Supporting Information for Angew. Chem. Int. Ed. Z 17211

"Solid phase capture-release strategy in soluble polymer supported oligosaccharide synthesis"

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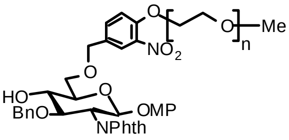
Contents: Preparation of compounds 2, **4**, **6**, **7**, **8**, **9**, **10**, **12**, **14**, **15**, **17**, **18**, **19**, **20**, and **21**.



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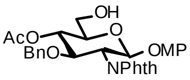

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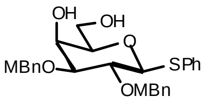

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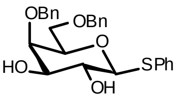

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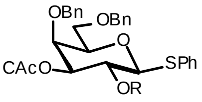
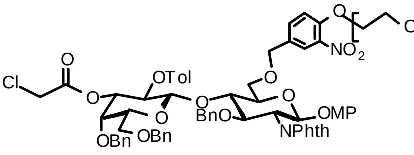


	R
8	**H**
9	**Tol**



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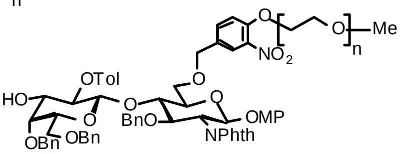

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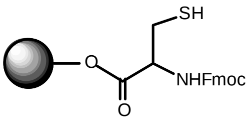

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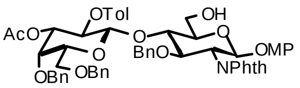

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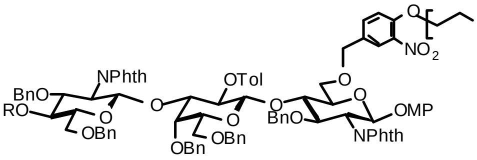
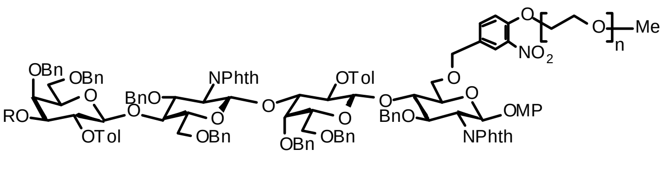
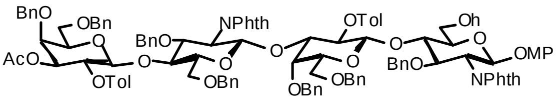


	R
17	CAc
18	H



	R
19	CAc
20	H



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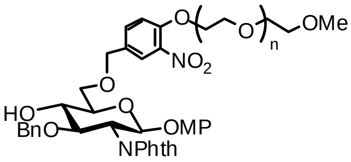
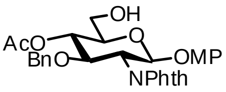
General Procedures. ^{1}H- and ^{13}C-NMR spectra were taken by JEOL EX-400 as solutions in $CDCl_3$ otherwise mentioned. Chemical shifts are expressed in ppm relative to the signal of either $CHCl_3$ or Me_4Si, adjusted to 7.24 or 0.00 ppm, respectively. Optical rotations were measured by JASCO DIP-310 as solutions in $CHCl_3$ at ambient temperature. MALDI-TOF MS spectra were recorded in the positive ion mode on a KOMPACT MALDI IV tDE (Shimazu/KRATOS) equipped with nitrogen laser with an emission wavelength of 337 nm. Molecular Sieves 4Å were purchased from Nakalai Tesque Inc. (Kyoto) and dried at 180 °C under vacuum prior to use. Kanto silica gel 60N (spherical, neutral) was used for column chromatography. TLC analysis was performed on Merck TLC (silica gel 60F254). For PEG-bound material, I_2 was used for detection on TLC analysis.



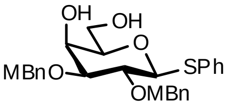
PEG-bound monosaccharide (2)

To a solution of *p*-methoxyphenyl 3-*O*-benzyl-6-*O*-2-deoxy-(4-hydroxy-3-nitrobenzyl)-2-phthalimido-β-D-glucopyranoside (**1**; 0.477 g, 0.868mmol) and poly (ethylene glycol) methyl ether (Aldrich, average MW ca 550; 1.14 g, ca 1.7 mmol) in THF (15 mL) was added DEAD (0.273 mL, 1.73 mmol) and PPh_3 (0.455 g, 1.73 mmol). The mixture was stirred for 18 h at room temperature and quenched with acetic acid. After co-evaporation of the mixture with toluene *in vacuo*, the residue was purified by silica gel column chromatography (neat AcOEt AcOEt/MeOH = 4/1) to give compound **2** (0.966 g, 99%). ^{1}H-NMR δ 7.78-6.68 (m, 16H), 5.66 (d, *J* = 8.3 Hz, 1H, H-1), 4.74 (d, *J* = 12.2 Hz, 1H, PHCH_2), 4.56 (m, 3H), 3.37 (s, 3H, CH_3O).



p-Methoxyphenyl 4-*O*-acetyl-3-*O*-benzyl-2-deoxy-2-phthalimido-b-D-glucopyranoside (4)

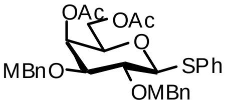
To a solution of compound **2** (50.5 mg, 42.4 mmol) in THF (0.40 mL) were added acetylacetone (0.2 mL) and zinc-copper couple (100 mg). After being stirred for 16 h at ambient temperature, the reaction mixture was filtered through Celite, then evaporated *in vacuo* and exposed to high vacuum for 6 h. To a solution of the obtained residue in THF (0.5 mL) were added acetic anhydride (0.2 mL) and triethylamine (0.3 mL). After the mixture was stirred overnight, the reaction was quenched by addition of methanol and co-evaporated with toluene *in vacuo*. The residue was subjected to silica gel column chromatography (neat AcOEt AcOEt/MeOH = 4/1) to afford compound **3** **(**57 mg) which was successively dissolved in 1,2-dichloroethane (0.6 mL) followed by addition of DDQ (28.9 mg, 127 µmol) and water (0.12 mL). After the mixture was stirred for 4 h, the reaction was quenched with an aqueous solution of ascorbic acid (0.7%)/citric acid (1.3%)/NaOH (0.9%), and diluted with AcOEt, washed with sat. $NaHCO_3$ and brine, then dried over Na_2SO_4 and evaporated *in vacuo*. Silica gel chromatography of the residue (AcOEt/hexane = 1/1) gave title compound **4** (19.8 mg, 92 % overall): $[\alpha]_D$ +74.2 (*c* 0.3); ^{1}H-NMR δ 7.69-6.69 (m, 13H), 5.68 (d, *J* = 8.1 Hz, 1H, H-1), 5.15 (t, *J* = 8.1 Hz, 1H, H-4), 4.60 (d, *J* = 11.9 Hz, 1H, PhCH_2), 4.30 (m, 2H, H-2 and H-3), 4.37 (d, *J* = 11.9 Hz, 1H, PhCH_2), 3.70 (m, 6H), 2.08 (s, 3H, CH_3CO); ^{13}C-NMR δ 170.1 155.1, 151.1, 133.8, 128.0, 127.6, 127.4, 118.4, 114.3, 97.4 (anomeric), 74.5, 74.1 (CH_2), 71.9, 61.5 (CH_2), 55.6, 55.4, 21.0 (CH_3); Anal Calcd for $C_{30}H_{29}NO_9$: C, 65.81; H, 5.34; N, 2.56. Found: C, 65.44; H, 5.23; N, 2.54.



Phenyl 2,3-di-*O*-*p*-methoxybenzyl-1-thio-b-D-galactopyranoside (6)

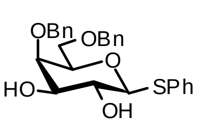
To a suspension of phenyl 1-thio-β-D-galactopyranoside (**5**; 32.00 g, 0.117 mol) in CH_3CN (300 mL) were added 2,2-dimethoxypropane (21.6 mL, 0.176 mol) and CSA (500 mg). After being stirred for 10 min at ambient temperature, the mixture was neutralized with Et_3N and evaporated *in vacuo*. The residue was exposed to high vacuum for 10 h. Then the resulting material was dissolved in DMF (200 mL) and cooled in ice-water cold bath. After addition of NaH (18.7 g, 0.468 mol) and *p*-methoxybenzyl chloride (47.6 mL, 0.351 mol), the mixture was stirred for 15 h at ambient temperature, then quenched with MeOH and co-evaporated with toluene *in vacuo*. The resulting residue was diluted with AcOEt, and washed with water. The aqueous layer was extracted with AcOEt twice. The combined organic layers were washed with brine, dried over Na_2SO_4 and evaporated *in vacuo*. Thus obtained crude material was successively dissolved in 60% aq. acetic acid (150 mL). The reaction mixture was stirred for 13 h at room temperature and extracted with AcOEt twice. The combined organic layers were washed with sat. aq $NaHCO_3$ and brine, and dried over Na_2SO_4. After evaporation, the residue was subjected to silica gel column chromatography (hexane/AcOEt = 1/1   1/2) to afford title compound **6** (33.5 g, 56%) : $[\alpha]_D$ +6.3 (*c* 1.0); ^{1}H-NMR δ 7.55-6.84 (m, 13H), 4.73 (d, *J* = 10.1 Hz, 1H) 4.65 (d, *J* = 10.1 Hz, 1H), 4.62 (s, 2H), 4.61 (d, *J* = 9.1 Hz, 1H, H-1), 4.00 (d, *J* = 3.4 Hz, 1H, H-4), 3.92 (m, 1H, H-6), 3.79 (s, 3H, O*Me*), 3.78 (s, 3H, O*Me*), 3.70 (t, *J* = 9.1 Hz, 1H, H-2), 3.53 (dd, *J* = 9.1, 3.4 Hz, 1H, H-3), 3.45 (m, 1H, H-5); ^{13}C-NMR δ 159.2, 159.0, 133.5, 131.4, 130.1, 129.6, 129.3, 128.7, 127.2, 113.8, 113.6, 114.8, 87.5 (anomeric), 82.0, 77.9, 76.6 (CH_2), 75.3 (CH_2), 71.9, 67.3, 62.6, 55.3 (CH_3), 55.2 (CH_3); Anal Calcd for $C_{28}H_{32}O_7S$: C, 65.60; H, 6.29. Found: C, 65.38; H, 6.36.

The presence of 4,6-hydroxyl groups was confirmed by acetylation of title compound.



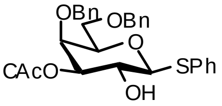
Phenyl 4,6-di-*O*-acetyl-2,3-di-*O*-*p*-methoxybenzyl-1-thio-b-D-galactopyranoside

^{1}H-NMR: δ 7.58-6.83 (m, 13H), 5.51 (d, 1H, H-4), 4.65 (m, 4H), 4.42 (d, *J* = 10.8 Hz, 1H), 4.16 (d, *J* = 6.6 Hz, 2H), 3.80 (m, 7H), 3.62 (d, *J* = 7.4 Hz, 1H), 2.14 (s, 3H, CH_3CO), 2.06 (s, 3H, CH_3CO); ^{13}C-NMR δ 170.2 170.0, 159.1, 159.1, 133.2, 132.0, 129.6, 129.4, 128.8, 128.5, 128.0, 127.4, 125.1, 113.7, 113.6, 87.6 (anomeric), 80.6, 77.3, 76.3, 75.3 (CH_2), 74.4, 71.1 (CH_2), 66.6, 62.3 (CH_2), 55.3 (CH_3), 55.2 (CH_3), 20.9 (CH_3), 20.8 (CH_3); $[\alpha]_D$ +40.6 (*c* 1.0); Anal Calcd for $C_{32}H_{36}O_9S$: C, 64.41; H, 6.08. Found: C, 64.73; H, 6.14.



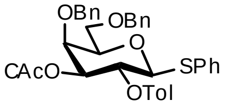
Phenyl 4,6-di-*O*-benzyl-1-thio-b-D-galactopyranoside (7)

To a solution of compound **6** (22.8 g, 44.4 mmol) in DMF (150 mL) were added NaH (7.10 g, 0.177 mol) and benzyl bromide (15.8 mL, 0.133 mol). After stirring of the mixture for 5 h, triethylamine (9.3 mL) was added to destroy the excess of benzyl bromide, and stirring was continued for 30 min at 4 °C. The mixture was diluted with AcOEt and washed with water. The aqueous layer was extracted with AcOEt and the combined organic layers were washed with brine, then dried over Na_2SO_4, and evaporated *in vacuo*. The obtained residue was successively dissolved in CH_2Cl_2 (300 mL). To the solution were added DDQ (26.9 g, 0.118 mol) and water (100 mL). The mixture was stirred overnight, then extracted with AcOEt and washed with water and brine, and the organic layer was dried over Na_2SO_4 and evaporated *in vacuo*. The residue was purified through silica gel column (hexane/AcOEt = 4/1   1/2) to afford compound **7** (15.8 g, 79%): $[\alpha]_D$ –2.1 (*c* 1.6); ^{1}H-NMR δ 7.56-7.25 (m, 15H), 4.73 (d, *J* = 10.1 Hz, 1H), 4.68 (d, *J* = 10.1 Hz, 1H), 4.51 (m, 3H, Ph*CH₂*), 3.93 (d, *J* = 2.4 Hz, 1H, H-4), 3.70 (m, 5H); ^{13}C-NMR δ 132.0, 128.7, 128.2, 127.6, 127.5, 127.4, 88.4 (anomeric), 77.5., 76.0, 75.3, 75.0 (CH_2), 73.5 (CH_2), 70.3, 68.4 (CH_2), 62.6, 55.3 (CH_3), 55.2 (CH_3); Anal Calcd for $C_{26}H_{28}O_5S$: C, 69.00; H, 6.24. Found: C, 69.05; H, 6.24.



Phenyl 4,6-di-*O*-benzyl-3-*O*-chloroacetyl-1-thio-b-D-galactopyranoside (8)

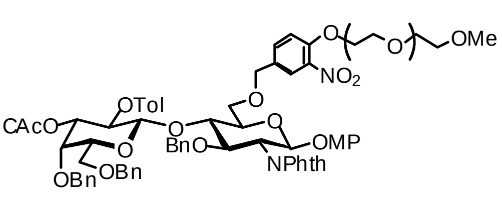
To a solution of **7** (6.20 g, 13.6 mmol) in pyridine (22.1 mL)-CH_2Cl_2 (200 mL) were added a solution of chloroacetic anhydride (1.87 g, 10.9 mmol) in CH_2Cl_2 (50 mL) dropwise at –40 °C. After stirring for 1 h, chloroacetic anhydride (0.46 g, 2.73 mmol) was added, and stirring was continued for 2 h at -40 °C. The mixture was washed with 2M HCl, cold sat. $NaHCO_3$ and brine, and dried over Na_2SO_4.. The obtained residue after evaporation was chromatographed on silica gel (hexane/ AcOEt = 4/1) to afford compound **8** (2.39 g, 33%): $[\alpha]_D$ + 7.5 (*c* 0.5); ^{1}H-NMR δ 7.69-7.22 (m, 15H), 4.97 (dd, *J* = 10.2, 2.9 Hz, 1H, H-4), 4.03 (d, *J* = 14.9 Hz, 1H, ClC*H₂*(=O)), 3.83 (d, *J* = 14.9 Hz, 1H, ClC*H₂*(=O)); ^{13}C-NMR δ 132.2, 128.8, 128.3, 128.1, 127.8, 127.7, 127.6, 88.8 (anomeric), 78.1, 73.5 (CH_2), 67.3, 40.7 (CH_2). Anal Calcd for $C_{28}H_{29}O_6S$: C, 63.57; H, 5.53. Found: C, 63.75; H, 5.63.



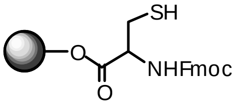
Phenyl 4,6-di-*O*-benzyl-3-*O*-chloroacetyl-1-thio-2-O-toluyl-b-D-galactopyranoside (9)

To an ice-water cooled solution of compound **8** (5.20 g, 9.82 mmol) in pyridine (39.7 mL)-CH_2Cl_2 (50 mL) were added toluoyl chloride (2.59 mL, 19.6 mmol). The mixture was stirred for 3 h with gradual warming up to ambient temperature, quenched by addition of methanol, diluted with $CHCl_3$ and washed with 2 M HCl, water and brine, dried over Na_2SO_4, and evaporated *in vacuo.* The residue was subjected to silica gel column chromatography (hexane/AcOEt = 8/1   4/1) to afford compound **9** (5.43 g, 85%): $[\alpha]_D$ + 31.8 (*c* 1.5); ^{1}H-NMR δ 7.89-7.16 (m, 19H), 5.63 (t, *J* = 10.0 Hz, 1H, H-2), 5.21 (dd, *J* = 10.0, 3.1Hz, 1H, H-3), 4.84 (s, *J* = 10.0 Hz, 1H, H-1), 4.65 (d, *J* = 11.7 Hz, 1H, PhC*H₂*), 4.58 (d, *J* = 11.7 Hz, 1H, PhC*H₂*), 4.52 (d, *J* = 11.7 Hz, 1H, PhC*H₂*), 4.46 (d, *J* = 11.7 Hz, 1H, PhC*H₂*), 4.10 (d, *J* = 3.1 Hz, 1H, H-4), 3.67 (m, 4H, H-6 and ClC*H₂*CO), 2.41 (s, 3H); ^{13}C-NMR δ 164.9, 143.9, 137.7, 137.4, 132.7, 132.1, 129.7, 129.0, 128.8, 128.6, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 127.6, 86.7 (anomeric), 77.3, 76.5, 74.9 (CH_2), 74.1, 73.6 (CH_2), 68.3, 67.9 (CH_2) , 40.4 (CH_2), 21.8 (CH_3); Anal Calcd for $C_{36}H_{35}ClO_7S$: C, 66.81; H, 5.45. Found: C, 67.17; H, 5.47.

PEG-bound disaccharide (10)

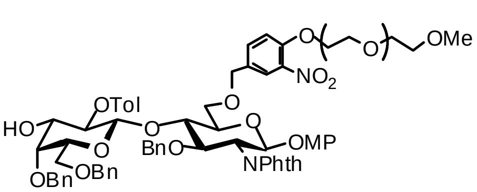


To a mixture of compound **2** (50.0 mg, 42.0 μmol), compound **9** (54.4 mg, 84.0 μmol) and molecular sieves 4Å (50 mg) in CH_2Cl_2 (1.0 mL) was added DMTST mixed with molecular sieves 3Å (148 mg, 1.13 mmol/g) at –20 °C under Ar atmosphere and stirring was continued for 14 h at –20 °C to 0 °C. The mixture was filtered through Celite and evaporated *in vacuo*. The residue was subjected to silica gel column chromatography (neat AcOEt   AcOEt/MeOH = 4/1) gave compound **10** (68.0 mg, 94%).



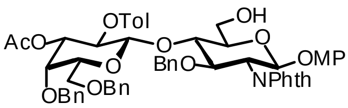
Deprotection of tert-butylthio group in Fmoc-Cys(tBu-thio) loaded on Wang Resin (12)

Fmoc-Cys(*t*Buthio) loaded Wang Resin **11** (350 mg, 0.64 mmol/g from Novabiochem) was solvated in 4:6:1 EtOH/CH_2Cl_2/H_2O (3.0 mL) (The solvent was purged with Ar prior to use.) under Ar atmosphere. n-Bu_3P (279 µL, 1.12 mmol) was added and the mixture was stirred for 3 h. The resins were filtered, rinsed with CH_2Cl_2, MeOH and CH_2Cl_2 and exposed to high vacuum for 3 h to afford thiol-containing resin **12** (314 mg, 98 %). (In regard to period of storage of the resin, one week storage under Ar atmosphere is guaranteed at least.)



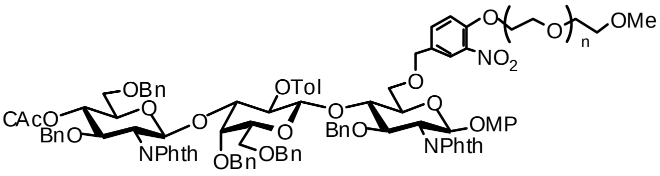
Catch and release to give disaccharide (14)

A solution of compound **10** (68.0 mg, 39.3 µmol) in 1:1 CH_3CN/CH_2Cl_2 (2.0 mL) was transferred to a glass tube containing resin **12** (135 mg, 118 µmol) under Ar atmosphere and diisopropylethylamine (20.5 µL, 118 µmol) was added. The mixture was shaken for 14 h as monitored the decrease of disaccharide **10** by coloring test with *p*-nitrobenzylpyridine and piperidine. The resins were filtered and rinsed with $CHCl_3$, MeOH, $CHCl_3$, and dry diethyl ether. The resins were exposed to high vacuum for 6 h. The obtained resins were swollen in THF (0.67 mL) and 4-(aminomethyl)pyridine (67.4 mg, 590 µmol) was added. After shaking the mixture for 12 h, the resins were filtered and washed with THF (10 mL), $CHCl_3$ (10 mL), and MeOH (20 mL). To the stirring combined filtrate and washing was added Amberlyst 15E until pH value turned to around 6 and filtered and washed with THF. The filtrate was co-evaporated with toluene *in vacuo*. The residue was subjected to silica gel column chromatography (neat AcOEt AcOEt/MeOH = 4/1) to afford compound **14** (53.2 mg, 82%): ^{1}H-NMR δ 5.52 (d, *J* = 8.0 Hz, 1H, H-1^{GlcN}), 5.30 (dd, *J* = 10.0, 8.0 Hz, 1H, H-2^{Gal}), 4.77 (d, *J* = 8.0 Hz, 1H, H-1^{Gal}), 3.37 (s, 3H, *Me*O), 2.40 (s, 3H, PhCH_3); ^{13}C-NMR δ 100.9 (anomeric), 97.3 (anomeric).



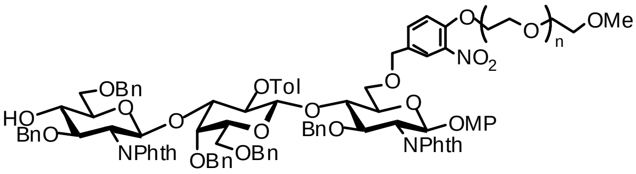
p-Methoxyphenyl *O*-(3-*O*-acetyl-4,6-di-*O*-benzyl-2-*O*-toluoyl-b-D-galactopyranosyl)-(1®4)-3-*O*-benzyl-2-deoxy-2-phthalimido-b-D-glucopyranoside (15)

To a solution of compound **14** (54.0 mg, 32.7 mmol) in THF (0.30 mL) were added acetylacetone (0.15 mL) and zinc-copper couple (108 mg). After being stirred for 18 h at ambient temperature, the reaction mixture was filtered through Celite, then evaporated *in vacuo* and exposed to high vacuum for 6 h. To a solution of the obtained residue in THF (3.0 mL) were added acetic anhydride (1.0 mL) and triethylamine (2.0 mL). The mixture was stirred overnight, quenched by addition of methanol and co-evaporated with toluene *in vacuo*. The residue was subjected to silica gel column chromatography (neat AcOEt AcOEt/MeOH = 4/1) to afford *N*-acetoamido compound (56.2 mg) which was successively dissolved in 1,2-dichloroethane (1.0 mL) followed by addition of DDQ (13.3 mg, 58.8 µmol) and water (0.15 mL). After the mixture was stirred for 3 h, the reaction was quenched with an aqueous solution of ascorbic acid (0.7%)/citric acid (1.3%)/NaOH (0.9%), diluted with AcOEt, washed with sat. $NaHCO_3$ and brine, dried over Na_2SO_4 and evaporated *in vacuo*. Silica gel chromatography of the residue (AcOEt/toluene = 1/7) gave title compound **15** (28.1 mg, 86% overall): $[\alpha]_D$ +22.1 (*c* 0.5); ^{1}H-NMR δ 7.96 (d, 1H), 7.67-6.63 (m, 25H), 5.67 (dd, *J* = 10.2, 8.1 Hz, 1H, H-2^{Gal}), 5.58 (d, *J* = 8.0 Hz, 1H, H-1^{GlcN}), 5.16 (dd, *J* = 10.2, 3.0 Hz, 1H, H-3^{Gal}), 4.83 (d, *J* = 8.1 Hz, 1H, H-1^{Gal}), 4.01 (d, *J* = 3.0 Hz, 1H, H-4^{Gal}), 3.79 (m, 1H), 2.42 (s, 3H, C*H*$_3$Ph), 1.85 (s, 3H, C*H*$_3$CO); Anal Calcd for $C_{58}H_{57}NO_{15}$: C, 69.10; H, 5.70; N, 1.39. Found: C, 69.27; H, 5.79; N, 1.35.



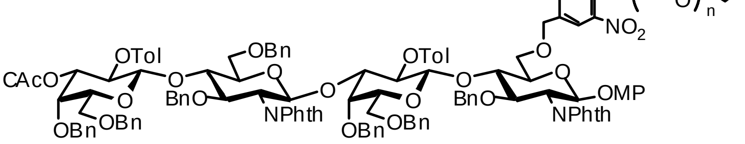
PEG-bound trisaccharide (17)

To a mixture of compound **14** (67.1 mg, 40.6 µmol) and compound **16** (57.7 mg, 81.3 µmol) in CH_2Cl_2 (1.8 mL) was added 10% TMSOTf in CH_2Cl_2 at –20 °C under Ar atmosphere and stirring was continued for 1 h at –20 °C. The mixture was directly subjected to silica gel column chromatography (neat AcOEt AcOEt/MeOH = 4/1) gave compound **17** (84.5 mg, 95%).



Catch and release to give trisaccharide (18)

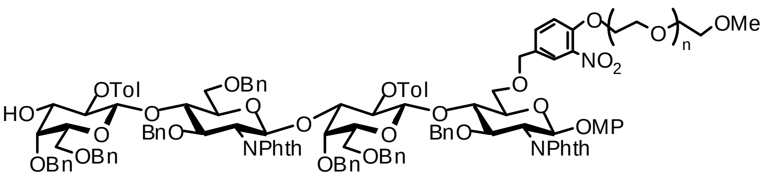
A solution of compound **17** (52.0 mg, 22.9 µmol) in 1:1 CH_3CN/CH_2Cl_2 (1.1 mL) that had been purged with Ar was transferred to a glass tube containing resin **12** (131 mg, 114 µmol) under Ar atmosphere and diisopropylethylamine (19.9 µL, 114 µmol) was added. The mixture was shaken for 22 h as monitored the decrease of trisaccharide **17** by coloring test with 4-(4-nitrobenzyl)pyridine and piperidine. The resins were filtered and rinsed with $CHCl_3$, MeOH, $CHCl_3$, and dry diethyl ether. The resins were exposed to high vacuum for 14 h. The obtained resin was swollen in THF (2.0 mL) and 4-(aminomethyl)pyridine (65.3 mg, 570 µmol) was added. After shaking the mixture for 19 h, the resins were filtered and washed with THF (10 mL), $CHCl_3$ (10 mL), and MeOH (20 mL). To the stirring combined filtrate and washing was added Amberlyst 15E until pH value turned to around 6 and filtered and washed with THF. The filtrate was co-evaporated with toluene *in vacuo*. The residue was subjected to silica gel column chromatography (neat AcOEt AcOEt/MeOH = 4/1) to afford compound **18** (38.2 mg, 79%).



PEG-bound tetrasaccharide (19)

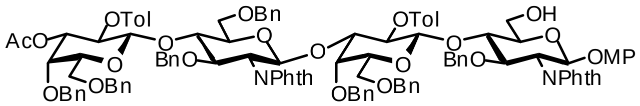
To a mixture of compound **19** (20.0 mg, 9.42 µmol), compound **9** (12.2 mg, 18.8 µmol) and molecular sieves 4Å (10 mg) in CH_2Cl_2 (0.5 mL) was added DMTST mixed with molecular sieves 3Å (33.3 mg, 1.13 mmol/g) at 0 °C under Ar atmosphere and stirring was continued for 3 h at 0 °C and 2 h at 10 °C. The mixture was filtered through Celite and evaporated *in vacuo*. The residue was subjected to silica gel column chromatography (neat AcOEt AcOEt/MeOH = 4/1) gave compound **19** (22.1 mg, 88%): ^{1}H-NMR δ 7.80-6.54 (m, 30H), 5.41 (d, *J* = 8.6 Hz, 1H), 5.26 (d, *J* = 8.6 Hz, 1H), 5.13 (t, *J* = 9.2 Hz), 4.71 (s, 2H), 3.32 (s, 3H).

Catch and release to give tetrasaccharide (20)



A solution of compound **19** (22.1 mg, 8.31 μmol) in 1:1 CH_3CN/CH_2Cl_2 (1.1 mL) (The solvent was purged with Ar prior to use.) was transferred to a glass tube containing resin **12** (95.5 mg, 83.1 μmol) under Ar atmosphere and diisopropylethylamine (14.4 μL, 83.1 μmol) was added. The mixture was shaken for 23 h as monitored by coloring test described above. The resins were filtered and rinsed with $CHCl_3$, MeOH, $CHCl_3$, and dry diethyl ether. The resins were exposed to high vacuum for 14 h. The obtained resins were swollen in THF (1.5 mL) and 4-(aminomethyl)pyridine (23.7 mg, 207 μmol) was added. After shaking for 20 h the resin was filtered and washed with THF (10 mL), $CHCl_3$ (10 mL), and MeOH (20 mL). To the stirring combined filtrate and washing was added Amberlyst 15E until pH value turned to around 6 and filtered and washed with THF. The filtrate was co-evaporated with toluene *in vacuo*. The residue was subjected to silica gel column chromatography (neat AcOEt AcOEt/MeOH = 4/1) to afford compound **20** (17.2 mg, 80%).

Tetrasaccharide (21)



To a solution of compound **20** (45.3 mg, 17.54 mmol) in THF (0.30 mL) were added acetylacetone (0.15 mL) and zinc-copper couple (90 mg). After being stirred for 18 h at ambient temperature, the reaction mixture was filtered through Celite, then evaporated *in vacuo* and exposed to high vacuum for 6 h. To a solution of the obtained residue in THF (3.0 mL) were added acetic anhydride (1.0 mL) and triethylamine (2.0 mL). The mixture was stirred for 14 h, quenched by addition of methanol and co-evaporated with toluene *in vacuo*. The residue was subjected to silica gel column chromatography (neat AcOEt AcOEt/MeOH= 4/1) to afford *N*-acetoamido compound which was successively dissolved in 1,2-dichloroethane (1.0 mL) followed by addition of DDQ (5.9 mg, 26.3 μmol) and water (0.15 mL). The mixture was stirred for 3 h, quenched with an aqueous solution of ascorbic acid (0.7%)/citric acid (1.3%)/NaOH (0.9%), diluted with AcOEt, washed with sat $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and evaporated *in vacuo*. Silica gel chromatography of the residue (AcOEt/toluene = 1/5) gave title compound **21** (24.5 mg, 72 % overall). ^{1}H-NMR δ 5.58 (d, *J* = 10.2, 8.1 Hz, 1H), 5.46 (d, *J* = 8.2 Hz, 1H), 5.38 (d, *J* = 10.2, 8.1 Hz, 1H), 5.12 (d, *J* = 7.8 Hz, 1H), 5.04 (m, 2H), 3.65 (s, 3H), 2.44 (s, 6H), 1.84 (s, 3H). ^{13}C-NMR δ 170.0 164.7, 164.1, 155.0, 150.35, 143.9, 138.9, 138.6, 138.5, 138.1 138.0, 137.8, 137.6, 133.6, 129.6, 129.4, 129.1, 128.8, 128.3, 128.2, 128.1, 128.0, 128.0, 127.8, 127.7, 127.6, 127.5, 127.5, 127.4, 127.4, 127.2, 126.9, 126.5, 126.4, 123.1, 118.2, 114.2, 101.1, 100.7, 99.4, 97.2, 80.1, 77.8, 75.0, 74.8, 74.7, 74.5, 74.3, 74.2, 73.7, 73.7, 73.4, 73.3, 73.1, 71.7, 70.7, 68.7, 67.5, 60.4, 56.0, 55.5, 29.8, 21.8, 20.8.