiosulfate solution (7 mL) and saturated sodium biocarbonate (7 mL) and extracted with CH_2Cl_2. The organic layer was concentrated and flash column chromatographed to afford the product (43 mg, 53%).

^1H NMR ($CDCl_3$, 300 MHz): δ 7.69 - 7.66 (d, 2H, ArH), 7.54 - 7.40 (m, 8H, ArH), 7.16 - 6.76 (m, 4H, ArH), 6.02 - 5.99 (d, J=9.6 Hz, 1H), 5.68 (S, 1H), 5.18 - 5.15 (d, J=9.6 Hz, 1H) 4.83 - 4.76 (d, 1H), 4.64 - 4.50 (m, 3H), 4.43 - 4.30 (m, 3H), 3.89 - 3.74 (m, 2H), 2.65 (S, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.94, 171.71, 163.34, 162.31, 143.49, 140.22, 138.32, 137.28, 134.13, 130.05, 129.87, 129.84, 129.35, 128.63, 128.53, 128.34, 128.27,

128.23, 128.15, 127.61, 127.34, 126.38, 126.26, 101.65, 82.31, 76.65, 75.94, 75.17, 74.72, 69.30, 68.61, 53.73, 45.15, 25.75.

FAB-MS: m/z, 818.9 (M^+)

1-N-(acetyl)-[N-(4-chloromethyl)-benzoyl]-2-deoxy-2-tetrachlorophthalimido-3-O- benzoyl-4,6-O-benzylidine-β-D-glucopyranosyl amine.

A solution of pentenyl glycoside (100 mg, 0.12 mmol) and 4-chloromethyl benzoic acid (51 mg, 0.3 mmol) were treated with NBS (60 mg, 0.33 mmol) in CH_3CN (6mL) at RT under argon atmosphere for 2hrs. The reaction was quenched with 10% sodium thiosulfate solution (7 mL) and saturated sodium biocarbonate (7 mL) and extracted with CH_2Cl_2. The organic layer was concentrated and flash column chromatographed to afford the product (80 mg, 71 %).

^1H NMR ($CDCl_3$, 300 MHz): δ 7.87 -7.84 (d, 2H, ArH), 7.74 - 7.72 (d, 2H, ArH), 7.53 - 7.45 (m, 3H, ArH), 7.41 - 7.35 (m, 3H, ArH), 7.33 - 7.29 (m, 4H, ArH), 6.24 - 6.21 (d, J=9.6Hz, 1H) 6.09 - 6.02 (t, J=9.6 Hz, 1H), 5.59 - 5.53 (t, J=9Hz, 2H), 4.60 (s, 2H), 4.47 - 4.41 (dd, J_1, J_2=5.1, 10.1 Hz, 1H), 4.08 - 4.02 (t, J=9.6 Hz, 1H), 3.94 - 3.87 (t, J=10.2 Hz, 1H), 3.81 -3.77 (dd, J_1,J_2 = 4.5, 9.6 Hz, 1H), 2.07 (s, 3H).

FAB-MS m/z : 832 (M^+)

1 - N- (acetyl) -[N- (3, 5 -dinitro)-benzoyl]- 2- deoxy- 2- tetrachlororphthalimido- 4, 6 - O - benzylidene - β- D- glucopyranosyl amine.

To a solution of pentenyl glycoside (59 mg, 0.1 mmol) and 3,5-dinitro benzoic acid (25 mg, 0.12 mmol) in CH_3CN (4 mL) was added NBS (40 mg, .225 mmol). The solution was protected from light and stirred at RT under argon atmosphere for 3hrs. The reaction was quenched by adding 10% sodium thiosulfate solution (7 mL) and saturated $NaHCO_3$ solution (7 mL) and then extracted with CH_2Cl_2. The organic layer was dried, concentrated and the residue on flash column chromatography afforded the product (42mg, 54%) as a colorless paste.

^{1}H NMR ($CDCl_3$, 300 MHz): - δ 9.05-9.04 (d,1H,ArH), 8.71-8.70 (d, 1H, ArH), 7.94 (s, 1H, ArH), 7.51-7.16 (m, 5H. ArH), 6.03- 6.00 (d, J =9.6 Hz, 1H), 4.59 (s, 1H), 4.61-4.49 (m, 1H), 4.48- 4.32 (m, 1H), 3.91 - 3.56 (m, 3H), 3.01 (bs, 1H), 2.02 (s, 3H).

FAB- MS m/z : 769.9 (M^+-1)

1 - N- (acetyl) -[N- (4-chloromethyl)-benzoyl]- 2- deoxy- 2- azido- 4, 6 -O- benzylidene - 3 - benzyl- α- D- glucopyranosyl amine.

To a solution of pentenyl glycoside (25 mg, 0.05 mmol) and 4-chloromethyl benzoic acid (11 mg, 0.06 mmol) in CH_3CN (4 mL) was added NBS (20 mg, .11 mmol). The solution was protected from light and stirred at RT under argon atmosphere for 3hrs. The reaction was quenched by adding 10% sodium thiosulfate solution (3 mL) and saturated $NaHCO_3$ solution (3 mL) and then extracted with CH_2Cl_2. The organic layer was dried, concentrated and the residue on flash column chromatography afforded the product (28 mg, 97%) as a colorless paste.

^{1}H NMR ($CDCl_3$, 300 MHz): - δ 7.81 -7.79 (d, 2H, ArH), 7.53 - 7.51 (d, 4H, ArH), 7.45 -7.38 (m, 4H, ArH). 7.34 - 7.23 (m, 4H. ArH), 6.29 - 6.26 (d, J = 7.1 Hz. 1H), 5. 61 (s, 1H). 4.97 - 4.93 (d, 1H), 4.75- 4.71 (d, 1H), 4.63 - 4.56 (m, 3H), 4.48 - 4.39 (m, 1H), 4.33 - 4.28 (dd, 1H), 4.19-4.13 (t, J = 7.1 Hz, 1H), 3.81 - 3.75 (t, J = 8.7 Hz, 1H), 3.71 - 3.64 (t, J = 7.5 Hz, 1H), 1.98 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): - δ 173.84, 173. 42, 142. 95, 137.90, 137.32, 135.59, 129.98, 129, 07, 129.02, 128.36, 128.27, 128.16, 127.81, 126.09, 101.45, 82.94, 81.36, 78.45, 76.42, 76.14, 74.83, 69.14, 65.41, 61.53, 45.06, 26.77.

FAB-MS m/z : 577.14 (M^+), 575.13 (M^+-2)

1 - N- (acetyl) -[N- (3, 5- dinitro)-benzoyl]- 2- deoxy- 2- azido- 4, 6 -O- benzylidene - 3- benzyl- α- D- glucopyranosyl amine.

To a solution of pentenyl glycoside (45 mg, 0.1 mmol) and 3,5-dinitrobenzoic acid(25 mg, 0.12 mmol) in CH_3CN (4 mL) was added NBS (40 mg, .225 mmol). The solution was protected from light and stirred at RT under argon atmosphere for 3hrs. The reaction was

quenched by adding 10% sodium thiosulfate solution (7 mL) and saturated $NaHCO_3$ solution (7 mL) and then extracted with CH_2Cl_2. The organic layer was dried, concentrated and the residue on flash column chromatography afforded the product (62 mg, 99%) as a colorless paste.

^1H NMR ($CDCl_3$, 300 MHz): - δ 9.13 - 9.12 (bs, 1H, ArH), 8.828-8.820 (d, 2H, ArH), 7.53 -7.50 (m, 2H, ArH), 7.45-7.40 (m, 3H, ArH), 7.30- 7.22 (m, 5H, ArH), 5.93 - 5.90 (d, J = 7.1Hz, 1H), 5.63 (s,1H), 4.96 -4.93 (d, 1H), 4.72 -4.69 (d, 1H). 4.53 -4.47 (t, J=7.7Hz, 1H), 4.43- 4.29 (m, 2H), 4.23 -4.18 (t, J = 7.1 Hz, 1H), 3.84 -3.78 (t, J = 7.7, 9.6 Hz, 1H), 3.74- 3.66 (t, J =9.6 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): - δ 174.18, 171.46, 148.58, 139.01, 137.44, 137.02, 129.17, 128.51, 128.39, 128.34, 128.30, 127.97, 126.05, 125.96, 121.66, 101.53, 83.06, 82.59, 78.14, 74.87, 68.81, 65.21, 60.99, 23.59.

FAB-MS m/z : 658.4 (M^+-1+K)

<u>1 - N- (acetyl) -[N- (4-chlorormethyl)-benzoyl]- 2- deoxy- 2- azido- 4, 6 -O- benzylidene - α- D- glucopyranosyl amine.</u>

To a solution of pentenyl glycoside (50 mg, 0.13 mmol) and 4-cloromethyl benzoic acid (28 mg, 0.16 mmol) in CH_3CN (4 mL) was added NBS (55 mg, 0.31 mmol). The solution was protected from light and stirred at RT under argon atmosphere for 3hrs. The reaction was quenched by adding 10% sodium thiosulfate solution (7 mL) and saturated $NaHCO_3$ solution (7 mL) and then extracted with CH_2Cl_2. The organic layer was dried, concentrated and the residue on flash column chromatography afforded the product (60mg, 95%) as a colorless paste.

^1H NMR ($CDCl_3$, 300 MHz): - δ 7.81- 7.79 (d, 2H, ArH), 7.53 - 7.47 (m, 4H, ArH), 7.41 - 7.38 (m, 3H, ArH), 6.31 - 6.28 (d, J = 9Hz, 1H), 5.56 (s, 1H), 4.68 - 4.63 (m, 2H), 4.43 - 4.36 (m, 1H), 4.31 -4.26 (dd, J_1, J_2 = 5.1, 10.2 Hz, 1H), 4.13 - 4.06 (m, 1H), 3.68 -3.61 (t, J =10.2 Hz, 1H), 3.60 - 3.54 (t, J = 9.6 Hz, 1H), 2.96 (bs, 1H), 1.98 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): - δ 173.91, 173.52, 143.06, 137.01, 135.45, 129. 95, 129.37, 129.09, 128.88, 128.46, 128.42, 128.38, 127.85, 126.38, 126.23, 81.88, 81.29, 70.96, 69.01, 65.24, 62.27, 45.03, 26.73.

FAB-MS m/z : - 487.1 (M^+-1)

1 - N- (acetyl) -[N- (3,5 -dinitro)-benzoyl]- 2- deoxy- 2- azido- 4, 6 -O- benzylidene - α- D- glucopyranosyl amine.

To a solution of pentenyl glycoside (50 mg, 0.14 mmol) and 3,5-dinitrobenzoic acid (35 mg, 0.17 mmol) in CH_3CN (4 mL) was added NBS (55 mg, 0.31 mmol). The solution was protected from light and stirred at RT under argon atmosphere for 1hr. The reaction was quenched by adding 10% sodium thiosulfate solution (7 mL) and saturated $NaHCO_3$ solution (7 mL) and then extracted with CH_2Cl_2. The organic layer was dried, concentrated and the residue on flash column chromatography afforded the product (74mg, 99%) as a colorless paste.

^{1}H NMR ($CDCl_3$, 300 MHz): - δ 9.14 - 9.12 (t, 1H, ArH), 8.81 - 8.80 (d, 2H, ArH), 7.52 - 7.49 (m, 2H, ArH), 7.40 - 7.37 (t, 3H, ArH), 5.93- 5.90 (d, J = 7.8 Hz, 1H), 5.55 (s, 1H), 4.63 -4.56 (t, J = 8.7 Hz, 1H), 4.40 - 4.28 (m, 2H), 4.19 - 4.09 (m, 1H), 3.70 - 3.63 (t, J = 10.2 Hz, 1H), 3.62 - 3.55 (t, J = 9.3 Hz, 1H), 2.98 (bs, 1H), 2.36 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): - δ 174.50, 171. 73, 148.79, 139.18, 136.97, 129.71, 128.69, 128.64, 126.54, 121.88, 102.39, 83.16, 81.78, 71.50, 68.93, 65.24, 61.86, 23.83.

FAB-MS m/z : - 529.1 (MH^+), 531.1(M^++3).

1-N-(acetyl)-[N-(4-chloromethyl)-benzoyl]-2-deoxy-2-tetrachlorophthalimido-3, 4-O-benzoyl-6-O- *tert*- butyl dimethylsilyl-β-D-glucopyranosyl amine.

To a solution of pentenyl glycoside (83 mg, 0.1 mmol) and 4-chloromethyl benzoic acid (18 mg, 0.11 mmol) in CH_3CN (4ML) was added NBS (40 mg, 0.225 mmol). The solution was protected from light and stirred at RT under argon atmosphere for 2hrs. The reaction was quenched by adding 10% sodium thiosulfate solution (7 mL) and

saturated $NaHCO_3$ solution (7 mL) and then extracted with CH_2Cl_2. The organic layer was concentrated and the residue on flash column chromatography (10% EtOAc-Hexane) afforded the product (40 mg, 0.04 mmol, 43%) as a white amorphous solid.

^1H NMR ($CDCl_3$,300 MHz): δ 7.96 - 7.86 (m, 3H, ArH), 7.82 - 7.72 (m, 3H, ArH), 7.51 - 7.25 (m, 8H, ArH) 6.18 - 6.14 (d, J=9.6 Hz, 1H), 6.04 - 5.98 (t, J=8.1 Hz, 1H) 5.76 - 5.69 (t, J=8.1 Hz, 1H), 5.62 - 5.54 (m, 1H), 4.60 (bs, 2H), 4.12 - 4.07 (m, 1H), 3.98 - 3.79 (m, 1H), 2.17 (s, 3H), 0.89 (s, 21H), 0.012 (s, 3H), 0.001 (s, 3H).

FAB-MS, m/z: 963.1 (MH^+)

N-(acetyl)-[N-(4-chloromethyl)-benzoyl]-2-deoxy-2-tetrachlorophthalimido-3,4,6-tri-O-benzoyl-β-D-glucopyranosyl amine.

To a solution of pentenyl glycoside (41 mg, 0.05 mmol) and 4-chloromethyl benzoic acid (9 mg, 0.55 mmol) in acetonitrite (2 mL) was added NBS (20 mg, 0.11 mmol). The solution was protected from light and stirred at RT under argon atmosphere for 3hrs. The reaction was quenched with 10% sodium thiosulfate solution (3 mL), and saturated $NaHCO_3$ solution (3 mL) and then extracted with CH_2Cl_2, evaporated off the solvent and the crude residue on flash column chromatogrpahy (25% EtoAc: Hexane) afforded the product (25 mg, 53%) as an amorphous solid.

^1H NMR ($CDCl_3$,300 MHz): δ 8.08 - 8.00 (d, 3H, ArH), 7.91 - 7.87 (d, 2H, ArH), 7.79 - 7.73 (t, 3H, ArH), 7.49 - 7.23 (m, 12H, ArH), 6.30 - 6.24 (t, J=8.7 Hz, 1H), 6.10 - 6.04 (t, J=9.3 Hz, 1H), 5.77 - 5.60 (m, 2H), 4.71 - 4.63 (t, 7.5 Hz, 1H), 4.55 - 4.42 (m, 2H), 4.49 (bs, 2H), 4.21 - 4.15 (m, 1H), 2.13 (s, 3H).

^{13}C NMR ($CDCl_3$,100 MHz): δ 172.95, 171.49, 166.17, 165.96, 165.09, 163.73, 161.86, 143.51, 133.59, 133.54, 133.36, 133.18, 130.56, 130.09, 130.02, 129.87, 129.85, 129.80, 129.76, 129.55, 129.49, 129.03, 128.83, 128.66, 128.55, 128.51, 128.44, 128.39, 128.22, 128.11, 92.56, 81.42, 77.22, 75.26, 71.96, 69.48, 63.08, 52.62, 44.89, 25.27.

FAB-MS m/z: 953.0(M^+)

Analysis cald. for$C_{45}H_{31}Cl_5N_2O_{11}$: C, 56.71 H, 3.28, N, 2.94; Cl, 18.60: Found C, 56.41; H, 3.38; N, 2.79; Cl, 18.32.

1-N-(acetyl)-[N-(2-iodo)-benzoyl)-2-deoxy-2-tetrachlorophthalimido-3, 4 -di-O-benzoyl-6-O-*tert*- butyl dimethylsilyl-β-D-glucopyranosyl amine.

To a solution of pentenyl glycoside (83 mg, 0.1 mmol) and 2-iodo benzoic acid (37 mg, 0.12 mmol) in dry CH_2CN (4 mL) was added NBS (40 mg, 0.225 mmol). The solution was protected from light and stirred at RT under argon atmosphere for 2hrs. The reaction was quenched by adding 10% sodium thiosulfate (7 mL) and saturated $NaHCO_3$ solution (7 mL) and then extracted with CH_2Cl_2. The organic layer was dried, concentrated and the residue on flash column chromatography (10% EtOAc-Hexane) afforded (58 mg, 50%) the product as a colorless amorphous solid.

^1H NMR ($CDCl_3$,300 MHz): δ 7.92 - 7.84 (m, 3H, ArH), 7.74 - 7.71 (d, 2H, ArH), 7.46 - 7.23 (m, 10H), 6.11 - 6.02 (m, 2H), 5.72 - 5.66 (t, J=9.3 Hz, 1H), 5.61 - 5.54 (t, J=9.6 Hz, 1H), 3.82 - 3.70 (m, 3H), 2.35 (s, 3H), 0.85 (s, 9H), 0.009 (d, 6H).

^{13}C NMR ($CDCl_3$,100 MHz): δ 173.06, 172.18, 166.01, 164.92, 163.61, 162.22, 140.58, 133.44, 133.33, 133.24, 132.62, 132.15, 130.15, 129.90, 129.85, 129.72, 129.52, 128.43, 128.24, 81.78, 78.64, 72.29, 69.71, 63.17, 53.03, 27.53.

FAB-MS m/z: 1040.2 (M^+), 1039.2(M^+-1).

Analysis cald. for $C_{43}H_{39}Cl_4IN_2O_{10}Si$: C, 49.07; H, 3.73; Cl, 13.80; I, 12.85; N, 2.73: Found C, 49.48; H, 3.99, Cl, 13.52; I, 12.67, N, 2.40.

1-N-(acetyl)-[N-(4-bromomethyl)-benzoyl)-2-deoxy-2-tetrachlorophthalimido-3,4,6-tri-O-benzoyl-β-D-glucopyranosyl amine.

To a solution of pentenyl glycoside (240 mg, 0.29 mmol) and 4-bromomethyl benzoic acid (74 mg, 0.34 mmol) in CH_3CN (4 mL) was added NBS (116 mg, 0.65 mmol). The solution was protected from light and stirred at RT under argon for 7hrs. The reaction was quenched by adding 10% sodium thiosulfate solution (7 mL) followed by saturated $NaHCO_3$ (7 mL) solution and then extracted with CH_2Cl_2. The organic layer was concentrated and the residue on flash column chromatography (25% EtOAc-Hexane) afforded the product (276 mg, 96%) as a colorless solid.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.07 - 7.98 (m, 3H, ArH), 7.91 - 7.87 (d, 2H, ArH), 7.75 - 7.73 (m, 3H, ArH), 7.67 - 7.22 (m, 11H, ArH), 6.31 - 6.28 (d, J=9.3 Hz, 1H), 6.12 - 6.06 (t, J=9.3Hz, 1H), 5.74 - 5.68 (t, J=9.6 Hz, 1H), 5.64 - 5.57 (t, J=10.2 Hz, 1H), 4.52 - 4.45 (m, 2H), 4.35 (bs, 2H), 4.23 - 4.18 (m, 1H), 2.12 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 176.67, 171.69, 166.17, 166.11, 165.30, 163.94, 162.07, 144.15, 133.78, 133.69, 133.58, 133.49, 133.31, 130.21, 130.04, 129.75, 129.70, 129.65, 128.94, 128.76, 128.72, 128.64, 128.58, 128.53, 81.59, 75.45, 72.44, 69.72, 63.27, 52.83, 31.74, 25.44.

FAB-MS, m/z: 997.0(M^+), 996.0 (M^+-1)

1-N-(acetyl)-[N-(2,4-dinitro)-benzoyl]-2-deoxy-2-tetrachlorophthalimido-3,4,6-tri-O-benzoyl-β-D-glucopyranosyl amine.

To a solution of pentenyl glycoside (124 mg, 0.15 mmol) and 2,4-dinitro benzoic acid (38 mg, 0.18 mmol) in CH_3CN (4 mL) was added NBS (60 mg, 0.33 mmol). The solution was stirred in darkness at RT under argon atmosphere for 6hrs. The reaction was quenched by adding 10% sodium thiosulfate solution (7 mL) and saturated $NaHCO_3$ solution (7 mL) and extracted with CH_2Cl_2. The residue on flash column chromatography (40% EtOAc-Hexane) afforded the product in 67% yield (98 mg, 67%).

^{1}H NMR ($CDCl_3$,300 MHz): δ 8.96 (bs, 1H, ArH) 8.32 - 8.29 (d, 1H, ArH), 8.07 - 8.05 (d, 2H, ArH), 7.90 - 7.88 (d, 2H, ArH) 7.78 - 7.74 (d, 2H, ArH), 7.63 - 7.42 (m, 5H, ArH), 7.38 - 7.26 (m, 5H, ArH), 6.41 - 6.38 (d, J=9.6 Hz, 1H), 6.28 - 6.22 (t, J=9.6 Hz, 1H), 5.83 - 5.76 (t, J=9.6 Hz, 1H), 4.75 - 4.70 (dd, J_1, J_2 = 11.7, 3 Hz, 1H), 4.57 - 4.51 (m, 2H), 4.22 - 4.20 (m, 1H), 2.57 (s, 3H, ArH).

^{13}C NMR ($CDCl_3$,100 MHz): δ 172.26, 167.22, 165.99, 165.86, 165.06, 164.15, 162.37, 147.98, 144.98, 140.81, 140.62, 133.75, 133.72, 133.58, 133.72, 133.25, 129.89, 129.85, 129.76, 129.66, 129.30, 128.86, 128.68, 128.48, 128.44, 128.34, 128.18, 120.12, 75.45, 69.15, 62.83, 51.96, 30.91.

FAB-MS, m/z: 997.3 (M^+-1)

1-N-(acetyl)-[N-(2-nitro)-benzoyl]-2-deoxy-2-tetrachlorophthalimido-3,4,6-tri-O-benzoyl-β-D-glucopyranosyl amine.

To a solution of pentenyl glycoside (100 mg, 0.12 mmol) and 2-nitrobenzoic acid (24 mg, 0.14 mmol) in CH_3CN (4 mL) was added NBS (48 mg, 0.27 mmol). The solution was protected from light and stirred at RT under argon for 7hrs. The reaction was quenched with 10% sodium thiosulfate (7 mL) and saturated $NaHCO_3$ solution (7 mL) and extracted with CH_2Cl_2. The organic layer was dried, concentrated and the residue on flash column chromatography (30% EtOAc-Hexane) afforded the product (100 mg, 88%) as a colorless solid.

^1H NMR ($CDCl_3$, 300 MHz): δ 8.21 - 8.18 (d, 1H, ArH), 8.09 - 8.06 (d, 2H, ArH), 8.03 - 8.00 (d, 1H, ArH), 7.91- 7.89 (d, 1H, ArH), 7.86 - 7.84 (d, 2H, ArH), 7.74 - 7.72 (d, 2H, ArH), 7.63 - 7.57 (m, 2H, ArH), 7.52 - 7.23 (m, 9H, ArH), 6.14 - 6.08 (d, J=9.6Hz, 1H), 6.03 - 6.00 (d, J=9.6 Hz, 1H), 5.67 - 5.61 (t, J=9.6 Hz, 1H), 4.69 - 4.63 (m, 1H), 4.54 - 4.41 (m, 1H), 3.94 - 3.93 (m, 1H), 2.55 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.55, 169.65, 166.21, 166.08, 165.31, 164.31, 162.47, 140.97, 140.71, 134.49, 133.84, 133.80, 133.66, 133.34, 131.88, 130.36, 130.27, 130.05, 130.02, 129.98, 129.91, 129.68, 128.91, 128.80, 128.62, 128.22, 75.12, 71.47, 69.46, 63.36, 60.61, 51.84, 21.25.

FAB-MS, m/z: 952.1 (MH^+), 949.1 (M^+-3)

1-N-(acetyl)-[N-(3,5-dinitro)-benzoyl]-2-deoxy-2-tetrachlorophthalimido-3,4-di-O-benzoyl-6-O-*tert*-butyl dimethylsilyl-β-D-glucopyranosyl amine.

To a solution of pentenyl glycoside (82 mg, 0.1 mmol) and 3,5,dinitrobenzoic acid (32 mg, 0.15 mmol) in CH_3CN (4 mL) was added NBS (40 mg, 0.225 mmol). The solution was protected from light and stirred at RT under argon atmosphere for 3hrs. The reaction was quenched by adding 10% sodium thiosulfate solution (7 mL) and saturated $NaHCO_3$ solution (7 mL) and extracted with CH_2Cl_2. The organic layer was concenrated and the residue on flash column chromatography (20% EtOAc-Hexane) afforded the product (60 mg, 61%) as a white solid.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.21 - 9.20 (1H, t, ArH), 8.74 - 8.73 (d, 2H, ArH), 8.00 - 7.77 (m, 4H, ArH), 7.55 - 7.30 (m, 6H, ArH), 6.38 - 6.34 (d, J=10.2 Hz, 1H), 6.17 - 6.10 (t, J=9.6 Hz, 1H), 5.80 - 5.74 (t, J=9.6 Hz, 1H), 5.44 - 5.37 (t, J=10.2Hz, 1H), 4.02 - 3.90 (m, 3H), 2.56 (s, 3H), 0.90 (s, 9H), 0.06 - 0.05 (d, 6H).

^{13}C NMR ($CDCl_3$,100 MHz): δ 173.35, 170.36, 166.61, 160.27, 149.08,148.75, 138.63, 134.23, 134.04, 130.43, 130.26, 129.62, 129.28, 128.96, 128.58, 128.48, 122.37, 82.50, 78.97, 72.60, 69.21, 62.56, 53.59, 26.37, 26.32, 26.25, 18.80, -5.05, -5.00.

FAB-MS, m/z: 1007 (M^+-1)

1-N-(acetyl)-[N-(4-bromomethyl-3-nitro)-benzoyl]-2-deoxy-2-tetrachlorophthali-mido-3,4-di-O-benzoyl-6-O-*tert*-butyl dimethyl silyl-β-D-glucopyranosyl amine.

To a solution of pentenyl glycoside (83 mg, 0.1 mmol) and 4-bromomethyl, 3-nitrobenzoic acid (31 mg, 0.12 mmol) in CH_3CN (4 mL) was added NBS (40 mg, 0.225 mmol). The solution was protected from light and stirred at RT under argon atmosphere for 7hrs. The reaction was quenched with 10% sodium thiosulfate solution (7 mL) and saturated $NaHCO_3$ (7 mL) and then extracted with CH_2Cl_2. The organic layer was concentrated and the residue on flash column chromatography (20% EtOAc-Hexane) afforded the product (62 mg, 60%) as a white solid.

^{1}H NMR ($CDCl_3$,300 MHz): δ 8.25 - 8.24 (d, 1H, ArH), 7.98 - 7.95 (m, 2H, ArH), 7.86 - 7.84 (m, 2H, ArH), 7.71 - 7.69 (d, 1H, ArH), 7.65 - 7.62 (d, 1H, ArH), 7.46 - 7.22 (m, 6H, ArH), 6.24 - 6.20 (d, J=9.6 Hz, 1H), 6.01 - 5.95 (t, J=10.2 Hz, 1H), 5.68 - 5.58 (q, J=9.3 Hz, 1H), 5.44 - 5.37 (t, J=10.5 Hz, 1H), 4.85 - 4.73 (m, 2H), 3.95 - 3.82 (m, 3H), 2.32 (s, 3H), 0.83 (s, 9H), 0.01 (d, 6H).

^{13}C NMR ($CDCl_3$100 MHz,): δ 172.86, 171.54, 166.68, 165.46, 164.63, 162.44, 148.49, 138.09, 136.01, 134.73, 134.07, 133.97, 133.81, 130.52, 82.49, 79.01, 72.88, 69.68, 63.00, 53.50, 28.31, 26.46, 26.40, 18.94, -4.77, -4.88.

FAB-MS, m/z: 1051.1 (M^+-1).

1-N-(acetyl)-[N-(3,5-dinitro)-benzoyl]-2-deoxy-2-tetrachlorophthalimido-3,4,6-tri-O-benzoyl-β-D-glucopyranosyl amine.

To a solution of pentenyl glycoside (164 mg, 0.2 mmol) and 3,5-dinitrobenzoic acid (50.8 mg, 0.24 mmol) in CH_3CN (4 mL) was added NBS (80 mg, 0.450 mmol). The solution was protected from light and stirred at RT under argon atmosphere for 3hrs. The reaction was quenched with 10% sodium thiosulfate solution (7 mL) and saturated $NaHCO_3$ solution (7 mL) and then extracted with CH_2Cl_2. The organic layer was concentrated and the residue on flash column chromatography (25% EtOAc-Hexane) afforded the product (180 mg, 96%) as a white amorphous solid.

^1H NMR ($CDCl_3$, 300 MHz): δ 9.14 (s, 1H, ArH), 8.75 - 8.74 (d, 1H, ArH), 8.07 - 8.01 (t, 1H, ArH), 7.96 - 7.94 (d, 2H, ArH), 7.88 - 7.85 (d, 2H, ArH), 7.76 - 7.73 (d, 2H, ArH), 7.58 - 7.26 (m, 9H, ArH), 6.46 - 6.42 (d, J=10.2 Hz, 1H), 6.17 - 6.11 (t, J=10.2 Hz, 1H), 5.84 - 5.78 (t, J=10.2 Hz, 1H), 5.44 - 5.38 (t, J=10.2 Hz, 1H), 4.80 - 4.76 (dd, J_1, J_2=2.1, 12.3 Hz), 4.54 - 4.46 (m, 1H), 4.32 - 4.26 (m, 1H), 2.41 (s, 3H).

^{13}C NMR ($CDCl_3$,100 MHz): δ 172.33, 170.17, 166.32, 166.29, 165.14, 164.30, 162.21, 148.78, 141.00, 137.87, 134.02, 133.87, 133.76, 133.70, 133.57, 133.47, 130.56, 130.48, 130.35, 130.20, 130.10, 130.01, 129.93, 129.91, 129.83, 129.71, 129.58, 129.35, 129.11, 128.80, 128.69, 128.67, 128.65, 128.56, 128.55, 122.43, 82.05, 75.47, 71.88, 69.14, 62.47, 53.27, 24.72.

FAB-MS, m/z: 997.3 (M^+-1)

<u>1-N-(acetyl)-[N-(3-nitro)-benzoyl]-2-deoxy-2-tetrachlorophthalimido-3,4,6-tri-O-benzoyl-β-D-glucopyranosyl amine.</u>

To a solution of pentenyl glycoside (82 mg, 0.1 mmol) and 3-nitrobenzoic acid (20 mg, 0.12 mmol) in CH_3CN (2 mL) was added NBS (40 mg, 0.225 mmol). The solution was protected from light and stirred at RT under argon atmosphere for 4hrs. The reaction was quenched with 10% sodium thiosulfate solution (7 mL) and saturated $NaHCO_3$ solution (7mL) and then extracted with CH_2Cl_2. The organic layer was concentrated and the residue on flash column chromatography (20% EtOAc-Hexane) afforded the product (57 mg, 60%) as a white solid.

^{1}H NMR ($CDCl_3$,300 MHz): δ 8.55 - 8.54 (t, 1H, ArH), 8.41- 8.37 (m, 1H, ArH), 8.10 - 8.07 (m, 1H, ArH), 8.03 - 7.99 (d, 2H, ArH), 7.89 - 7.86 (d, 2H, ArH), 7.76 - 7.73 (d, 2H, ArH), 7.59 - 7.42 (m, 6H, ArH), 7.35 - 7.27 (m, 4H, ArH), 6.37 - 6.33 (d, J=9.6 Hz, 1H), 6.11 - 6.05 (t, J=10.2, 9.6 Hz, 1H), 5.79 - 5.73 (t, J=10.2, 9.6 Hz, 1H), 5.58 - 5.51 (t, J=10.2, 9.6 Hz, 1H), 4.76 - 4.70 (dd, J=3, 12.6 Hz, 1H), 4.53 - 4.47 (dd, J=4.1, 12.6 Hz, 1H), 4.22 - 4.16 (m, 1H), 2.27 (s, 3H).

^{13}C NMR ($CDCl_3$,100 MHz): δ 171.66, 171.63, 165.98,165.90, 164.99, 163.94, 161.89, 148.31, 135.54, 134.42, 133.70, 133.64, 133.36, 130.09, 130.00, 129.88, 129.83, 129.70, 129.36, 128.51, 128.45, 128.42, 127.97, 127.89, 124.43, 81.64, 75.29, 71.85, 69.20, 62.70, 52.80, 25.12.

FAB-MS, m/z: 950(M^+), 949 (M^+-1)

1-N-(acetyl)-[N-benzoyl]-2-deoxy-2-tetrachlorophthalimido-3,4-di-O-benzoyl-6-O-*tert*-butyl dimethylsilyl-β-D-glucopyranosyl amine.

To a solution of pentenyl glycoside (83 mg, 0.1 mmol) and benzoic acid (19 mg, 0.15 mmol) in CH_3CN (4 mL) was added NBS (40 mg, 0.225 mmol). The solution was protected from light and stirred at RT under argon atmosphere for 4hrs. The reaction was quenched with 10% sodium thiosulfate solution (7 mL) and saturated $NaHCO_3$ (7 mL) and then extracted with dichloromethane. The organic layer was concentrated and the residue on flash column chromatography (15% EtOAc-Hexane) afforded the product (56 mg, 62%) as a white amorphous solid.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.89-7.86 (d, 2H, ArH), 7.82-7.80 (d, 2H, arH), 7.75-7.72 (d, 2H, ArH), 7.63-7.57 (t, 1H, arH), 7.50- 7.23 (m, 8H, ArH), 6.28-6.25 (d, J=9.6 Hz, 1H), 6.06- 6.00 (t, J=9.3 Hz, 1H), 5.63-5.56 (m, 2H), 3.88-3.82 (m, 3H), 2.13 (s, 3H), 0.854 (s, 9H), 0.01 (d, 6H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.05, 172.49, 166.64, 165.57, 164.32, 162.53, 139.93, 139.04, 138.96, 138.92, 135.94, 135.57, 135.52, 135,47, 135.35, 135.20, 134.75, 134.49, 133.96, 133.93, 82.23, 78.96, 72.91, 70.11, 63.40, 53.65, 26.49, 26.42, 26.04, 18.94, -4.74, -4.80.

FAB-MS m/z : 915.07 (MH+)