Supporting Information

STICS: Surface-Tethered Iterative Carbohydrate Synthesis

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1. General

Column chromatography was performed on silica gel 60 (EM Science, 70-230 mesh), reactions were monitored by TLC on Kieselgel 60 F\textsubscript{254} (EM Science). The compounds were detected by examination under UV light and by charring with 10% sulfuric acid in methanol or potassium permanganate solution. Solvents were removed under reduced pressure at \textless 40 \degree C. Dichloromethane was distilled from CaH\textsubscript{2} directly prior to application. Methanol was dried by refluxing with magnesium methoxide, distilled and stored under argon. Pyridine was dried by refluxing with CaH\textsubscript{2} and then distilled and stored over molecular sieves (3Å). Reagent grade solvents, such as N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from Acros. Molecular sieves (3Å), used for reactions, were crushed and activated \textit{in vacuo} at 390\degree C during 8 h in the first instance and then for 2-3 h at 390\degree C directly prior to application. 10 carat white gold sheets were purchased from Hoover and Strong, Richmond, VA. Concentrated nitric acid (trace metal grade, Fisher Scientific) was used for dealloying. Optical rotations were measured at ‘Jasco P-1020’ polarimeter. \textsuperscript{1}H-NMR spectra were recorded at 300MHz, \textsuperscript{13}C-NMR spectra were recorded at 75MHz (Bruker Avance). HRMS determinations were made with the use of JEOL MStation (JMS-700) Mass Spectrometer.
2. Synthesis of anchors

2.1 Tripod

![Chemical structure](image)

Tris(p-toluenesulfonyl) pentaerythritol (14). Toluenesulfonyl chloride (28 g, 0.15 mol) was added to a stirred solution of pentaerythritol (13, 5.0 g, 37 mmol) in dry pyridine (100 mL) and the resulting mixture was stirred under argon for 16 h at rt. After that, the reaction mixture was concentrated under reduced pressure, the residue was dissolved in CH$_2$Cl$_2$ (600 mL) and washed successively with water (150 mL), sat. aq. NaHCO$_3$ (150 mL), and water (2 x 150 mL). The organic phase was separated, dried over MgSO$_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (acetone-toluene gradient elution) to give the title compound as a white solid (35 g, 80% yield). Analytical data for 14 were in a good agreement with those reported previously.$^1$

2,2,2-Tris(thiocyanatomethyl)ethanol (15). Potassium thiocyanate (1.81 g, 18.6 mmol) was added to a stirred solution of 14 (858 mg, 1.4 mmol) in dry DMF (5 mL) under argon at rt. The reaction mixture was stirred at 140 °C for 8 h. After that, the resulting dark solution was poured into cold water, left for 16 h at 5 °C, and then extracted with CH$_2$Cl$_2$ (3 x 100 mL). The combined organic phase was dried over MgSO$_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate-toluene gradient elution) to give...
the compound 2 as colorless syrup (313 mg, 71% yield). Analytical data for 15 were in a good agreement with those reported previously.²

2.2 Thiaadamantane

7-Ethoxycarbonyl-2,4,9-trithiaadamantane (19). A flow of ozone/oxygen obtained from ozone generator was bubbled through a solution of ethyl triallylaceta³ (16, 1.76 g, 8.46 mmol) in dry CH₂Cl₂ (60 mL) at –78 °C. The bubbling was continued until the reaction mixture displayed a light blue color (~3 h). The excess of ozone was then removed by bubbling argon through the mixture for 10 min. After that, dimethyl sulfide (1.86 mL, 25.4 mmol) was added dropwise at –78 °C. The reaction mixture was gradually warmed to rt and kept for additional 16 h. After that, the reaction mixture was concentrated under reduced pressure and dried in vacuo to obtain crude 17 as a colorless syrup (1.8 g, 99% yield). The latter was dissolved in 1,4-dioxane (50 mL) and Lawesson’s reagent (12.2 g, 30.3 mmol) was added under argon at rt. The resulting mixture was stirred at 80 °C for 6 h. After that, the reaction mixture was cooled to rt, filtered through a pad of Celite, concentrated under reduced pressure, and dried to give crude compound
18 as a colorless syrup (2.1 g, 95%). The latter was dissolved in CH$_2$Cl$_2$ (100 mL), BF$_3$-Et$_2$O (3.6 mL, 25.2 mmol) was added dropwise, and the resulting mixture was kept at reflux for 20 h. After that, the reaction mixture was cooled to rt, diluted with CH$_2$Cl$_2$ (400 mL) and washed successively with 5M K$_2$CO$_3$ (50 mL) and water (3 x 50 mL). The organic phase was separated, dried over MgSO$_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (acetone/toluene) to afford the title compound 19 as a pale yellow solid (940 mg, 42% yield). Analytical data for 19 were in a good agreement with those reported previously.$^4$

7-Hydroxymethyl-2,4,9-trithiaadamantane (20). A solution of 19 (250 mg, 0.95 mmol) in THF (2 mL) was added to a stirred suspension of LiAlH$_4$ (72 mg, 1.9 mmol) in dry THF (1 mL) and the resulting mixture was stirred under argon for 30 min at rt. After that, sat. aq. NH$_4$Cl (~5 mL) was added until two phases were clearly seen. The aqueous layer was separated and extracted with CH$_2$Cl$_2$ (3 x 50 mL). The organic phase and the extracts were combined, dried over MgSO$_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (acetone-toluene gradient elution) to afford the title compound as white solid (112 mg, 53% yield). Analytical data for 20: $R_f$ = 0.58 (acetone/toluene, 1/1, v/v); $^1$H-n.m.r.: $\delta$, 1.68 (bs, 1H, OH), 2.57 (d, 6H, J = 2.8 Hz, CCH$_2$C), 3.63 (s, 1H, CH$_2$OH), 4.33 (t, 3H, SCH) ppm; $^{13}$C-n.m.r.: $\delta$, 32.3, 40.8, 42.3, 73.8 ppm; HR-FAB MS [M+H]$^+$ calcd for C$_8$H$_{13}$OS$_3$ 221.0129, found 221.0121
3. Synthesis of acceptor-linker-anchor conjugates

3.1 Tripod

Methyl 2,4-di-O-benzyl-6-O-[3-(2,2,2-tris(thiocyanatomethyl)ethoxycarbonyl)propanoyl]-α-D-glucopyranoside (22). A mixture of N,N'-dicyclohexylcarbodiimide (DCC, 0.93 g, 4.5 mmol) and 4-(N,N-dimethylamino)pyridine (DMAP, 118 mg, 0.96 mmol) in dry CH₂Cl₂ (10 mL) was added to a stirred solution of methyl 2,4-di-O-benzyl-6-O-(3-hydroxycarbonylpropanoyl)-α-D-glycopyranoside² (21, 1.82 g, 3.85 mmol) and anchor 15 (0.98 g, 3.2 mmol) in dry CH₂Cl₂ (20 mL) under argon at 0 °C. The reaction mixture was gradually warmed up and stirred for 1 h at rt. After that, the reaction mixture was diluted with CH₂Cl₂ (200 mL) and washed successively with water (3 x 40 mL). The organic phase was separated, dried over MgSO₄ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (acetone-toluene gradient elution) to afford the title compound as a white solid (1.47 g, 80% yield). Analytical
data for 22: Rf = 0.4 (acetone/toluene, 1/4, v/v), [α]D21 +44.6° (c = 1, CHCl3); 1H-n.m.r.: δ, 2.66 (d, 4H, COCH2CH2CO), 2.75 (d, 1H, OH), 3.25 (s, 6H, 3 x CH2SCN), 3.34 (s, 3H, OCH3), 3.37-3.43 (m, 2H, H-2, 4), 3.79 (m, 1H, H-5), 4.10 (dd, 1H, J3,4 = 8.4 Hz, H-3), 4.23 (s, 2H, OCH2C), 4.30 (d, 2H, H-6a, 6b), 4.62 (d, 1H, J1,2 = 3.5 Hz, H-1), 4.65-4.70 (m, 3H, CH2Ph), 4.91 (d, 1H, CH2Ph), 7.27-7.46 (m, 10H, aromatic) ppm; 13C-n.m.r.: δ, 14.3, 21.1, 28.9, 29.1, 36.8, 45.5, 55.4, 60.5, 63.5, 63.8, 68.3, 73.2, 73.7, 74.5, 79.7, 97.5, 111.4, 128.0, 128.2 (x 4), 128.2, 128.6 (x 3), 128.7 (x 3), 138.0, 138.3, 171.5, 172.4 ppm; HR-FAB MS [M+Na]+ calcd for C33H37N3O9S3Na 738.1590, found 738.1568.

Methyl 2,4-di-O-benzyl-6-O-[3-(4-mercaptomethyl-1,2-dithiolan-4-yl)methoxycarbonyl]-α-D-glucopyranoside (23). A solution of 22 (380 mg, 0.50 mmol) in diethyl ether/THF (10 mL, 1/1, v/v) was added to a stirred suspension of LiAlH4 (38 mg, 1.0 mmol) in diethyl ether (3 mL) and the resulting mixture was stirred under argon for 1 h at rt. After that, sat. aq. NH4Cl (~10 mL) was added until two phases were clearly seen. The aqueous layer was separated and extracted with diethyl ether (3 x 50 mL). The organic phase and the extracts were combined, dried over MgSO4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (acetone-toluene gradient elution) to afford the title compound as a pale-yellow syrup (212 mg, 62% yield). Analytical data for 23: Rf = 0.5 (1/4 acetone/toluene), [α]D20 +45.8° (c = 1, CHCl3); 1H-n.m.r.: δ, 1.19 (dd, 1H, SH), 2.56 (s, 4H, COCH2CH2CO), 2.96 (s, 4H, CH2SSCH2), 3.18 (s, 2H, CH2SH), 3.26 (s, 3H, OCH3), 3.28-3.36 (m, 2H, H-2, 4), 3.72 (m, 1H, H-5), 4.04 (dd, 1H, J3,4 = 8.7 Hz, H-3), 4.14 (s, 2H, OCH2C), 4.22 (d, 2H, H-6a, 6b), 4.54 (d, 1H, J1,2 = 4.4 Hz, H-1), 4.55-4.67 (m, 3H, CH2Ph), 4.85 (d, 1H, CH2Ph), 7.19-7.36 (m, 10H, aromatic) ppm; 13C-n.m.r.: δ, 28.9, 29.0, 39.7, 45.9, 45.9, 55.3, 55.4, 63.6, 66.0, 68.2, 73.2,
73.7, 74.5, 77.0, 79.6, 127.9, 128.2 (x2), 128.2 (x3), 128.5 (x2), 128.7 (x2), 138.0, 138.2, 171.6, 172.0 ppm; HR-FAB MS [M+Na]+ calcd for C$_{30}$H$_{38}$O$_9$S$_3$Na 661.1576, found 661.1535.

3.2 Thiaadamantane

![Thiaadamantane reaction scheme](image)

**6-O-Acetyl-2,3,4-tri-O-benzoyl-1-(3-hydroxycarbonylpropanoyl)-α/β-D-glycopyranose (25).** DMAP (33 mg, 0.27 mmol) and succinic anhydride (108 mg, 1.08 mmol) were added to a solution of 6-O-acetyl-2,3,4-tri-O-benzoyl-α/β-D-glycopyranose*(24)* (289 mg, 0.54 mmol) in dry pyridine (4 mL) and the resulting mixture was stirred under argon for 3 h at rt. After that, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to afford the title compound as a colorless syrup (277 mg, 80% yield, α/β = 1.5/1). Analytical data for α-25; R$_f$ = 0.37 (acetone/toluene, 3/7, v/v); $^1$H-n.m.r.: δ, 2.08 (s, 3H, COCH$_3$), 2.23 (s, 4H, COCH$_2$CH$_2$CO), 4.02 (dd, 1H, J$_{5,6b}$ = 2.0 Hz, H-6b), 4.10 (dd, 1H, J$_{5,6a}$ = 4.0 Hz, H-6a), 4.22 (m, 1H, H-5), 5.31 (dd, 1H, J$_{2,3}$ = 11.5 Hz, H-2), 5.50 (dd, 1H, J$_{4,5}$ = 9.8 Hz, H-4), 5.93 (dd, 1H, J$_{3,4}$ = 10.1 Hz, H-3), 6.47 (d, 1H, J$_{1,2}$ = 3.6 Hz, H-1), 7.05-8.00 (m, 15H, aromatic) ppm; $^{13}$C-n.m.r. (α/β): δ, 20.9, 28.6,
28.7, 28.9, 29.2, 53.6, 68.6, 68.8, 70.2, 70.4, 70.5, 70.6, 70.8, 70.9, 71.1, 77.0, 77.2, 89.9, 90.0, 128.6, 128.7, 128.8, 128.9, 129.0, 129.9, 130.0, 130.2, 133.6, 133.7, 133.8, 134.2, 164.7, 165.3, 165.5, 166.1, 170.2, 170.8, 170.9, 171.1, 177.0, 177.2 ppm; HR-FAB MS [M+Na]^+ calcd for C_{33}H_{30}O_{13}Na 657.1584, found 657.1568

6-O-Acetyl-2,3,4-tri-O-benzoyl-1-O-[3-(2,4,9-trithiaadamantane-7-yl)methoxycarbonylpropanoyl]-α/β-D-glycopyranose (26). A solution of DCC (72 mg, 0.35 mmol) and DMAP (14.2 mg, 0.12 mmol) in dry CH₂Cl₂ (1 mL) was added to a stirred solution of 25 (147 mg, 0.23 mmol) and 20 (47 mg, 0.21 mmol) in dry CH₂Cl₂ (2 mL) was added under argon at 0 °C. The resulting mixture was warmed to rt and stirred for 1 h, after that, it was diluted with CH₂Cl₂ (30 mL) and washed with water (3 x 10 mL). The organic phase was separated, dried over MgSO₄ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to afford the title compound as a white foam (102 mg, 76% yield). Analytical data for α-26: Rf = 0.5 (ethyl acetate/hexane, 1/1, v/v); ¹H-n.m.r.: δ, 2.06 (s, 3H, COCH₃), 2.45 (d, 6H, J = 3.2 Hz, 3 x SCHCH₂S), 2.51 (s, 4H, COCH₂CH₂CO), 3.58 (dd, 2H, OCH₂C), 4.20-4.32 (m, 5H, H-6a,6b, 3 x SCHS), 4.44 (m, 1H, H-5), 5.50 (dd, 1H, J₂,₃ = 3.7 Hz, H-2), 5.67 (dd, 1H, J₄,₅ = 10.0 Hz, H-4), 6.10 (dd, 1H, J₃,₄ = 10.1 Hz, H-3), 6.69 (d, 1H, J₁,₂ = 3.5 Hz, H-1), 7.27-7.95 (m, 15H, aromatic) ppm; ¹³C-n.m.r.: δ, 20.9, 25.1, 25.8, 28.9, 29.0, 30.9, 34.2, 40.3, 42.1, 42.2, 49.4, 62.1, 68.8, 70.2, 70.4, 70.6, 73.6, 77.0, 77.2, 77.5, 90.0, 128.7, 128.7, 128.9, 129.0, 129.1, 129.2, 130.0, 130.3, 133.7, 133.8, 134.2, 164.7, 165.4, 165.0, 170.8, 171.3, 171.6 ppm; HR-FAB MS [M+Na]^+ calcd for C_{41}H_{40}O_{13}S₃Na 859.1529, found 859.1501
2,3,4-Tri-O-benzoyl-1-O-[3-(2,4,9-trithiaadamantane-7-yl)methoxycarbonylpropanoyl]-
α/β-D-glycopyranose (27). Acetyl chloride (0.1 mL) was added to a solution of compound 26
(137 mg, 0.16 mmol) in CH2Cl2/methanol (3 mL, 1/1, v/v) and the resulting mixture was stirred
for 2 h at rt. After that, the reaction mixture was neutralized by addition of triethylamine (~0.5
mL) and concentrated under reduced pressure. The residue was purified by column
chromatography on silica gel (ethyl acetate-hexane gradient elution) to afford the title compound
as a white foam (80 mg, 61% yield). For characterization purposes, the anomers could be
obtained individually in nearly equal amounts. Analytical data for α−27: Rf= 0.30 (ethyl
acetate/hexane, 1/1, v/v); ¹H-n.m.r.: δ, 2.44 (d, 6H, J= 3.5 Hz, 3 x SCHCH2C), 2.51 (s, 4H,
COCH2CH2CO), 2.70 (bs, 1H, OH), 3.58 (dd, 2H, OCH2C), 3.72 (dd, 1H, J6a,6b = 13.1 Hz, H-6a),
3.80 (dd, 1H, H-6b), 4.24 (m, 4H, H-5, 3 x SCS), 5.50 (dd, 1H, J2,3 = 3.7 Hz, H-2), 5.58 (dd,
1H, J4,5 = 9.8 Hz, H-4), 6.17 (dd, 1H, J3,4 = 10.0 Hz, H-3), 6.71 (d, 1H, J1,2 = 3.6 Hz, H-1), 7.36-
8.20 (m, 15H, aromatic) ppm; ¹³C-n.m.r.: δ, 25.1, 25.8, 28.8, 29.0, 30.9, 34.1, 40.2, 42.1, 49.3,
61.0, 69.1, 70.2, 70.2, 73.0, 73.6, 90.1, 128.6, 128.7 (x 2), 128.7 (x 3), 129.0, 129.2, 129.2, 130.0
(x 2), 130.2 (x 4), 133.6, 134.0, 134.2, 164.7, 166.0, 166.3, 171.3, 171.6 ppm. Analytical data for
β−27: Rf= 0.23 (ethyl acetate/hexane, 1/1, v/v); ¹H-n.m.r.: δ, 2.54 (d, 6H, J= 3.5 Hz, 3 x
SCHCH2C), 2.68-2.84 (m, 4H, COCH2CH2CO), 3.75 (dd, 1H, H-6a), 3.80 (dd, 2H, OCH2C),
3.83 (dd, 1H, H-6b), 4.20 (m, 1H, H-5), 4.28 (m, 3H, 3 x SCS), 5.52 (dd, 1H, J2,3 = 3.8 Hz, H-
2), 5.60 (dd, 1H, J4,5 = 10.0 Hz, H-4), 6.21 (dd, 1H, J3,4 = 10.0 Hz, H-3), 6.65 (d, 1H, J1,2 = 3.8
Hz, H-1), 7.27-8.00 (m, 15H, aromatic) ppm; ¹³C-n.m.r.: δ, 28.9, 29.2, 31.0, 40.2 (x 2), 42.1,
61.1, 69.0, 70.2, 70.5, 72.8, 73.9, 90.0, 128.6 (x 2), 128.6, 128.7 (x 2), 128.7 (x 5), 128.8, 128.8,
129.0, 129.9 (x 3), 130.1 (x 2), 130.2 (x 2), 133.6, 133.7, 134.0, 165.5, 166.0, 166.3, 170.6, 172.0
ppm; HR-FAB MS [M+Na]⁺ calcd for C39H38O12S3Na 817.1423, found 817.1420.
3.3 Lipoic Acid conjugates

6-O-Acetyl-2,3,4-tri-O-benzoyl-1-O-[5-(1,2-dithiolan-3-yl)pentanoyl]-α/β-D-glycopyranose (29). A solution of DCC (194 mg, 0.94 mmol) and DMAP (34 mg, 0.28 mmol) in dry CH₂Cl₂ (2 mL) was added to a stirred solution of hemiacetal 24 (350 mg, 0.66 mmol) and lipoic [5-(1,2-dithiolan-3-yl)pentanoyl] acid (28, 162 mg, 0.79 mmol) in CH₂Cl₂ (4 mL) at 0 °C under argon. The resulting solution was warmed to rt and stirred for 16 h. After that, the reaction mixture was diluted with CH₂Cl₂ (50 mL), washed with water (10 mL), sat. aq. NaHCO₃ (10 mL), and water (2 x 10 mL). The organic phase was separated, dried over MgSO₄ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to afford the title compound as a white foam (340 mg, 72% yield, \( \alpha/\beta = 1.4/1 \)).

Analytical data for \( \alpha-29 \): Rf = 0.25 (ethyl acetate/hexane, 3/7, v/v); \(^1\)H-n.m.r.: \( \delta \), 1.20-3.30 (m, 13H, lipoic aglycone protons), 2.07 (s, 3H, COCH₃), 4.24 (dd, 1H, \( J_{5,6b} = 2.8 \) Hz, H-6b), 4.30 (dd, 1H, \( J_{5,6a} = 3.9 \) Hz, H-6a), 4.42 (m, 1H, H-5), 5.43 (dd, 1H, \( J_{2,3} = 3.8 \) Hz, H-2), 5.60 (dd, 1H,
J_{4,5} = 9.9 \text{ Hz, H-4)}, 6.20 (dd, 1H, J_{3,4} = 10.2 \text{ Hz, H-3}), 6.62 (d, 1H, J_{1,2} = 3.4 \text{ Hz, H-1}), 7.36-8.20 (m, 15H, aromatic) ppm; \text{^{13}C-n.m.r. (}\alpha/\beta): \delta, 20.9, 20.9, 24.6, 24.8, 28.5, 28.5, 28.8, 28.8, 33.8, 33.8, 34.1, 34.5, 34.7, 38.6, 38.6, 40.2, 40.4, 40.4, 56.1, 56.3, 56.4, 62.1, 62.2, 68.7, 68.8, 69.8, 70.3, 70.5, 70.6, 89.3, 90.1, 128.6, 128.7, 128.7, 128.8, 128.9, 128.9, 129.0, 129.0, 129.1, 129.9, 130.0, 130.1, 130.2, 133.5, 133.7, 134.2, 164.7, 165.3, 165.4, 165.4, 165.9, 166.0, 170.8, 170.8, 171.4, 172.4 ppm; HR-FAB MS [M+Na]+ calcd for C_{37}H_{38}O_{11}S_{2}Na 745.1753, found 745.1750.

**2,3,4-Tri-O-benzoyl-1-O-[5-(1,2-dithiolan-3-yl)pentanoyl]-\alpha/\beta-D-glycopyranose (30).** The title compound was prepared from 29 (201 mg, 61% yield, \alpha/\beta = 1.4/1) as described for the synthesis of 27. Analytical data for \alpha-30: \text{Rf} = 0.58 (ethyl acetate/hexane, 1/1, v/v); \text{^1H-n.m.r.: } \delta, 3.50-3.80 (m, 2H, H-6a, 6b), 4.10 (m, 1H, H-5), 5.42-5.52 (m, 2H, H-2, 4), 6.13 (dd, 1H, H-2), 6.63 (d, 1H, J_{1,2} = 3.5 \text{ Hz, H-1}), 7.27-8.20 (m, 15 H, aromatic) ppm; \text{^{13}C-n.m.r. (}\alpha/\beta): \delta, 21.5, 24.8, 25.0, 28.7, 29.0, 34.0, 34.4, 34.7, 34.9, 38.8, 38.9, 40.4, 40.6, 40.6, 56.3, 56.5, 56.6, 60.8, 61.2, 61.3, 69.2, 69.3, 70.0, 70.3, 70.5, 70.9, 73.0, 73.2, 89.6, 90.4, 128.6, 128.8, 128.9, 128.9, 129.0, 129.0, 129.2, 129.3, 130.1, 130.2, 130.4, 130.5, 133.8, 134.0, 134.2, 134.4, 165.0, 165.7, 166.1, 166.3, 166.5, 166.6, 171.8, 172.6 ppm; HR-FAB MS [M]+ calcd for C_{35}H_{36}O_{10}S_{2} 680.1750, found 680.1729.
4. Synthesis of other building blocks

Methyl 2,3,4-Tri-\textit{O}-benzyl-6-\textit{O}-(3-hydroxycarbonylpropanoyl)-\alpha-D-glycopyranoside (31). The title compound was obtained from methyl 2,3,4-tri-\textit{O}-benzyl-\alpha-D-glycopyranoside (32)\textsuperscript{7} in 93\% yield as described for the synthesis of compound 25. Analytical data for 31: \(R_f = 0.57\) (acetone/toluene, 1/1, v/v); \([\alpha]_{D}^{18} = 17.7^\circ\) (c = 1, CHCl\(_3\)); \(^1\)H-n.m.r.: \(\delta\), 2.50 (s, 4H, COCH\(_2\)CH\(_2\)CO), 3.28 (s, 3H, OCH\(_3\)), 3.39 (dd, 1H, \(J_{4,5} = 9.5\) Hz, H-4), 3.46 (dd, 1H, \(J_{2,3} = 3.4\) Hz, H-2), 3.73 (m, 1H, H-5), 3.93 (dd, 1H, \(J_{3,4} = 9.2\) Hz, H-3), 4.22 (m, 2H, H-6a, 6b), 4.45-4.60 (m, 3H, \(J_{1,2} = 3.4\) Hz, H-1, CH\(_2\)Ph), 4.68-4.94 (m, 4H, CH\(_2\)Ph), 7.10-7.30 (m, 15H, aromatic), 10.1 (bs, 1H, COOH) ppm; \(^{13}\)C-n.m.r.: \(\delta\), 55.3, 63.3, 68.6, 73.4, 75.1, 75.9, 77.4, 79.9, 82.1, 98.1, 127.8, 128.0, 128.1, 128.2, 128.5, 128.6, 137.9, 138.1, 138.6, 171.9, 177.7 ppm; HR-FAB MS [M]\(^+\) calcd for C\(_{32}\)H\(_{36}\)O\(_9\)Na 587.2257, found 587.2247.

2-Benzoxazolyl 2,3,4-tri-\textit{O}-benzoyl-6-\textit{O}-(\textit{tert}-butyldiphenylsilyl)-1-thio-\beta-D-glucopyranoside (10). \textit{Ter}-butyldiphenylsilyl chloride (0.19 mL, 0.72 mmol) and imidazole (81 mg, 1.2 mmol) were added to a solution of 2-benzoxazolyl 2,3,4-tri-\textit{O}-benzoyl-1-thio-\beta-D-glucopyranoside\textsuperscript{8} (300 mg, 0.48 mmol) in DMF (2 mL). The resulting mixture was stirred for 8 h at rt, after that the volatiles were removed under reduced pressure and the residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to afford the title compound as a white foam (399 mg, 96\% yield). Analytical data for 10: \(R_r = 0.3\) (ethyl acetate/hexane, 1/4, v/v); \([\alpha]_{D}^{20} = 65.7^\circ\) (c = 1, CHCl\(_3\)); \(^1\)H-n.m.r.: \(\delta\), 0.91 (s, 9H, C(CH\(_3\))\(_3\)), 3.82 (m, 2H, H-6a,6b), 4.09 (m, 1H, H-5), 5.65-5.80 (m, 2H, H-2, 4), 5.94-6.05 (m, 2H, H-1, 3), 7.10-
7.87 (m, 29H, aromatic) ppm; $^{13}$C-n.m.r.: $\delta$, 19.5, 26.9, 63.1, 69.1, 71.2, 74.7, 77.6, 80.2, 84.1, 110.5, 119.4, 124.8, 124.9, 127.9, 128.0, 128.7, 128.8, 128.8, 129.1, 129.2, 129.5, 129.9, 130.0, 130.2, 130.3, 133.3, 133.6, 133.7, 133.9, 136.0, 136.1, 142.0, 152.3, 161.6, 165.3, 165.7, 166.2 ppm; HR-FAB MS [M]$^+$ calcd for C$_{50}$H$_{45}$NO$_9$SNa 886.2482, found 886.2470.

5. **General procedure for preparing nanoporous gold (NPG) plates**

A 10 carat white gold sheet of 0.25 mm thickness was cut into 8mm x 8mm pieces, which were then dealloyed by immersion in concentrated nitric acid for 72 h and then thorough rinsed with milli-Q water. NPG pieces were previously characterized using field-emission SEM, tapping mode AFM, electrochemistry, and BET adsorption isotherm measurements for determination of surface area. Energy dispersed spectroscopy confirmed the presence of only gold after the dealloying. The BET measurements gave a surface area of 6.5 m$^2$ g$^{-1}$ for the NPG prepared from these alloy sheets.$^9$
6. **General procedure for loading glycosyl acceptor on gold plates. Preparation of 5-7.**

Single NPG plate was immersed in a 5 mM solution of glycosyl acceptor-linker-anchor conjugate (23, 27 or 30) in CH₂Cl₂ (1.0 mL) for 48 h at rt. Similarly, ten-plate assembly was immersed in a 5 mM solution of conjugate 27 in CH₂Cl₂ (7.0 mL). After that, the excess reagents was rinsed by repeatedly dipping the plate or the conjugate in CH₂Cl₂ (3-5 x 1 or 7 mL, respectively), and the solvent excess was removed under reduced pressure (2 h) to afford anchored glycosyl acceptors 5-7. The loading was determined by comparing the results of gravimetric analysis of plates prior and after the loading procedure. The Table 1 summarizes the results obtained.

**Table 1. Determination of the surface coverage**

<table>
<thead>
<tr>
<th>Acceptor</th>
<th># plates</th>
<th>Loading, mg Max/aver</th>
<th>Loading, µmol Max/aver</th>
<th>Plate weight, mg</th>
<th>Surface coverage Max/aver</th>
</tr>
</thead>
<tbody>
<tr>
<td>23 → 5</td>
<td>1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.03 0.97</td>
<td>1.50 1.41</td>
<td>126.76</td>
<td>1.82 µmol/m² 1.67 µmol/m²</td>
</tr>
<tr>
<td>27 → 6</td>
<td>1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.05 0.90</td>
<td>1.33 1.18</td>
<td>133.79</td>
<td>1.53 µmol/m² 1.37 µmol/m²</td>
</tr>
<tr>
<td>27 → 6</td>
<td>10&lt;sup&gt;b&lt;/sup&gt;</td>
<td>7.20 7.00</td>
<td>9.10 8.85</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>30 → 7</td>
<td>1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.71 0.58</td>
<td>1.04 0.85</td>
<td>83.36</td>
<td>1.92 µmol/m² 1.53 µmol/m²</td>
</tr>
</tbody>
</table>

<sup>a</sup> - 10 x 10 mm plates were used

<sup>b</sup> - 8 x 8 mm plates were used
7. Synthesis of disaccharides 8 and 9 by glycosylation of NPG-supported glycosyl acceptors 5-7 on a single NPG plate

Method A: General procedure for MeOTf-promoted glycosylation. A mixture of the glycosyl donor (1, 3 or 4, 9.0 µmol, 6 mg), acceptor conjugate (5, 6 or 7, 0.9 µmol, 0.6 mg), and freshly activated molecular sieves (3Å, 20 mg) in dry CH₂Cl₂ (1.0 mL) was agitated under argon for 2-3 h. MeOTf (0.017 mmol, 3 µL) was added and the reaction mixture was agitated under argon for 16-48 h at rt. After that, the excess reagents was removed by repeatedly dipping the plate in CH₂Cl₂ (3-5 x 1 mL), and the solvent excess was removed by briefly drying the plate under reduced pressure (10 min – 1 h). The NPG plate covered with bound disaccharides was then agitated in 1N solution of NaOMe in methanol (1.0 mL) for 16 h at rt, while maintaining the pH = 8-9. The reaction mixture was then neutralized with Dowex (H⁺) and the NPG plate was removed and rinsed by dipping in MeOH (3-5 x 1 mL). Dowex (H⁺) was filtered off and washed successively with methanol (5 x 2 mL). The combined methanol filtrate and washings were combined and concentrated under reduced pressure and dried in vacuo. The resulting crude mixture containing fully or partially deprotected disaccharides was dissolved in pyridine (0.5 mL), cooled to 0 °C and benzoyl chloride (10 µL) was added. The reaction mixture was stirred under argon for 5 h at rt, then quenched with methanol (1 mL) and the volatiles were evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to allow the corresponding disaccharides 8 or 9. The yield of disaccharide was obtained using standardized HPLC calibration plots (see Charts 1 and 2).
Method B: General procedure for TMSOTf-promoted glycosylation. A mixture of the glycosyl donor (2 or 4, 11.0 μmol, 8 mg), acceptor conjugate (5, 6 or 7, 1.0 μmol, 0.7 mg), and freshly activated molecular sieves (3Å, 20 mg) in dry CH₂Cl₂ (1.0 mL) was agitated under argon for 2-3 h. TMSOTf (0.017 mmol, 4 μL) was added and the reaction mixture was agitated under argon for 16-48 h at rt. After that, the excess reagents was removed by repeatedly dipping the plate in CH₂Cl₂ (3-5 x 1 mL), and the solvent excess was removed by briefly drying the plate under reduced pressure (10 min – 1 h). The NPG plate covered with bound disaccharides was then agitated in 1N solution of NaOMe in methanol (1.0 mL) for 16 h at rt, while maintaining the pH = 8-9. The reaction mixture was then neutralized with Dowex (H⁺) and the NPG plate was removed and rinsed by dipping in MeOH (3-5 x 1 mL). Dowex (H⁺) was filtered off and washed successively with methanol (5 x 2 mL). The combined methanol filtrate and washings were combined and concentrated under reduced pressure and dried in vacuo. The resulting crude mixture containing fully or partially deprotected disaccharides was dissolved in pyridine (0.5 mL), cooled to 0 °C and benzoyl chloride (10 μL) was added. The reaction mixture was stirred under argon for 5 h at rt, then quenched with methanol (1 mL) and the volatiles were evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to allow the corresponding disaccharides 8 or 9. The yield of disaccharide was obtained using standardized HPLC calibration plots (see Charts 1 and 2).
Chart 1. HPLC calibration plot for 8.

\[ y = (5.814 \times 10^7)x + 3.626 \times 10^6 \]
\[ R^2 = 0.99 \]

Chart 2. HPLC calibration plot for 9.

\[ y = (2.586 \times 10^7)x + 5.381 \times 10^6 \]
\[ R^2 = 0.97 \]
Methyl 6-O-benzoyl-3-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-2,4-di-O-benzyl-α-D-glucopyranoside (8). The title compound was obtained from acceptor 5 and donors 1 (Method A, 31%), 2 (Method B, 39%), 3 (Method A, 32%) or 4 (Method A, 42%). Analytical data for 8: R_f= 0.25 (ethyl acetate/hexanes, 3/7, v/v), [α]_D\textsuperscript{24} = -0.94° (c = 1, CHCl₃); \textsuperscript{1}H-n.m.r: δ, 3.30 (s, 3H, OCH₃), 3.41 (dd, 1H, J₂,₃ = 3.6 Hz, H-2), 3.56 (dd, 1H, J₄,₅ = 8.8 Hz, H-4), 3.89 (m, 1H, H-5), 4.20-4.25 (m, 2H, H-3’, 5’), 4.35 (d, 1H, J₁,₂ = 3.5 Hz, H-1), 4.40 (dd, 1H, J₅,₆a = 5.2 Hz, J₆a,₆b = 11.9 Hz, H-6a), 4.46-4.58 (m, 3H, H-3, 6a’, 6b), 4.61 (dd, 1H, H₅',₆b' = 3.1 Hz, H₆a',₆b' = 12.0 Hz, H-6b’), 4.73 (dd, 2H, H-2’, 4’), 5.20 (d, 1H, J₁',₂' = 11.0 Hz, H-1’), 5.60 (d, 1H, CH₂Ph), 5.72-5.80 (m, 2H, CH₂Ph), 6.00 (d, 1H, CH₂Ph), 7.15-8.20 (m, 35H, aromatic) ppm; \textsuperscript{13}C-n.m.r.: δ, 55.1, 60.5, 63.3, 63.7, 68.6, 70.0, 72.1, 72.7, 73.3, 73.9, 74.9, 75.4, 79.5, 80.8, 97.6, 101.2, 127.8, 127.9, 128.2, 128.3, 128.4, 128.4, 128.5, 128.6, 128.6, 128.9, 129.4, 129.7, 129.8, 129.9, 130.0, 130.1, 133.0, 133.1, 133.3, 133.5, 133.5, 138.0, 138.1, 148.7, 165.3, 165.4, 166.0, 166.2, 166.3 ppm; HR-FAB MS [M+Na]⁺ calcd for C₆₂H₅₆O₁₆Na 1079.3466, found 1079.3446

1,2,3,4-Tetra-O-benzoyl-6-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-α/β-D-glucopyranose (9). The title compound was obtained from acceptors 6 or 7 and donors 1-4 as shown in Table 1 of the article. Analytical data for 9 was in a good agreement to those reported previously.\textsuperscript{6}
8. Synthesis of trisaccharides 12 and 34 by sequential glycosylation of NPG-supported glycosyl acceptor 6 on a NPG 10-plate assembly.

O-(2,3,4,6-Tetra-O-benzoyl-β-D-glucopyranosyl)-(1→6)-O-(2,3,4-tri-O-benzoyl-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzoyl-α/β-D-glucopyranose (12). NPG stick containing glycosyl acceptor conjugate 6 (7 mg, 9.0 µmol) was placed into the reaction vessel containing a mixture of the glycosyl donor 10 (39 mg, 0.05 mmol) and freshly activated molecular sieves (3Å, 120 mg) in dry CH₂Cl₂ (7.0 mL). The assembly was agitated under argon for 3 h, MeOTf (17 µL, 0.14 mmol) was added and the reaction vessel was agitated under argon for 20 h at rt. The excess reagents was removed by repeatedly dipping the stick in CH₂Cl₂ (3-5 x 7 mL), and the solvent excess was removed by drying the stick under reduced pressure (1 – 2 h). After that, the NPG stick was placed into the reaction vessel containing a solution of 1M Bu₄NF (27 µL, 0.03 mmol) in THF (7 mL). The reaction vessel was agitated at rt for 16 h. The excess reagents was removed by repeatedly dipping the stick in CH₂Cl₂ (3-5 x 7 mL), and the solvent excess was removed by drying the stick under reduced pressure (1 – 2 h). After that, the NPG stick was placed into the reaction vessel containing a mixture of the glycosyl donor 4 (33 mg, 0.05 mmol) and freshly activated molecular sieves (3Å, 100 mg) in dry CH₂Cl₂ (7.0 mL). The assembly was agitated under argon for 3 h, MeOTf (17 µL, 0.14 mmol) was added and the reaction vessel was agitated under argon for 20 h at rt. The excess reagents was removed by repeatedly dipping the stick in CH₂Cl₂ (3-5 x 7 mL), and the solvent excess was removed by drying the stick under reduced pressure (1 – 2 h). After that, the NPG stick covered with bound trisaccharides was agitated in 1N solution of NaOMe in methanol (7.0 mL) for 16 h at rt, while maintaining the pH
The reaction mixture was then neutralized with Dowex (H⁺) and the NPG stick was removed and rinsed by dipping in MeOH (3-5 x 7.0 mL). Dowex (H⁺) was filtered off and washed successively with methanol (5 x 2 mL). The combined methanol filtrate and washings were combined and concentrated under reduced pressure and dried in vacuo. The resulting crude mixture containing fully deprotected trisaccharides was dissolved in pyridine (0.5 mL), cooled to 0 °C and benzoyl chloride (30 μL) was added. The reaction mixture was stirred under argon for 5 h at rt, then quenched with methanol (1 mL) and the volatiles were evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel (ethyl acetate-hexane gradient elution) to allow the title trisaccharides 12 as a colorless foam in 52% yield (α/β = 3.3/1). Analytical data for 12: Rf= 0.5 (1/1 ethyl acetate/hexanes), ¹H-n.m.r: (α-12); δ, 3.50 (dd, 1H, J₅,₆ₐ= 4.1 Hz, J₆ₐ,₆ₕ= 11.0 Hz, H-6a), 3.88 (d, 2H, H-5’,6b’), 4.00 (d, 1H, H-6a’), 4.04 (dd, 1H, J₅,₆ₕ= 4.0 Hz, H-6b), 4.30 (m, 1H, H-5), 4.42-4.52 (m, 2H, H-5”,6b”), 4.56 (d, 1H, J₁’,₂=7.7 Hz, H-1’), 4.66 (d, 1H, H-6a”), 5.05 (dd, 1H, J₄’,₅= 9.5 Hz, H-4’), 5.16 (dd, 1H, J₂’,₃= 7.7 Hz, H-2’), 5.25 (d, 1H, J₁”，₂”= 7.9 Hz, H-1””), 5.51 (dd, 1H, J₂”’,₃”= 7.9 Hz, H-2””), 5.62-5.72 (m, 2H, H-3’,4”), 5.75 (dd, 1H, J₂,₃= 3.7 Hz, H-2), 5.80 (dd, 1H, J₄,₅= 9.9 Hz, H-4), 6.17 (dd, 1H, J₃”,₄”=9.8 Hz, H-3”), 6.27 (dd, 1H, J₃,₄= 10.0 Hz, H-3), 6.86 (d, 1H, J₁,₂= 3.7 Hz, H-1), 7.15-8.12 (m, 55H, aromatic) ppm; ¹³C-n.m.r.: δ, 29.9, 31.1, 63.5, 68.1, 68.6, 69.7, 69.8, 70.3, 70.5, 70.8, 71.3, 72.0, 72.4, 72.5, 72.8, 72.9, 74.8, 77.6, 90.3, 100.6, 101.6, 128.4, 128.5, 128.5, 128.5, 128.6, 128.6, 128.7, 128.9, 129.1, 129.1, 129.1, 129.1, 129.3, 129.3, 129.5, 129.5, 129.5, 130.0, 130.0, 130.1, 130.3, 130.5, 133.1, 133.3, 133.3, 133.5, 133.5, 133.5, 133.6, 133.7, 133.9, 164.7, 165.2, 165.4, 165.5, 165.5, 165.6, 165.8, 166.0, 166.1, 166.4 ppm; HR-FAB MS [M+Na]⁺ calcd for C₉₅H₇₆O₂₇Na 1671.4472, found 1671.4425. Also obtained herein was compound 9 in 20% yield.
O-(2,3,4,6-Tetra-O-benzoyl-β-D-galactopyranosyl)-(1→6)-O-(2,3,4-tri-O-benzoyl-α/β-D-glucopyranosyl)-(1→6)-2,3,4-tri-O-benzoyl-α/β-D-glucopyranosyl (34). The title compound was obtained from building blocks 6, 10, and 2-benzoxazolyl 2,3,4,6-tetra-O-benzoyl-1-thio-β-D-galactopyranoside (33) as a pale yellow foam in 31% yield (α/β = 4.1/1). Analytical data for 34: Rf = 0.5 (1/1 ethyl acetate/hexanes), 1H-n.m.r.; δ, 3.54 (dd, 1H, J5,6α = 3.5 Hz, J6α,6β = 10.8 Hz, H-6α), 3.90 (m, 1H, H-5’’), 3.97-4.01 (m, 2H, H-6a’’), 4.10 (dd, 1H, J5,6β = 3.4 Hz, H-6b), 4.35 (m, 1H, H-5), 4.48 (dd, 1H, J5’,6a’ = 6.0 Hz, H-5’), 4.53 (d, 1H, J1’,2’ = 7.6 Hz, H-1’), 4.60 (dd, 1H, H-6b’), 4.65 (dd, 1H, J6a’,6b’ = 10.8 Hz, H-6a’), 5.15 (dd, 1H, J4’,5’ = 9.7 Hz, H-4’), 5.29 (dd, 2H, J1’’,2’’ = 8.0 Hz, J2’,3’ = 9.8 Hz, H-1’’,2’), 5.68 (m, 2H, H-2,3’), 5.78 (m, 2H, H-2’’,4), 5.91 (dd, 1H, H-3’’), 6.14 (d, 1H, J4’’,5’’ = 3.2 Hz, H-4’’), 6.28 (dd, 1H, J3,4 = 10.0 Hz, H-3), 6.84 (d, 1H, J1,2 = 3.7 Hz, H-1), 7.20-8.14 (m, 55H, aromatic) ppm; 13C-n.m.r.: δ, 62.5, 67.7, 68.3, 69.2, 69.6, 70.6, 70.8, 71.3, 71.5, 71.8, 71.9, 72.9, 75.3, 76.6, 90.4, 100.5, 101.9, 128.4, 128.4, 128.5, 128.5, 128.6, 128.6, 128.7, 128.7, 128.9, 128.9, 129.0, 129.1, 129.2, 129.3, 129.3, 129.5, 129.6, 129.7, 129.9, 129.9, 130.1, 130.2, 130.3, 130.3, 130.4, 133.0, 133.3, 133.4, 133.4, 133.5, 133.5, 133.6, 133.7, 133.9, 134.0, 164.9, 165.2, 165.2, 165.3, 165.4, 165.6, 165.7, 165.8, 165.9, 166.2, 166.3, 171.4 ppm; HR-FAB MS [M+Na]+ calcd for C95H76O27Na 1671.4472, found 1671.4425. Also obtained herein were compound 9 and 1,2,3,4-Tetra-O-benzoyl-6-O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-α/β-D-glucopyranose (35) in 26% and 8% yield, respectively. Analytical data for 35 was in a good agreement to those reported previously.11
9. Reusing the anchored NPG plates

The adamantine monolayer covered NPG 10-plate assembly (36) left over after the cleavage of trisaccharide 11 (see the synthesis of 12) was investigated with the purpose of direct reapplication. For this purpose DCC/DMAP mediated coupling with model compound 31 was performed as described for the solution phase couplings (see for example the synthesis of compound 26). After agitating for 20 h (1 h for the synthesis of 26) and washing-drying sequence, the stick was subjected to the treatment with NaOMe in MeOH (16 h) as described for the synthesis of compounds 8 or 9. As a result, compound 32 was obtained in 83% yield (3.5 mg, 7.47 µmol). Analytical data for 32 was in a good agreement to those reported previously.7
10. Copies of NMR spectra for all new compounds
Supplementary Material (ESI) for Chemical Communications
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11. References