Supplementary Material (ESI) for Chemical Communications

Solution-Phase Oligosaccharide Synthesis in a Cycloalkane-Based Thermomorphic System

Shokaku Kim[a], *Ai Tsuruyama*[b] , *Akihiro Ohmori*[b] , *and Kazuhiro Chiba*[a]*

[a] Laboratory of Bio-organic Chemistry, Tokyo University of Agriculture an Technology, 3-5-8 Saiwai-cho, Fuchu, Tokyo 183-8509, Japan, [b] Yokohama Technical Center, Moritex Corporation. 1-3-3 Azamino-Minami, Aoba-ku, Yokohama, Kanagawa 225-0012, Japan

Email_chiba@cc.tuat.ac.jp

Table of Contents.

1. General Information.

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ with TMS as the initial standard on JEOL JNM-LA400 spectrometer. The following abbreviations were used to explain multiplicities: s, singlet; d, doublet; t, triplet; m, multiple. TLC analysis was carried out with Merk Silica Gel 60 F254 plates, detection of compounds was achieved by UV absorption (254 nm) and by charring after spraying with ceric ammonium sulfate in 10% aqueous H_2SO_4. Column chromatography was performed with Kieselgel 60 Silica Gel (Merk, 0.04-0.063 mm). All reagents and solvents were purchased from Kanto

chemical, Tokyo Kasei Kogyo, Aldrich and Wako and used as received. High-performance liquid chromatography (HPLC) was carried out using a JASCO LC 2000 series, PU-2080 plus Intelligent HPLC pump, MX-2080-53 3-Line degasser, MS-2080-31 Solvent Mixing Module, UV-2075 Plus Intelligent UV/ VIS detector with Imtakt Unison UK silica UKS06 (normal phase; 130A, 3 μm, 250 × 4.6 mm). Mass spectra were measured using an Applied Biosystems Japan., Ltd. Voyager DE-STR /NT-O MALDI-TOF with α-cyano-4-hydroxycinnamic acid as the matrix.

Typical Glycosylation Procedure. To a solution of acceptor (0.1-0.3 mmol) in methylcychlohexane (4 ml) was added flame-dried MS AW-300 (0.3 g) and a solution of the trichloroacetamide donor (2.0 equiv) in propionitrile (2 ml). After stirring for 1 h at room temperature, the mixture was treated with 0.5 equiv of TMSOTf. After stirring for 30 min at 25 ^{o}C, the homogenous reaction mixture was neutralized with triethylamine followed by addition of acetonitrile (2 ml) and partitioned between nitriles (EtCN/MeCN=1/1 v/v) and MCH (× 3) at 25 ^{o}C. The combined MCH layers were concentrated and precipitated with MeOH to give the corresponding oligosaccharide.

Typical procedure of TBDPS protecting group. A solution of TBDPS-protected compound in MCH/EtCN (2/1, v/v, 30 ml) was treated with acetic acid (6.0 equiv) and tetrabutylammoniumfluoride 1.0 M solution in THF (3.0 equiv). After stirring for 10 h at room temperature, the reaction mixture was added to MeCN (10 ml) to form a biphasic-solution at room temperature. The reaction mixture was extracted with MCH three times. The combined MCH layers were concentrated, and precipitated with MeOH to give the deprotected oligosaccharide derivative.

2. Experimental procedure

Methyl 2,3,4-tri-*O*-octadecanoyl-α-D-glucopyranoside (1).

α-D-methylglucoside (89.0 g, 0.46 mol) in anhydride CH_2Cl_2 (600 ml) was treated with triethylamine (196 ml, 1.4 mol), 4-dimethylaminopyridine (DMAP, 4.38 g, 0.036 mol) and trityl chloride (100 g, 0.35 mol). After stirring for 2 days at room temperature, the reaction mixture was poured into H_2O (200 ml) and washed three times. The organic layer was dried with $MgSO_4$, concentrated to a minimal volume

and precipitated with MeOH to give methyl 6-*O*-trityl-α-D-glucoside (73.3 g, 48 %). A solution of 6-trityl-α-D-methylglucoside (72.4 g, 0.166 mol) in CH_2Cl_2 (1 L) was added to triethylamine (463 ml, 3.32 mol) and DMAP (2.1 g, 0.017 mol), then cooled on ice. Stearoyl chloride (300 g, 0.99 mol) was added dropwise at 0 ^oC for 30 min and stirred over night at room temperature. The reaction mixture was filtered in vacuo and washed with n-hexane (200 ml). The filtrate was concentrated and precipitated with 2-propanol to give desired product (164 g, 80%). A solution of 2,3,4-tri-*O*-octadecanoyl- 1-methoxy-6-trityl-α-D-glucopyranoside (40.9 g, 0.032 mol) and triisopropylsilane (18.07 g, 0.114 mol) in CH_2Cl_2 (500 ml) was stirred at 0 ^oC. Trifluoroacetic acid (TFA, 11.64 g, 0.102 mol) was added dropwise for 30 min. After stirring for 2 h at 0 ^oC, the reaction mixture was concentrated and diluted in n-hexane (200 ml). The residue was washed with DMF (100 ml × 2), MeCN (100 ml × 3). n-Hexane layer was concentrated and precipitated with 2-propanol to give compound **1** (31 g, 95 %); ^{1}H-NMR(400MHz, $CDCl_3$) δ5.57 (1H, t, *J*=9.76 Hz), 5.00 (1H, t, *J*=9.76 Hz), 4.96 (1H, d, *J*=3.66 Hz), 4.86 (1H, dd, *J*=10.02, 3.66 Hz), 3.78-3.67 (2H, m), 3.60-3.54 (1H, m), 3.40 (3H, s), 2.40-2.18 (6H, m), 1.63-1.46 (6H, m), 1.25 (84H, m), 0.88 (9H, t, *J*=6.83 Hz); ^{13}C-NMR(100MHz, $CDCl_3$) δ173.4, 172.9, 172.4, 96.8, 70.9, 69.3, 69.2, 68.7, 61.1, 55.4, 34.3, 34.2, 34.1, 31.9, 29.8, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3, 29.3, 29.2, 29.2, 29.1, 25.1, 25.0, 24.9, 22.8, 14.2. MALDI-TOF-MS: m/z calcd. for $C_{61}H_{116}NaO_9$ ($M+Na^+$): 1016.85, Found: 1015.73.

Solubility measurement of hydrophobic monosaccharide in various solvents. Compound **1** was dissolved to each solution (6 ml) in excess quantity of saturated concentration at 25 ^oC. After the solution was heated to 55 ^oC for 15 min to solve compound **1**, the solution was cooled down to 25 ^oC. After more than 2 h at 25 ^oC, the insoluble compound **1** was filtered out with PTFE filter (0.2 μm). The filtrate was concentrated and evaporated in vacuo. The solubility of compound **1** was calculated by weight of the residue.

***O*-2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-α-D-glucopyranosyl trichloroacetimidate (2)**.

A solution of phenyl 2,3,4-tri-*O*-benzoyl-6-(*t*-butyldiphenylsilyl)-1-thio-α-D–glucopyranoside (2.0g, 2.43 mmol) in acetone-H_2O (9:1, v/v, 30 ml) was treated with N-bromosuccinimide (1.75 g, 9.72 mmol) at 25 ^oC. The reaction mixture was stirred for 2 h at 25 ^oC, concentrated and purified by flash chromatography (hexane-EtOAc=4:1) to give Phenyl *S*-2, 3, 4-tri-*O*-benzoyl-6-*t*-butyldiphenylsilyl-1-thio-α-D-glucopyranoside (1.36 g, 77.5%). This compound (1.0 g, 1.68 mmol) in CH_2Cl_2 (5 ml) was treated with trichloroacetonitrile (0.86 g, 5.47 mmol) and DBU (0.21 g, 1.36 mmol). The reaction mixture was stirred for 16 h at 25 ^oC, concentrated and purified by flash chromatography (0.2% TEA hexane-EtOAc, 6:1) to give compound 3 (0.78 g, 65.5%); ^{1}H-NMR(400MHz, $CDCl_3$) δ8.57 (1H, s), 7.96-7.85 (6H, m), 7.66-7.15 (19H, m), 6.86 (1H, d, *J*=3.4 Hz,), 6.20 (1H, t, *J*=10.0 Hz), 5.8 (1H, t, *J*=9.77 Hz), 4.38 (1H, m), 3.85 (2H, d, *J*=3.42 Hz), 3.66 (1H, dd, *J*=10.24, 3.66 Hz), 1.02 (9H, s) ;^{13}C-NMR(100MHz, $CDCl_3$) δ165.6, 165.4, 164.9, 160.4, 135.5, 132.8, 132.8, 129.9, 129.9, 129.7, 129..6, 129.0, 128.6, 128.3, 127.6, 127.5, 90.9, 73.5, 62.3, 26.7, 26.7, 19.2. MALDI-TOF-MS: m/z calcd. for $C_{45}H_{42}NNaO_9Si$ ($M+Na^+$): 896.16, Found: 896.10.

Methyl *O*-(2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-octadecanoyl-β-D-glucopyranoside (3a).

To a solution of compound **1** (0.3 g, 0.3 mmol) in MCH (4 ml) was added flame-dried MS AW-300 (0.3 g) and a solution of compound **2** (0.53 g, 0.6 mmol) in EtCN (2 ml). After stirred for 1h at room temperature, the mixture was treated with TMSOTf (29 μl, 0.15 mmol). After stirring for 30 min at 25 ^oC, the homogenous reaction mixture was neutralized with Et_3N followed by addition of MeCN (2 ml) and partitioned between nitriles (EtCN/MeCN=1/1 v/v) and MCH (× 3). The combined MCH layers were concentrated and precipitated with MeOH to give compound **3a** (0.49 g, 97% yield; 95% purity) as a white powder; ^{1}H-NMR(400MHz, $CDCl_3$) δ7.94(2H, dd, *J*=7.08, 8.55 Hz), 7.88-7.80(4H, m), 7.68(2H, dd, *J*=7.81, 9.28 Hz), 7.58(2H, dd, *J*=8.06, 9.28 Hz), 7.56-7.46(2H, m), 7.44-7.24(11H, m), 7.21(2H, t, *J*=7.57 Hz), 5.84 (1H, t, *J*=9.77 Hz), 5.63(1H, t, *J*=9.52 Hz), 5.51(1H, dd, *J*=7.81, 9.77 Hz),

5.43 (1H, t, *J*=9.77 Hz), 4.87 (1H, d, *J*=7.81 Hz), 4.81(1H, t, *J*=10.25 Hz), 4.70 (1H, dd, *J*=3.66, 10.20 Hz), 4.64 (1H, d, *J*=3.66 Hz), 3.97-3.90 (2H, m), 3.85 (1H, s), 3.63-3.58 (1H, m), 2.32-2.13 (6H, m), 1.62-1.43 (6H, m), 1.25(84H, m), 1.03(9H, s), 0.88 (9H, t, *J*=6.84 Hz); ^{13}C-NMR (100MHz, $CDCl_3$) δ172.7, 172.3, 172.2, 165.7, 164.9, 164.7, 135.4, 135.3, 133.0, 132.9, 132.8, 132.8, 129.6, 129.6, 129.5, 129.4, 129.2, 129.0, 128.8, 128.2, 128.1, 127.5, 127.4, 101.4, 96.0, 75.1, 73.1, 71.9, 69.5, 69.1, 68.8, 68.4, 68.3, 62.5, 54.6, 34.1, 34.0, 33.9, 31.9, 30.0, 29.6, 29.5, 29.5, 29.3, 29.3, 29.2, 29.2, 29.1, 29.0, 26.6, 24.9, 24.8, 24.7, 22.7, 19.1, 14.1 MALDI-TOF-MS: m/z calcd. for $C_{104}H_{156}NaO_{17}Si$ ($M+Na^+$): 1728.10, Found: 1728.71.

Methyl *O*-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-octadecanoyl-α-D-glucopyranoside (4a).

A solution of compound **3a** (0.6 g, 0.35 mmol) in MCH/EtCN (2/1, v/v, 30 ml) was treated with acetic acid (0.12 g, 2.00 mmol) and tetrabutylammoniumfluoride 1.0 M solution in THF (TBAF, 1.00 ml, 1.00 mmol) at room temperature. After stirring for 12 h, MeCN (10 ml) was added to formed biphasic solution at room temperature. The reaction mixture was extracted with MCH three times. The combined MCH layers were concentrated and precipitated with MeOH to give compound **4a** (0.48 g, 93%) as a white powder; ^{1}H-NMR(400MHz, $CDCl_3$) δ7.98-7.91(4H, m), 7.82(2H, dd, *J*=8.30, 9.52 Hz), 7.57-7.47(2H, m), 7.45-7.33(5H, m),7.27(2H, t, *J*=7.81 Hz), 5.93 (1H, t, *J*=9.77 Hz), 5.51(1H, dd, *J*=9.77, 7.81 Hz), 5.47 (1H, t, *J*=9.52 Hz), 5.43 (1H, t, *J*=9.77 Hz), 4.91 (1H, d, *J*=7.81 Hz), 4.87 (1H, t, *J*=9.52 Hz), 4.72 (1H, dd, *J*=3.66, 10.25 Hz), 4.65 (1H, d, *J*=3.66 Hz), 3.96-3.84 (3H, m), 3.81-3.70 (2H, m), 3.64 (1H, dd, *J*=7.08, 10.98 Hz), 3.03 (3H, s), 2.28-2.14 (6H, m), 1.61-1.45 (6H, m), 1.25 (84H, m), 0.88 (9H,t, *J*=6.84 Hz); ^{13}C-NMR(100MHz, $CDCl_3$) δ172.8, 172.7, 172.4, 166.0, 165.6, 164.9, 133.6, 133.2, 129.9, 129.8, 129.8, 129.8, 129.7, 129.6, 129.2, 128.7, 128.4, 128.2, 101.0, 96.1, 74.8, 72.8, 72.5, 71.7, 71.3, 70.8, 70.0, 69.5, 69.3, 68.8, 68.3, 61.2, 54.9, 34.2, 34.2, 34.1, 32.0, 29.8, 29.7, 29.4, 29.2, 29.1, 25.0, 24.9, 24.8, 22.8, 14.1; MALDI-TOF-MS: m/z calcd. for $C_{88}H_{138}NaO_{17}$ ($M+Na^+$): 1489.98, Found: 1489.77.

Methyl O-(2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-octadecanoyl-α-D-glucopyranoside (3b).

Compound **4a** (0.3 g, 0.20 mmol) and compound **2** (0.4 g, 0.46 mmol) were coupled by the same procedure as described in the synthesis of disaccharide derivatives to give trisaccharide derivative **3b** as a white powder (0.38 g, 86% yield; 90% purity); ^{1}H-NMR(400MHz, $CDCl_3$) δ8.01-7.92 (4H, m), 7.89-7.78(6H, m), 7.75(2H, dd, *J*=8.29, 1.22 Hz), 7.65-7.61(2H, m), 7.55-7.47(6H, m), 7.46-7.30(12H, m), 7.29-7.21(6H, m), 7.16(2H, t, *J*=7.56 Hz), 5.84 (1H, t, *J*=9.76 Hz), 5.80 (1H, t, *J*=9.76 Hz), 5.61 (1H, t, *J*=9.27 Hz), 5.44 (1H, dd, *J*=9.51, 8.05 Hz), 5.373 (1H, t, *J*=9.76 Hz), 5.32 (1H, t, *J*=9.76 Hz), 4.91 (1H, d, *J*=8.05 Hz), 4.81 (1H, t, *J*=9.76 Hz), 4.70 (1H, d, *J*=3.66 Hz), 4.67 (1H, d, *J*=7.81 Hz), 4.59 (1H, dd, *J*=10.25, 3.66 Hz), 4.16-3.91 (2H, m), 3.86-3.72 (5H, m), 3.62-3.58 (1H, m), 3.28-3.22 (1H, dd, *J*=5.37, 11.47 Hz), 3.11 (3H, s), 2.29-2.06 (6H, m), 1.64-1.41 (6H, m), 1.26-1.11 (84H, m), 0.98 (9H, s), 0.88 (9H, t, *J*=6.84 Hz); ^{13}C-NMR(100MHz, $CDCl_3$) δ172.6, 172.4, 172.1, 165.7, 165.5, 165.1, 164.9, 164.9, 164.8, 135.6, 135.5, 135.4, 135.4, 133.6, 133.3, 133.0, 133.0, 132.9, 132.8, 132.6, 130.0, 129.9, 129.8, 129.8, 129.7, 129.7, 129.5, 129.4, 129.3, 129.1, 129.0, 128.9, 128.8, 128.8, 128.7, 128.3, 128.2, 128.1, 127.7, 127.5, 127.5, 101.3, 96.3, 91.0, 75.1, 73.9, 73.2, 72.9, 72.1, 71.8, 70.7, 70.4, 70.1, 69.9, 69.5, 69.0, 68.6, 68.2, 67.8, 63.8, 62.6, 55.1, 34.3, 34.2, 34.1, 34.1, 32.0, 30.4, 29.8, 29.8, 29.7, 29.6, 29.6, 29.6, 29.4, 29.3, 29.3, 29.1, 26.6, 25.0, 25.0, 24.9, 22.8, 19.1, 14.2 MALDI-TOF-MS: m/z calcd. for $C_{131}H_{178}NaO_{25}Si$ ($M+Na^+$): 2202.23 Found: 2202.74.

Methyl *O*-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-octadecanoyl-α-D-glucopyranoside (4b).

Compound **3b** (0.24 g, 0.11 mmol) were deprotected by the same procedure as described in the deprotection procedure of TBDPS group to give compound **4b** as a colorless powder (0.17 g, 90%); ^{1}H-NMR(400MHz, $CDCl_3$) δ7.98-7.87 (8H, m), 7.82-7.74 (4H, m), 7.60-7.31 (14H, m), 7.30-7.23 (4H, m), 5.86 (1H, t, *J*=9.76 Hz), 5.80 (1H, t, *J*=9.76 Hz), 5.60 (1H, t, *J*=9.52 Hz), 5.41 (1H, dd, *J*=9.76, 7.81

Hz), 5.39 (1H, t, *J*=9.52 Hz), 5.31(1H, dd, *J*=9.76, 7.81 Hz), 5.26 (1H, t, *J*=9.76 Hz), 4.91 (1H, d, *J*= 7.81 Hz), 4.82 (1H, t, *J*= 9.76 Hz), 4.75 (1H, d, *J*=7.81 Hz), 4.68-4.66 (1H, m), 4.64 (1H, d, *J*=3.66 Hz), 4.11 (1H, dd, *J*=10.74, 3.66 Hz), 3.99-3.94 (1H, m), 3.89 (1H, dd, *J*=10.74, 5.37 Hz), 3.83-3.70 (4H, m), 3.64-3.54 (1H, m), 3.43 (1H, dd, *J*=11.23, 6.59 Hz), 3.06 (3H, s), 2.96-2.86(1H, m), 2.32-2.10 (6H, m), 1.65-1.42 (6H, m), 1.32-1.15 (84H, m), 0.89 (9H, t, *J*=6.84 Hz); ^{13}C-NMR(100MHz, $CDCl_3$) δ172.8, 172.5, 172.5, 165.8, 165.7, 165.7, 165.0, 165.0, 133.6, 133.2, 133.1, 130.0, 129.9, 129.8, 129.7, 129.4, 129.3, 129.0, 128.9, 128.7, 128.6, 128.4, 128.4, 128.3, 101.4, 100.6, 96.3, 74.7, 73.2, 72.8, 71.8, 71.6, 70.7, 70.5, 69.5, 69.3, 68.9, 68.4, 68.3, 68.0, 61.2, 55.0, 34.2, 34.1, 31.9, 29.7, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 24.9, 24.9, 24.8, 22.7, 14.1 MALDI-TOF-MS: m/z calcd. for $C_{115}H_{160}NaO_{25}$ ($M+Na^+$): 1964.11, Found: 1964.59.

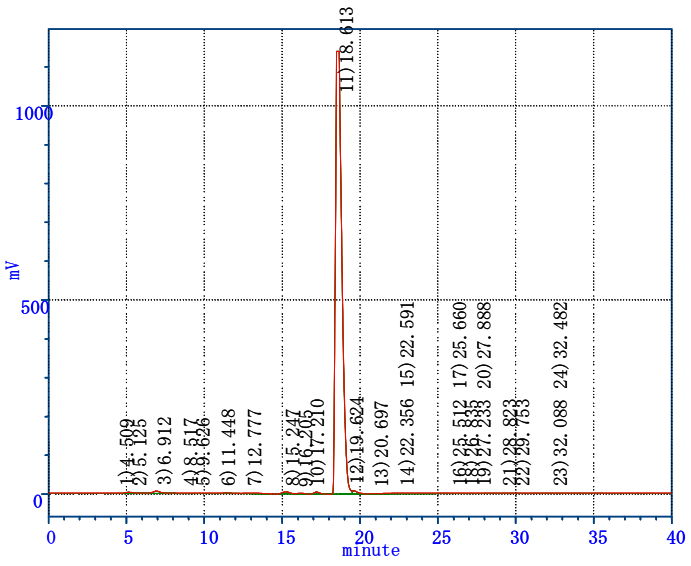
Methyl *O*-(2,3,4-tri-*O*-benzoyl-6-*O*-*t*-butyldiphenylsilyl-β-D-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-*D*-glucopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-octadecanoyl-α-D-glucopyranoside (3c).

Compound **4b** (0.13g, 0.07mmol) and compound **2** (0.15 g, 0.17 mmol) were coupled by the same procedure as described in the synthesis of disaccharide derivatives to give compound **3c** as a white powder (0.16 g, 86% yield; 93% purity); ^{1}H-NMR(400MHz, $CDCl_3$) δ8.06(2H, dd, *J*=7.08, 8.30 Hz), 8.00-7.85(8H, m), 7.82-7.73(6H, m), 7.72-7.66(2H, m), 7.61-7.13(37H, m), 6.01 (1H, d, *J*=5.37 Hz), 5.79 (1H, t, *J*=9.52 Hz), 5.78 (1H, t, *J*=9.52 Hz), 5.60-5.55 (2H, m), 5.48 (1H, d, *J*=8.78 Hz), 5.43-5.27 (4H, m), 4.86 (1H, d, *J*=7.81 Hz), 4.82 (1H, t, *J*=9.76 Hz), 4.69 (1H, d, *J*=3.66 Hz), 4.66 (1H. d, *J*=7.81 Hz), 4.60 (1H, dd, *J*=10.01, 3.66 Hz), 4.57- 4.55 (1H, m), 4.06-4.01 (1H, m), 3.98-3.89 (1H, m), 3.84-3.58 (7H, m), 3.52-3.40 (2H, m), 3.28 (1H, dd, *J*=11.24, 5.37 Hz), 3.10 (3H, s), 2.30-2.05 (6H, m), 1.60-1.42 (6H, m), 1.32-1.14 (84H, m), 0.93 (9H, s), 0.88 (9H, t, *J*=6.84 Hz); ^{13}C-NMR(100MHz, $CDCl_3$) δ172.5, 172.3, 172.1, 165.5, 165.4, 165.1, 164.9, 164.8, 164.8, 164.7, 164.2, 163.1, 135.4, 135.3, 134.3, 133.3, 133.2, 133.1, 133.0, 132.9, 132.9, 132.8, 132.8, 130.0, 129.8, 129.7, 129.7, 129.6, 129.5, 129.5, 129.4, 129.3, 129.2,129.2, 129.1, 128.7, 128.7, 128.7, 128.6, 128.3, 128.2, 128.1, 128.0,

128.0, 127.4, 127.3, 126.4, 120.7, 101.1, 101.0, 97.8, 96.2, 77.1, 73.8, 72.9, 72.6, 72.6, 71.8, 71.7, 70.6, 69.8, 69.4, 69.2, 68.5, 68.1, 67.8, 67.7, 63.3, 62.5, 55.0, 34.1, 34.0, 34.0, 31.9, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.3, 29.3, 29.2, 29.2, 29.0, 26.6, 24.9, 24.9, 24.8, 22.7, 19.1, 14.1 MALDI-TOF-MS: m/z calcd. for $C_{158}H_{200}NaO_{33}Si$ ($M+Na^+$): 2676.36, Found: 2676.44.

3. HPLC analysis

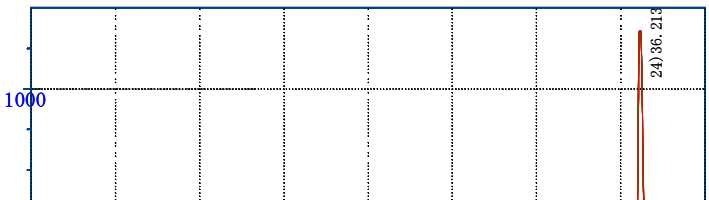
Purity of compound **3a-c** produced by CBT synthesis was analyzed by HPLC. Each compound which obtained precipitated with MeOH was analyzed by using Imtakt Unison UK silica UKS06 (250×4.6 mm) with a flow rate of 1mL/min, monitoring by UV at 280 nm. The initial conditions were 95% n-Hexane / 5% Ethyl acetate with a linear gradient to 80% n-Hexane / 20% Ethyl acetate (compound **3c**; 75% n-Hexane / 25% Ethyl acetate) in 25 min. The solvent composition was held at these final conditions for 15 min.



File:DisaccharideTBDPS.CHR
95:5→80:20 25min 15min

No.	R.T. (minute)	Area (uv*sec)	Area%
1	4.509	2735	0.0081
2	5.125	105733	0.3121
3	6.912	210200	0.6205
4	8.517	27285	0.0805
5	9.626	100333	0.2962
6	11.448	29927	0.0883
7	12.777	84892	0.2506
8	15.247	152170	0.4492
9	16.205	40007	0.1181
10	17.210	136138	0.4019
11	18.613	32234490	95.1512
12	19.624	196086	0.5788
13	20.697	11565	0.0341
14	22.356	104925	0.3097
15	22.591	184241	0.5439
16	25.512	88633	0.2616
17	25.660	13104	0.0387
18	26.835	65984	0.1948
19	27.233	9407	0.0278
20	27.888	31349	0.0925
21	28.823	16246	0.0480
22	29.753	16420	0.0485
23	32.088	3897	0.0115
24	32.482	11374	0.0336
	Total	33877141	

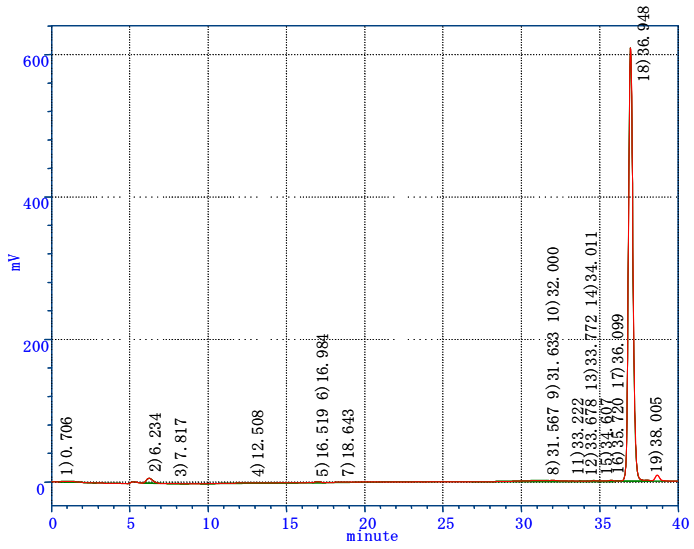
Fig.1 HPLC profile of **compound 3a**



File:Trisaccharide TBDPS.CHR
95:5→80:20 25min 15min

No.	R.T. (minute)	Area (uv*sec)	Area%
1	5.442	351265	0.9632
2	6.306	31121	0.0853
3	7.105	426037	1.1683
4	13.597	96262	0.2640
5	16.936	128245	0.3517
6	17.283	13550	0.0372
7	17.449	9345	0.0256
8	18.304	197757	0.5423
9	20.677	36651	0.1005
10	23.891	81752	0.2242

Fig.2 HPLC profile of **compound 3b**



File:TetrasaccharideTBDPS.CHR
95:5→75:25 25min 30min

No.	R.T. (minute)	Area (uv*sec)	Area%
1	0.706	79504	0.5952
2	6.234	206199	1.5438
3	7.817	11246	0.0842
4	12.508	61550	0.4608
5	16.519	65075	0.4872
6	16.984	36248	0.2714
7	18.643	26242	0.1965
8	31.567	189341	1.4176
9	31.633	16175	0.1211
10	32.000	95684	0.7164
11	33.222	29184	0.2185
12	33.678	1362	0.0102
13	33.772	2004	0.0150
14	34.011	14095	0.1055
15	34.607	43294	0.3241
16	35.720	67757	0.5073
17	36.099	11629	0.0871
18	36.948	12356590	92.5110
19	38.005	43702	0.3272
	Total	13356881	

Fig.3 HPLC profile of **compound 3c**