Supporting Information

A simple and practical real-time analysis of solid-phase reactions enabled by thin-layer chromatography

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General information.

All solvents, chemicals, and capillaries were commercially available. Flash column chromatography was packed with Silica Gel 60 (230-400 mesh, E. Merck.). Components for TLC analysis were pre-coated glass TLC plates of Silica Gel 60 F254 (0.25 mm, E. Merck), aqueous stain solution composed of Ce(NH₄)₂(NO₃)₆, (NH₄)₆Mo₇O₂₄, and H₂SO₄, and UV lamp (4 watt/ 254nm). Microwave reactions were carried out with a Discover SP (CEM). Handmade continuous-flow photoreactor was composed by UV lamp (15 watt/ 254 nm) and fluorinated ethylene propylene (FEP) double pipe. Optical rotations were measured on a JASCO P-2000 polarimeter at 20-25 °C. ¹H and ¹³C NMR spectra were processed with Bruker AV400, DRX500, AVIII-500, and N600 MHz instruments. Chemical shifts were locked at δ 7.24 for ¹H and δ77.00 for ¹³C of CHCl₃.

**Figure S1.** Few reaction mixture from the reaction vessel carried by a capillary.

**Figure S2.** A clean TLC plate for the absorption of the washing solutions.
Figure S3. The corresponding yield with different photo-induced reaction time.

Synthesis of 2,3-di-O-benzyl-4,6-O-benzylidene-β-D-glycopyranoside 2a and 2d.

A solution of 1,2,3,4,6-Penta-O-acetyl-β-D-galactopyranose \( S_1 \) (5.0 g, 12.8 mmol) and \( p \)-toluenethiol (1.9 g, 15.3 mmol) in \( CH_2Cl_2 \) (50 ml) was added BF\(_3\)-Et\(_2\)O (0.8 ml, 7.6 mmol) slowly at 0 °C. The reaction underwent at room temperature for 2 hours. The reaction mixture was neutralized by saturated NaHCO\(_3\) (aq). 1-tolyl-2,3,4,6-tetra-O-galactopyranoside \( S_2 \) was extracted by ethyl acetate and recrystallized in a yield of 95% (5.5 g, white-solid).\(^1\) \( S_2 \) (6.0 g, 13.2 mmol) in MeOH (60 ml) was added NaOMe (350 mg, 6.5 mmol) at room temperature. The overnight reaction was neutralized by Amberlite 120 (H\(^+\)). The desired 1-tolyl-galactopyranoside \( S_3 \) was obtained after filtration and evaporation in a quantitative yield (3.8 g, white-solid).\(^2\) To a solution of dried \( S_3 \)
(3.8 g, 13.2 mmol) in CH$_3$CN (30 ml), benzaldehyde dimethyl acetate (2.4 ml, 15.8 mmol) was mixed with, followed by the addition of camphorsulfonic acid (CSA, 610 mg, 2.6 mmol) at room temperature. The overnight reaction was quenched by trimethylamine. 1-toly-4,6-O-benzylidene galactopyranoside S4 was purified by column chromatography in a yield of 90% (4.4 g, white-solid). S4 (4.0 g, 10.7 mmol) in DMF (40 ml) was added benzyl bromide (BnBr, 2.8 ml, 23.5 mmol), followed by slowly adding sodium hydride (NaH, 60% dispersion in mineral oil, 940 mg, 23.5 mmol) at 0 °C. The reaction underwent at room temperature for overnight. The reaction mixture was quenched by water at 0 °C and 2a was extracted by ethyl acetate. The desired 2a was purified by column chromatography in the yield of 86% (5.1 g, white-solid). The synthesis of 2d (5.0 g, 12.8 mmol) followed the same procedure of 2a in the overall yield of 74% (5.3 g, white-solid). 

### Synthesis of 2,3,4,6-tetra-O-benzyl-β-D-glycopyranoside 2b and 2c.

![Synthesis of 2,3,4,6-tetra-O-benzyl-β-D-glycopyranoside 2b and 2c.](image)

A solution of S3 (3.0 g, 10.5 mmol) in DMF (30 ml) was mixed with BnBr (6.0 ml, 50.3 mmol), followed by slowly adding NaH (60% dispersion in mineral oil, 2.0 g, 50.3 mmol) at 0 °C. The reaction underwent at room temperature for overnight. The reaction mixture was quenched by water at 0 °C. The pure desired 2b was gave after recrystallization in the yield of 87% (5.9 g, white solid). The synthesis of 2c (3.0 g, 10.5 mmol) followed the same procedure of 2b in a yield of 92% (6.2 g, white-solid).

### Synthesis of O-tert-butyldiphenylsilyl-N-benzyloxy carbonyl-L-amino acids 6b and 6c.
A solution of N-benzyloxycarbonyl-L-amino acid S5 (7.9 mmol) in DMF (20 ml) was added methyl iodide (1.1 g, 7.9 mmol) and potassium carbonate (1.2 g, 8.7 mmol). The reaction mixture was kept at room temperature for 3 hours. The methylated products were purified by column chromatography in the yields of 50% (1.0 g, colorless-oil) for serine and 92% (1.9 g, white-solid) for threonine. The methylated amino acid (4.0 mmol) in DMF (10 ml) was mixed with TBDPSCl (2.2 g, 7.9 mmol), imidazole (810 mg, 11.9 mmol) and catalytic amount of DMAP. The reaction was processed at 45 °C for 7 hours. The desired products were purified by column chromatography in the yields of 90% (1.7 g, colorless-oil) for serine and 90% (1.8 g, white-solid) for threonine. The silyl product (500 mg, 1.0 mmol) in DMF (1 ml) was reacted with 15% NaOH (5 ml) for 2 hours. The reaction mixture was quenching by 1 N HCl(aq) and 6 was extracted by ethyl acetate. The desired amino acid 6 was obtained after removal of ethyl acetate in the quantitative yields (470 mg, white-solid for serine; 486 mg, colorless-oil for threonine).

**O-tert-butylidiphenylsilyl-N-benzyloxycarbonyl-L-serine (6b).** White-solid. [α]$_D^{26}$ +8.67 (c 0.21, CHCl$_3$); $^1$H NMR (600 MHz, CDCl$_3$) δ 7.60-7.56 (m, 4H, Ph-H), 7.42-7.20 (m, 11H, Ph-H), 5.61 (d, J = 8.34 Hz, 1H, NH), 5.13 (dt, J = 4.92, 12.27 Hz, 2H, CH$_2$Ph), 4.47 (d, J = 8.28 Hz, 1H, αH), 4.13 (dd, J = 2.52, 10.68 Hz, 1H, βHH), 3.90 (dd, J = 2.73, 10.23 Hz, 1H, βH), 1.00 (s, 9H, t-Bu); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 174.66 (C), 155.97 (C), 136.17 (C), 135.55 (CH), 135.46 (CH), 132.66 (C), 132.42 (C), 129.97 (CH), 129.94 (CH), 128.55 (CH), 128.21 (CH), 128.11 (CH), 127.82 (CH), 67.15 (CH$_2$), 55.65 (CH), 26.72 (CH$_3$), 19.25 (C). HRMS (ESI) calcd for C$_{27}$H$_{31}$NO$_5$Si [M + Na]$^+$ 500.1869, found 500.1872.

**O-tert-butylidiphenylsilyl-N-benzyloxycarbonyl-L-threonine (6c).** Colorless-oil. [α]$_D^{26}$ -1.07 (c 0.20, CHCl$_3$); $^1$H NMR (600 MHz, CDCl$_3$) δ 7.62 (d, J = 7.14 Hz, 4H, Ph-H), 7.44-7.34 (m, 11H, Ph-H), 5.55 (d, J = 8.58 Hz, 1H, NH), 5.13 (s, 2H, CH$_2$Ph), 4.45 (dt, J = 3.78, 6.41 Hz, 1H, βH), 4.34 (d, J =...
8.70 Hz, 1H, αH), 1.03 (d, J = 6.30 Hz, 3H, CH3), 1.01 (s, 9H, t-Bu); $^{13}$C NMR (150 MHz, CDCl3) δ 173.65 (C), 156.53 (C), 136.13 (C), 135.86 (CH), 135.82 (CH), 133.27 (C), 132.22 (C), 130.13 (CH), 129.94 (CH), 128.58 (CH), 128.26 (CH), 128.15 (CH), 127.78 (CH), 127.65 (CH), 69.96 (CH), 67.27 (CH2), 59.28 (CH), 26.84 (CH3), 19.79 (CH3), 19.22 (C). HRMS (ESI) calcd for C$_{28}$H$_{33}$NO$_3$Si [M + Na]$^+$ 514.2026, found 514.2032.

**TLC images of solid-phase reactions.**

![TLC images of solid-phase reactions.](image-url)
TLC of click reaction.

Eluent: Hex/EA = 2:1
TLC of sequential esterification, deprotection, and glycosylation.

Characterization of glycosyl pentyl esters 4a, 4b, and 4c and free linker 5.

5-\(N\text{-benzyloxycarbonyl}\)aminopentyl 2,3-di-\(O\text{-benzyl}-4,6-\(O\text{-benzylidene-β-D-galactopyranoside (4a)}\). White-solid. α form: \([\alpha]_{D}^{20} +29.34 (c 0.07, \text{CH}_2\text{Cl}_2); \text{H NMR (500 MHz, CDCl}_3) \delta 7.54 (d, J = 7.45 Hz, 2H, Ph-H), 7.43-7.27 (m, 18H, Ph-H), 5.48 (s, 1H, CHPh), 5.06 (s, 2H, CH\_2Ph), 4.89 (d, J = 11.00 Hz, 1H, CH\_2Ph), 4.78 (d, J = 11.00 Hz, 1H, CH\_2Ph), 4.76 (d, J = 12.48 Hz, 1H, CH\_2Ph), 4.73 (d, J = 12.48 Hz, 1H, CH\_2Ph), 4.73-4.70 (br, 1H, NH), 4.35 (d, J = 7.75 Hz, 1H, H-1), 4.27 (d, J = 12.30 Hz, 1H, H-6a), 4.09 (d, J = 3.40 Hz, 1H, H-4), 3.99 (d, J = 12.25 Hz, 1H, H-6b), 3.95 (dt, J = 5.91, 9.50 Hz, 1H, GalOCH\_H), 3.81 (t, J= 8.63, 1H, H-2), 3.54 (dd, J = 3.55, 9.65 Hz, 1H, H-3), 3.49 (dt, J = 6.03, 9.15 Hz, 1H, GalOCH\_H), 3.27 (s, 1H, H-5), 3.17-3.05 (quintet, J = 5.15 Hz, 2H, CH\_2), 1.70-1.59 (m, 2H, CH\_2), 1.54-1.44 (quintet, J = 7.11 Hz, 2H, CH\_2), 1.44-1.33 (m, 2H, CH\_2); \text{C NMR (125 MHz, CDCl}_3) \delta 156.32 (C), 138.88 (C), 138.41 (C), 137.83 (C), 136.65 (C), 128.86 (CH), 128.46
(CH), 128.29 (CH), 128.22 (CH), 128.07 (CH), 128.01 (CH), 127.83 (CH), 127.70 (CH), 127.61 (CH), 127.47 (CH), 126.44 (CH), 103.56 (CH), 101.25 (CH), 79.19 (CH), 78.40 (CH), 75.14 (CH), 73.94 (CH), 71.94 (CH), 69.54 (CH), 69.21 (CH), 66.49 (CH), 66.34 (CH), 53.40 (CH), 40.94 (CH), 29.61 (CH), 29.26 (CH), 23.28 (CH). HRMS (ESI) calcd for C_{40}H_{45}NO_{8}Na [M + Na]^+ 690.3043, found 690.3051.

5-N-benzyloxycarbonyl aminopentanol (5). White-solid. [α]_{D}^{21} -151.55 (c 0.10, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 7.36-7.26 (m, 5H, Ph-), 5.07 (s, 2H, CH₂Ph), 4.73 (br, 1H, NH), 3.62-3.51 (dt, J = 4.40, 5.70 Hz, 2H, CH₂), 3.19 (q, J = 6.48 Hz, 2H, CH₂), 1.61-1.47 (m, 4H, CH₂), 1.37 (quintet, J = 7.09 Hz, 2H, CH₂); ¹³C NMR (125 MHz, CDCl₃) δ 156.44 (C), 136.56 (C), 128.49 (CH), 128.08 (CH), 66.61 (CH₂), 66.62 (CH₂), 62.63 (CH₂), 40.90 (CH₂), 32.18 (CH₂), 29.72 (CH₂), 22.83 (CH₂). HRMS (ESI) calcd for C_{13}H_{19}NO_{3}Na [M + Na]^+ 260.1263, found 260.1261.

5-(N-benzyloxycarbonyl)aminopentyl 2,3,4,6-tetra-O-benzyl-β-D-galactopyranoside (4b). Colorless-oil. α form: [α]_{D}^{21}+23.86 (c 0.14, CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃) δ 7.35-7.22 (m, 25H, Ph-), 5.06 (s, 2H, CH₂Ph), 4.91 (d, J = 11.64 Hz, 1H, CH₂Ph), 4.87 (d, J = 10.98 Hz, 1H, CH₂Ph), 4.75 (d, J = 11.16 Hz, 1H, CH₂Ph), 4.70 (d, J = 13.20 Hz, 1H, CH₂Ph), 4.68 (d, J = 11.94 Hz, 1H, CH₂Ph), 4.60 (d, J = 11.64 Hz, 1H, CH₂Ph), 4.43 (d, J = 11.76 Hz, 1H, CH₂Ph), 4.39 (d, J = 11.64 Hz, 1H, CH₂Ph), 4.31 (d, J = 7.68 Hz, 1H, H-1), 3.92-3.88 (m, 1H, GalOCH₂H), 3.86 (d, J = 2.28 Hz, 1H, H-4), 3.78 (dd, J = 7.77, 9.69 Hz, 1H, H-2), 3.56 (d, J = 6.42 Hz, 2H, H-6), 3.53-3.44 (m, 3H, H-5, GalOCH₂H, H-3), 3.11 (quintet, 2H, CH₂), 1.68-1.59 (m, 2H, CH₂), 1.47 (quintet, J = 7.06 Hz, 2H, CH₂), 1.42-1.32 (m, 2H, CH₂); ¹³C NMR (150 MHz, CDCl₃) δ 156.32 (C), 138.83 (C), 138.65 (C), 138.53 (C), 137.95 (C), 136.67 (C), 128.48 (CH), 128.39 (CH), 128.32 (CH), 128.24 (CH), 128.13 (CH), 128.09 (CH), 128.03 (CH), 127.94 (CH), 127.84 (CH), 127.75 (CH), 127.50 (CH), 127.42 (CH), 103.94 (CH), 82.25 (CH), 79.56 (CH), 75.09 (CH₂), 74.48 (CH₂), 73.56 (CH), 73.52 (CH₂), 73.40 (CH), 73.02 (CH₂), 69.64 (CH₂), 68.89 (CH₂), 66.53 (CH₂), 40.96 (CH₂), 29.66 (CH₂), 29.32 (CH₂), 23.32 (CH₂). HRMS (ESI) calcd for C_{47}H_{53}NO_{8}Na [M + Na]^+ 782.3669, found 782.3678.
5-\((N\text{-benzyloxycarbonyl})\)aminopentyl 2,3,4,6-tetra-\(O\text{-benzyl-}\beta\text{-D-glucopyranoside}\) (4c).

Colorless oil. α form: \([\alpha]_{b}^{21}+12.62\) (c 0.13, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.37-7.22 (m, 23H, Ph-H), 7.13-7.10 (m, 2H, Ph-H), 5.06 (s, 2H, CH\(_2\)Ph), 4.91 (d, \(J = 11.15\) Hz, 1H, CH\(_2\)Ph), 4.90 (d, \(J = 10.90\) Hz, 1H, CH\(_2\)Ph), 4.78 (d, \(J = 10.95\) Hz, 1H, CH\(_2\)Ph), 4.76 (d, \(J = 11.05\) Hz, 1H, CH\(_2\)Ph), 4.70 (d, \(J = 11.10\) Hz, 1H, CH\(_2\)Ph), 4.58 (d, \(J = 12.20\) Hz, 1H, CH\(_2\)Ph), 4.52 (d, \(J = 12.65\) Hz, 1H, CH\(_2\)Ph), 4.50 (d, \(J = 11.55\) Hz, 1H, CH\(_2\)Ph), 4.35 (d, \(J = 7.85\) Hz, 1H, H-1), 3.92 (dt, \(J = 7.85, 9.50\) Hz, 1H, H-1), 3.71 (dd, \(J = 1.70, 10.83\) Hz, 1H, H-6a), 3.65 (dd, \(J = 5.00, 10.40\) Hz, 1H, H-6b), 3.62 (t, \(J = 9.00\) Hz, 1H, H-3), 3.54 (t, \(J = 9.50\) Hz, 1H, H-4), 3.54-3.49 (m, 1H, GluOCH\(_2\)H), 3.47-3.43 (m, 1H, H-5), 3.41 (t, \(J = 9.00\) Hz, 1H, H-2), 3.12 (quintet, \(J = 5.29\) Hz, 2H, CH\(_2\)), 1.64 (quintet, \(J = 6.35\) Hz, 2H, CH\(_2\)), 1.49 (quintet, \(J = 7.03\) Hz, 2H, CH\(_2\)), 1.45-1.35 (m, 2H, CH\(_2\)); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 156.35 (C), 138.61 (C), 138.53 (C), 138.16 (C), 138.10 (C), 128.49 (CH), 128.34 (CH), 128.10 (CH), 128.05 (CH), 127.94 (CH), 127.85 (CH), 127.75 (CH), 127.59 (CH), 103.60 (CH), 84.71 (CH), 82.26 (CH), 77.93 (CH), 75.65 (CH\(_2\)), 74.98 (CH\(_2\)), 74.83 (CH), 74.73 (CH\(_2\)), 73.45 (CH\(_2\)), 69.71 (CH\(_2\)), 69.01 (CH\(_2\)), 66.56 (CH\(_2\)), 40.93 (CH\(_2\)), 29.61 (CH\(_2\)), 29.34 (CH\(_2\)), 23.29 (CH\(_2\)). HRMS (ESI) calcd for C\(_{47}\)H\(_{53}\)NO\(_8\)Na [M + Na]\(^+\) 782.3669, found 782.3663.

Characterization of aminopentyl esters 7a, 7b, and 7c.

\(N\text{-9-fluorenylmethoxycarbonyl-L-serine}\) 5-\(N\text{-benzyloxycarbonyl-}\)aminopentyl ester (7a).

White solid. \([\alpha]_{b}^{20}+75.12\) (c 0.025, CH\(_2\)Cl\(_2\)); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.75 (d, \(J = 7.55\) Hz, 2H, Ph-H), 7.56 (d, \(J = 7.35\) Hz, 2H, Ph-H), 7.41-7.28 (m, 9H, Ph-H), 6.94 (d, \(J = 8.00\) Hz, 2H, Ph-H), 6.76 (d, \(J = 7.55\) Hz, 2H, Ph-H), 5.28 (d, \(J = 8.60\) Hz, 1H, NH), 5.12 (s, 2H, CH\(_2\)Ph), 4.84 (br, 1H, NH), 4.54 (dt, \(J = 5.35, 8.03\) Hz, 1H, αH), 4.45 (dd, \(J = 7.43, 10.62\) Hz, 1H, OCH\(_2\)CH), 4.37 (dd, \(J = 6.98, 10.68\) Hz, 1H, OCH\(_2\)CH), 4.21 (t, \(J = 6.73\) Hz, 1H, OCH\(_2\)CH), 4.03-3.92 (m, 2H, CH\(_2\)), 3.13-3.05 (m, 3H, βHH, CH\(_2\)), 2.86 (dd, \(J = 7.92, 13.08\) Hz, 1H, βHH), 1.43-1.26 (m, 6H, CH\(_2\), CH\(_2\), CH\(_2\)), \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 171.91 (C), 156.97 (C), 155.60 (C), 155.53 (C), 143.87 (C), 143.71 (C), 141.33 (C), 130.33 (CH), 128.57 (CH), 128.25 (CH), 128.16 (CH), 127.73 (CH), 127.06 (CH), 125.06 (CH), 125.01 (CH), 119.99 (CH), 115.73 (CH), 67.04 (CH\(_2\)), 66.94 (CH\(_2\)), 65.14 (CH\(_2\)), 55.42 (CH), 47.21 (CH), 40.97 (CH\(_2\)), 38.26 (CH\(_2\)), 29.87 (CH\(_2\)), 28.26 (CH\(_2\)), 23.07 (CH\(_2\)); HRMS (ESI) calcd for C\(_{37}\)H\(_{37}\)N\(_2\)O\(_7\) [M - H]\(^-\) 621.2601, found 621.2606.
O-tert-butyldiphenylsilyl-N-benzyloxy carbonyl-L-serine 5-N-benzyloxy carbonyl aminopentyl ester (7b). Colorless oil. \([\alpha]^{26}_D \) -80.10 (c 0.05, CH2Cl2); \(^1\)H NMR (600 MHz, CDCl3) \( \delta \) 7.62-7.54 (m, 4H, Ph-H), 7.43-7.26 (m, 16H, Ph-H), 5.62 (d, \( J = 9.36 \) Hz, 1H, NH), 5.09 (s, 2H, CH2Ph), 5.07 (s, 2H, CH2Ph), 4.72 (br, 1H, NH), 4.40 (d, \( J = 6.84 \) Hz, 1H, \( \alpha \)H), 4.15 (br, 1H, SerOCH2H), 4.07 (d, \( J = 9.24 \) Hz, 1H, \( \beta \)H), 3.22-3.09 (m, 2H, CH2), 1.61 (quintet, \( J = 5.88 \) Hz, 2H, CH2), 1.50-1.43 (m, 2H, CH2), 1.34-1.20 (m, 2H, CH2), 1.00 (s, 9H, t-Bu); \(^13\)C NMR (150 MHz, CDCl3) \( \delta \) 170.43 (C), 156.35 (C), 155.89 (C), 136.60 (C), 136.33 (C), 135.50 (CH), 135.08 (C), 132.77 (C), 129.90 (CH), 128.52 (CH), 128.09 (CH), 127.79 (CH), 66.97 (CH2), 66.61 (CH2), 65.39 (CH2), 64.46 (CH2), 55.99 (CH), 40.81 (CH2), 28.17 (CH2), 26.73 (CH3), 23.05 (CH3), 19.27 (C); HRMS (ESI) calcd for C40H48N2O7NaSi [M + Na]+ 719.3112, found 719.3129.

O-tert-butyldiphenylsilyl-N-benzyloxy carbonyl-L-threonine 5-N-benzyloxy carbonyl aminopentyl ester (7c). Colorless oil. \([\alpha]^{26}_D \) +1.67 (c 0.16, CH2Cl2); \(^1\)H NMR (600 MHz, CDCl3) \( \delta \) 7.60 (d, \( J = 6.84 \) Hz, 2H, Ph-H), 7.57 (d, \( J = 6.90 \) Hz, 2H, Ph-H), 7.42-7.28 (m, 16H, Ph-H), 5.55 (d, \( J = 9.66 \) Hz 1H, NH), 5.13 (s, 2H, CH2Ph), 5.07 (s, 2H, CH2Ph), 4.78 (br, 1H, NH), 4.42 (q, \( J = 6.24 \) Hz, 1H, \( \beta \)H), 4.22 (d, \( J = 8.94 \) Hz, 1H, \( \alpha \)H), 4.08 (dt, \( J = 10.50, 6.81 \) Hz 1H, ThrOCH2H), 3.89 (dt, \( J = 9.96, 5.82 \) Hz, 1H, ThrOCH2H), 3.17-3.11 (m, 2H, CH2), 1.54-1.49 (m, 2H, CH2), 1.45 (quintet, \( J = 5.72 \) Hz, 2H, CH2), 1.28 (quintet, \( J = 5.72 \) Hz, 2H, CH2), 1.03 (d, \( J = 6.24 \) Hz, 3H, \( \gamma \)H), 0.97 (s, 9H, t-Bu); \(^13\)C NMR (150 MHz, CDCl3) \( \delta \) 170.81 (C), 156.80 (C), 156.37 (C), 136.60 (C), 136.32 (C), 135.82 (C), 133.73 (C), 132.83 (C), 129.92 (CH), 129.78 (CH), 128.55 (CH), 128.50 (CH), 128.19 (CH), 128.13 (CH), 128.10 (CH), 127.64 (CH), 127.52 (CH), 70.10 (CH), 67.13 (CH2), 66.61 (CH2), 65.25 (CH2), 59.96 (CH), 40.82 (CH2), 29.52 (CH2), 28.01 (CH2), 26.82 (CH3), 23.04 (CH2), 20.71 (CH3), 19.18 (C). HRMS (ESI) calcd for C41H50N2O7NaSi [M + Na]+ 733.3285, found 733.3280.

Characterization of final products 11 and 15 in click reaction and sequential reactions.

5-(((5-(((Benzyloxy)carbonyl)amino)pentyl)oxy)methyl)-1H-1,2,3-triazol-1-yl) pentanoic acid (11). Brown solid. \([\alpha]^{21}_D \) +1.11 (c 0.100, CH3OD); \(^1\)H NMR (600 MHz, CD3OD) \( \delta \) 7.98 (s, 1H, COOH), 7.39-7.28 (m, 5H, Ph-H, triazole-H), 5.06 (s, 2H, CH2Ph), 4.56 (s, 2H, CH2), 4.40 (s, 1H,
NH), 3.57-3.48 (m, 2H, CH₂), 3.13-3.08 (m, 2H, CH₂), 1.64-1.57 (m, 2H, CH₂), 1.57-1.47 (m, 4H, CH₂), 1.37 (quintet, J = 7.2 Hz, 2H, CH₂), 1.36-1.27 (m, 4H, CH₂); ¹³C NMR (150 MHz, CD₃OD) δ 159.08 (C), 138.67 (C), 129.59 (CH), 129.07 (CH), 128.88 (CH), 71.55 (CH₂), 67.43 (CH₂), 64.89 (CH₂), 62.96 (CH₂), 41.90 (CH₂), 41.85 (CH₂), 33.40 (CH₂), 30.84 (CH₂), 30.41 (CH₂), 24.52 (CH₂), 24.25 (CH₂). HRMS (ESI) calcd for C₁₂H₂₉N₄O₅ [M - H] - 417.2145, found 417.2138.

O-(2,3,4,6-tetra-O-benzyl glucosyl)-L-serine 5-N-benzyloxy carbonyl amino pentyl ester (15a). Colorless oil. α:β = 1:1 (based on NMR). [α]²⁶D +18.78 (c 0.28, CHCl₃); α form: ¹H NMR (600 MHz, CDCl₃) δ 7.35-7.17 (m, 28H, Ph-H), 7.14-7.07 (m, 2H, Ph-H), 6.05 (d, J = 8.16 Hz, 1H, NH), 5.72 (d, J = 7.92 Hz, 1H, NH), 5.14-5.02 (m, 4H, CH₂Ph), 4.88 (d, J = 10.80 Hz, 1H, CH₂Ph), 4.76 (d, J = 10.92 Hz, 1H, CH₂Ph), 4.75 (d, J = 10.80 Hz, 1H, CH₂Ph), 4.71 (d, J = 3.48 Hz, 1H, H-1), 4.67 (d, J = 11.88 Hz, 1H, CH₂Ph), 4.56 (d, J = 11.88 Hz, 1H, CH₂Ph), 4.51 (d, J = 12.12 Hz, 1H, CH₂Ph), 4.47 (d, J = 4.32 Hz, 1H, αH), 4.46 (d, J = 12.12 Hz, 1H, CH₂Ph), 4.43 (d, J = 10.86 Hz, 1H, CH₂Ph), 4.31 (dd, J = 10.37, 3.30 Hz, 1H, βHβH), 4.20-4.00 (m, 2H, SerOCH₂), 3.84 (t, J = 9.30 Hz, 1H, H-3), 3.82-3.78 (m, 1H, βHH), 3.71 (d, J = 9.24 Hz, 1H, H-5), 3.65 (dd, J = 11.60, 1.50 Hz, 1H, H-6a), 3.59 (dd, J = 9.00, 1.44 Hz, 1H, H-6b), 3.58 (t, J = 9.25 Hz, 1H, H-4), 3.50 (dd, J = 9.69, 3.63 Hz, 1H, H-2), 3.14-3.02 (m, 2H, CH₂), 1.65-1.57 (m, 2H, CH₂), 1.48-1.37 (m, 2H, CH₂), 1.30-1.25 (m, 2H, CH₂); ¹³C NMR (150 MHz, CDCl₃) δ 169.89 (C), 156.40 (C), 156.01 (C), 138.68 (C), 138.11 (C), 138.02 (C), 138.01 (C), 138.95 (C), 129.59 (CH), 129.07 (CH), 128.88 (CH), 71.55 (CH₂), 67.43 (CH₂), 64.89 (CH₂), 62.96 (CH₂), 41.90 (CH₂), 41.85 (CH₂), 33.40 (CH₂), 30.84 (CH₂), 30.41 (CH₂), 24.52 (CH₂), 24.25 (CH₂).
O-(2,3,4,6-tetra-O-benzyl glucosyl)-L-theronine 5-N-benzyl-oxycarbonyl amino pentyl ester (15b). Colorless oil. α form: [α] D +16.67 (c 0.08, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.21 (m, 28H, Ph-H), 7.13-7.07 (m, 2H, Ph-H), 5.93 (d, J = 8.56 Hz, 1H, NH), 5.08 (s, 2H, CH₂Ph), 5.05 (s, 2H, CH₂Ph), 4.87 (d, J = 10.56 Hz, 1H, CH₂Ph) 4.86 (d, J = 3.68 Hz, 1H, H-1), 4.77 (d, J = 10.88 Hz, 1H, CH₂Ph), 4.76 (d, J = 10.92 Hz, 1H, CH₂Ph), 4.65 (d, J = 12.28 Hz, 1H, CH₂Ph), 4.6 (d, J = 10.92 Hz, 1H, CH₂Ph), 4.42 (d, J = 11.48 Hz, 2H, CH₂Ph), 4.32 (dd, J = 5.88, 1.76 Hz, 1H, βH), 4.23 (dd, J = 7.96, 1.64 Hz, 1H, αH), 4.00 (t, J = 6.20, 2H, ThrOCH₂), 3.87 (t, J = 9.22 Hz, 1H, H-3), 3.78 (d, J = 9.68 Hz, 1H, H-5), 3.69 (dd, J = 10.52, 3.24 Hz, 1H, H-6a), 3.62-3.55 (m, 2H, H-4, H-6b), 3.45 (dd, J = 9.92, 3.12 Hz, 1H, H-2), 3.13-3.06 (m, 2H, CH₂), 1.60-1.52 (m, 2H, CH₂), 1.45-1.37 (m, 2H, CH₂), 1.33-1.25 (m, 2H, CH₂), 1.28 (d, J = 6.32 Hz, 3H, CH₃); ¹³C NMR (150 MHz, CDCl₃) δ 170.75 (C), 156.85 (C), 156.40 (C), 138.67 (C), 138.13 (C), 137.95 (C), 137.85 (C), 136.69 (C), 136.35 (C), 128.48 (CH), 128.48 (CH), 128.36 (CH), 128.06 (CH), 127.99 (CH), 127.88 (CH), 127.83 (CH), 127.72 (CH), 127.55 (CH), 97.88 (CH), 81.71 (CH), 79.66 (CH), 77.64 (CH), 75.53 (CH₂), 75.27 (CH), 75.15 (CH₂), 73.49 (CH₂), 73.15 (CH₂), 70.97 (CH), 68.37 (CH₂), 67.07 (CH₂), 66.56 (CH₂), 65.28 (CH₂), 59.08 (CH), 40.78 (CH₂), 29.38 (CH₂), 28.03 (CH₂), 22.95 (CH₂), 19.17 (CH₃). HRMS (ESI) calcd for C₅₉H₆₄N₂O₁₂Na [M + Na]⁺ 1017.4507, found 1017.4513.

Reference


Current Data Parameters
NAME    cnw262-all spectrum
APPEND  1

P2 - Acquisition Parameters
data_  2015.733
time  14.03
CRF/EFN  spec
PFGseq  5 mm FABBO 90°
POLPOL  30°30
TE  31.788
CHOICE  CDCl3
IS  1
IN  1
MMR  4051.701 Hz
STIMES  0.123752 Hz
DG  3.8535162 sec
NB  90.72
f1  117.626 usec
f2  28.9999 usec
f3  209.0 E
f0  2.00000000 sec
f00  1

-------- CHANNEL 1 --------
DFOL  596.1520005 MHz
FOCL  18
f1  15.50 usec
LML  23.39000017 MHz

P2 - Processing parameters
f1  16394
f1  596.130020 MHz
FOL  0
LB  0 Hz
SF  0 Hz
FW  1.00