Supporting Information for:

Saccharide-Linked Ethynylpyridine Oligomers: Primary Structures Encode Chiral Helices

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Experimental Section

General. NMR spectra were recorded on a Varian Gemini 300 spectrometer using tetramethylsilane (TMS) as an internal reference. ESI-HRMS analyses were carried out on a JEOL JMS-T100LC mass spectrometer. IR, UV, and CD spectra were obtained by a JASCO spectrometers FT/IR-460plus, V-560, J-720WI, respectively. Melting points were determined with Yanako MP-500D and not corrected. THF was freshly distilled from sodium benzophenone ketyl before use. The following compounds, 2,6-Dibromopyridin-4-ol (**1**),[1] pentaacetylglycosides,[2] 3-bromopropyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (**12(β-Glc-3)**),[3] 3-bromopropyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (**12(β-Gal-3)**),[3] 3-bromopropyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (**12(α-Man-3)**),[4] 6-bromohexyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (**12(β-Glc-6)**),[5] and 6-iodo-2-pyridone[6] were prepared according to the procedures reported in the literature. A preparation method of 12-bromododecyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (**12(β-Glc-12)**) was recently reported.[7]

2,6-Dibromo-4-(3-butenoxy)pyridine (2). To a suspension of K_2CO_3 (32.4 g, 234 mmol) in acetone (250 mL) were added 2,6-dibromopyridin-4-ol (**1**) (9.9 g, 39 mmol) and 4-bromo-1-butene (21.1 g, 15.8 mL, 156 mmol) subsequently at room temperature. The mixture was refluxed for 5 h. The resulting mixture was filtered and evaporated, and the residue was purified by silica gel column chromatography (eluent; AcOEt/hexane = 1 : 9) to afford **2** (12 g, 98%) as a colorless solid. Mp 50−53 °C; IR (KBr) 3079, 1644, 1575, 1537, 1374, 1288 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.55 (q, J = 6.6 Hz, 2 H), 4.05 (t, J = 6.6 Hz, 2 H), 5.12−5.21 (m, 2 H), 5.78−5.88 (m, 1 H), 6.97 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 33.24, 68.40, 113.88, 118.17, 133.12, 144.17, 166.90; ESI-HRMS *m*/*z* calcd for $C_9H_{10}{}^{79}Br^{81}BrNO$ ($M + H^+$): 307.9108; found: 307.9108.

4-(3-Butenoxy)-2,6-diiodopyridine (3). To a mixture of CuI (0.38 g, 2.0 mmol), **2** (12.1 g, 39.4 mmol), and NaI (30 g, 197 mmol) were added diglyme (43 mL), *o*-xylene (100 mL), and 1,3-diaminopropane (0.29 g, 0.33 mL, 3.9 mmol) subsequently at room temperature. The mixture was stirred at 110 °C for 13 h. The resulting suspension was allowed to reach room temperature. Then to the mixture were added water and AcOEt. The organic layer was washed with additional water followed by brine, dried over $MgSO_4$, and concentrated. The residue was purified by silica gel column chromatography (eluent; AcOEt/hexane = 1 : 9) to afford **3** (15 g, 93%) as a colorless solid. Mp 64−67 °C; IR (KBr) 3099, 1644, 1557, 1519, 1364, 1221 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.52 (q, J = 6.3 Hz, 2 H), 4.01 (t, J = 6.6 Hz, 2 H), 5.12−5.19 (m, 2 H), 5.78−5.87 (m, 1 H), 7.22 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 33.20, 68.04, 115.92, 118.10, 121.26, 133.18, 164.68; ESI-HRMS *m*/*z* calcd for $C_9H_{10}I_2NO$ ($M + H^+$):

401.8851; found: 401.8851.

4-(3-Butenoxy)-2-(*tert*-butyldimethylsilylethynyl)-6-iodopyridine (4). To an *i*-Pr_2NH (15 mL) suspension of $PdCl_2(PPh_3)_2$ (17 mg, 0.025 mmol) and CuI (4.7 mg, 0.025 mmol) were added **3** (1.0 g, 2.5 mmol) and *tert*-butyldimethylsilylacetylene (70 mg, 0.093 mL, 0.50 mmol) at 0 °C. The mixture was stirred for 1 h at 0 °C, diluted with Et_2O, and filtered off the insoluble materials. The filtrate was concentrated and purified by silica gel column chromatography (eluent; AcOEt/hexane = 1 : 20) to afford **4** (0.20 g, 95%) as a colorless oil and recovered **3** (0.65 g, 80% recovery). IR (Nujol) 3079, 1575, 1532, 1377, 1250 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.18 (s, 6 H), 0.99 (s, 9 H), 2.53 (q, J = 6.6 Hz, 2 H), 4.03 (t, J = 6.6 Hz, 2 H), 5.11−5.20 (m, 2 H), 5.79−5.88 (m, 1 H), 6.93 (d, J = 1.8 Hz, 1 H), 7.19 (d, J = 2.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.47, 16.99, 67.86, 94.82, 103.18, 114.72, 117.79, 117.99, 120.77, 133.39, 144.31, 164.63; ESI-HRMS *m*/*z* calcd for $C_{17}H_{25}INOSi$ ($M + H^+$): 414.0750; found: 414.0750.

2-Bromo-4-(3-butenoxy)-6-(3-hydroxy-3-methyl-1-butynyl)pyridine (5). To an *i*-Pr_2NH (40 mL) suspension of $PdCl_2(PPh_3)_2$ (0.34 g, 0.49 mmol) and CuI (93 mg, 0.49 mmol) were added **2** (5.0 g, 16 mmol) and 2-methyl-3-butyn-2-ol (2.0 g, 2.3 mL, 24 mmol) at 0 °C. The mixture was stirred for 1 h at 0 °C, diluted with Et_2O, and filtered off the insoluble materials. The filtrate was concentrated and purified by silica gel column chromatography (eluent; AcOEt/hexane = 1 : 4) to afford **5** (4.0 g, 80%) as a yellow oil. IR (Nujol) 3348 (br), 3078, 2878, 1638, 1582, 1539, 1377, 1221 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.62 (s, 6 H), 2.52 (q, J = 6.6 Hz, 2 H), 3.76 (br s, 1 H), 4.04 (t, J = 6.6 Hz, 2 H), 5.11−5.20 (m, 2 H), 5.79−5.88 (m, 1 H), 6.87−6.93 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.13, 33.04, 65.15, 65.31, 67.86, 80.21, 95.32, 113.31, 113.57, 117.76, 133.15, 142.05, 143.76, 165.72; ESI-HRMS *m*/*z* calcd for $C_{14}H_{17}BrNO_2$ ($M + H^+$): 310.0442; found: 310.0447.

4-(3-Butenoxy)-2,6-bis(3-hydroxy-3-methyl-1-butynyl)pyridine (6). To an *i*-Pr_2NH (30 mL) suspension of $PdCl_2(PPh_3)_2$ (0.39 g, 0.55 mmol) and CuI (0.11 g, 0.55 mmol) were added **2** (5.0 g, 16 mmol) and 2-methyl-3-butyn-2-ol (8.2 g, 9.5 mL, 98 mmol) at room temperature. The mixture was stirred for 1 h at room temperature, diluted with Et_2O, and filtered off the insoluble materials. The filtrate was concentrated and purified by silica gel column chromatography (eluent; AcOEt/hexane = 2 : 1) to afford **6** (5.0 g, 99%) as a brown oil. IR (KBr) 3349 (br), 3082, 1645, 1583, 1556, 1359, 1221 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.62 (s, 12 H), 2.54 (q, J = 6.3 Hz, 2 H), 3.30 (br s, 2 H), 4.04 (t, J = 6.6 Hz, 2 H), 5.11−5.20 (m, 2 H), 5.78−5.91 (m, 1 H), 6.87 (d, J = 1.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.31, 33.29, 65.13, 67.65, 80.97, 94.83, 113.08, 117.79, 133.45, 144.13, 165.05; ESI-HRMS

m/*z* calcd for $C_{19}H_{24}NO_3$ ($M + H^+$): 314.1756; found: 314.1755.

4-(3-Butenoxy)-2-(*tert*-butyldimethylsilylethynyl)-6-(3-hydroxy-3-methyl-1-butynyl)pyridine (7). To an *i*-Pr_2NH (30 mL) suspension of $Pd[P(t\text{-}Bu)_3]_2$ (0.15 g, 0.30 mmol) and CuI (57 mg, 0.30 mmol) were added **5** (4.6 g, 15 mmol) and *tert*-butyldimethylsilylacetylene (4.2 g, 5.6 mL, 0.030 mmol) subsequently at room temperature. The mixture was stirred for 25 h at room temperature, diluted with Et_2O, and filtered off the insoluble materials. The filtrate was concentrated and purified by silica gel column chromatography (eluent; AcOEt/hexane = 1 : 4) to afford **7** (5.2 g, 94%) as a yellow oil. IR (Nujol) 3349 (br), 3079, 2884, 1645, 1581, 1553, 1350, 1227 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.18 (s, 6 H), 0.99 (s, 9 H), 1.61 (s, 6 H), 2.54 (q, *J* = 6.6 Hz, 2 H), 3.00 (s, 1 H), 4.04 (t, *J* = 6.6 Hz, 2 H), 5.11−5.20 (m, 2 H), 5.78−5.89 (m, 1 H), 6.88 (d, *J* = 2.4 Hz, 1 H), 6.91 (d, *J* = 2.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.54, 16.87, 26.33, 31.33, 33.29, 65.37, 67.57, 81.26, 93.44, 93.98, 103.96, 113.15, 113.91, 117.73, 133.45, 144.25, 144.33, 164.83; ESI-HRMS *m*/*z* calcd for $C_{22}H_{32}NO_2Si$ ($M + H^+$): 370.2202; found: 370.2202.

4-(3-Butenoxy)-2-(*tert*-butyldimethylsilylethynyl)-6-ethynylpyridine (8). To a NaH (16 mg, 0.40 mmol; commercial 60% dispersion was washed thoroughly with hexane prior to use) suspension in toluene (20 mL) was added **7** (0.37 g, 1.0 mmol) at room temperature. The mixture was refluxed for 30 min. To the mixture were added water and AcOEt at room temperature. The organic layer was washed with additional water followed by brine, dried over $MgSO_4$, and concentrated. The residue was purified by silica gel column chromatography (eluent; AcOEt/hexane = 1 : 4) to afford **8** (0.28 g, 90%) as a brown oil. IR (Nujol) 3310, 3080, 2885, 1579, 1556, 1365, 1226 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.19 (s, 6 H), 0.99 (s, 9 H), 2.54 (q, *J* = 6.9 Hz, 2 H), 3.10 (s, 1 H), 4.06 (t, *J* = 6.6 Hz, 2 H), 5.11−5.20 (m, 2 H), 5.80−5.89 (m, 1 H), 6.94 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.50, 16.89, 26.36, 33.30, 67.65, 82.45, 93.49, 103.89, 113.76, 114.12, 117.81, 133.45, 143.53, 144.54, 164.91; ESI-HRMS *m*/*z* calcd for $C_{19}H_{25}NNaOSi$ ($M + Na^+$): 334.1603; found: 334.1603.

4-(3-Butenoxy)-2,6-diethynylpyridine (9). To a NaH (7.2 mg, 0.30 mmol; commercial 60% dispersion was washed thoroughly with hexane prior to use) suspension in toluene (10 mL) was added **6** (0.24 g, 0.75 mmol) at room temperature. The mixture was refluxed for 30 min. To the mixture were added water and AcOEt at room temperature. The organic layer was washed with additional water followed by brine, dried over $MgSO_4$, and concentrated. The residue was purified by silica gel column chromatography (eluent; AcOEt/hexane = 1 : 4) to afford **9** (0.12 g, 82%) as a yellow solid. Mp 116−118 °C; IR (KBr) 3173, 3078, 2107, 1644, 1578, 1556, 1335 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ

2.54 (q, J = 6.3 Hz, 2 H), 3.11 (s, 2 H), 4.06 (t, J = 6.6 Hz, 2 H), 5.12−5.21 (m, 2 H), 5.79−5.92 (m, 1 H), 6.98 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 32.93, 67.44, 77.13, 81.97, 113.79, 117.50, 133.10, 143.30, 164.69; ESI-HRMS m/z calcd for $C_{13}H_{11}NNaO$ ($M + Na^+$): 220.0738; found: 220.0739.

4-(3-Butenoxy)-2,6-bis[[4-(3-butenoxy)-6-iodo-2-pyridyl]ethynyl]pyridine (10). To an i-Pr_2NH (60 mL) and THF (20 mL) suspension of $Pd(PPh_3)_4$ (0.13 g, 0.11 mmol) and CuI (22 mg, 0.11 mmol) were added **3** (14 g, 34 mmol) and **9** (1.1 g, 5.7 mmol) slowly at room temperature. The mixture was stirred for 5 h at room temperature, diluted with ether, and filtered off the insoluble materials. The filtrate was concentrated and purified by silica gel column chromatography (eluent; AcOEt/hexane = 1 : 4) to afford **10** (3.1 g, 72%) as a yellow oil. IR (Nujol) 3078, 2881, 1642, 1558, 1531, 1353, 1241 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.51−2.56 (m, 6 H), 4.02−4.10 (m, 6 H), 5.12−5.22 (m, 6 H), 5.80−5.89 (m, 3 H), 7.11−7.24 (m, 4 H), 7.24−7.25 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 33.24, 67.99, 86.74, 88.23, 114.59, 114.73, 117.81, 117.97, 118.00, 121.56, 133.24, 133.31, 143.63, 143.81, 164.73, 165.12; ESI-HRMS m/z calcd for $C_{31}H_{28}I_2N_3O_3$ ($M + H^+$): 744.0220; found: 744.0220.

Tetrameric building block 11. To an i-Pr_2NH (20 mL) and THF (18 mL) suspension of $Pd[P(t\text{-}Bu)_3]_2$ (25 mg, 0.049 mmol) and CuI (9.4 mg, 0.049 mmol) were added **10** (2.2 g, 3.0 mmol) and **8** (0.31 g, 0.98 mmol) slowly at room temperature. The mixture was stirred for 24 h at room temperature, and then to the mixture was added 3-aminopropyl-functionalized silica gel (0.50 g). After 1 h, the mixture was diluted with Et_2O, and filtered off the insoluble materials. The filtrate was concentrated and subjected to silica gel column chromatography (eluent; AcOEt/hexane = 1 : 7) to give recovered **10** (1.7 g, 73% recovery) and **11** (0.67 g, 74%) as a yellow solid. Mp 73−76 °C; IR (Nujol) 3075, 1716, 1643, 1583, 1548, 1376, 1249 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.20 (s, 6 H), 1.00 (s, 9 H), 2.54−2.61 (m, 8 H), 4.02−4.10 (m, 8 H), 5.13−5.22 (m, 8 H), 5.80−5.92 (m, 4 H), 6.98 (d, J = 2.4 Hz, 1 H), 7.10−7.15 (m, 6 H), 7.25 (d, J = 2.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.49, 16.93, 26.38, 33.21, 33.29, 67.74, 67.88, 67.96, 86.66, 87.25, 87.34, 87.50, 87.70, 88.27, 93.65, 103.88, 113.81, 114.54, 114.57, 114.70, 114.77, 117.78, 117.84, 117.92, 117.99, 121.54, 133.21, 133.29, 133.42, 143.63, 143.75, 143.78, 143.84, 143.97, 144.02, 144.57, 164.70, 164.94, 165.07; ESI-HRMS m/z calcd for $C_{50}H_{51}IN_4NaO_4Si$ ($M + Na^+$): 949.2622; found: 949.2619.

3-Bromopropyl 2,3,4,6-tetra-*O*-acetyl-(α/β)-D-glucopyranoside (12(α-Glc-3) and 12(β-Glc-3)). Typical procedure of glycosidation. To a solution of penta-*O*-acetyl-β-D-glucopyranose (10 g, 26 mmol) and 3-bromopropanol (4.3 g, 31 mmol) in CH_2Cl_2 (60 mL) was added $BF_3{\cdot}Et_2O$ (18 mL, 128 mmol) dropwise over a period of 90 min at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and

then for further 23 h at room temperature. The reaction mixture was poured into an ice/water mixture with stirring. The organic layer was separated and washed successively with additional water, saturated aqueous $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4 and concentrated. The resulting residue was purified by column chromatography on silica gel (eluent; AcOEt/hexane = 1 : 4) to afford **12(α-Glc-3)** and **12(β-Glc-3)**[3] (**12(α-Glc-3)**: 1.9 g, 12%; **12(β-Glc-3)**: 3.6 g, 36%). **12(α-Glc-3)**: a colorless oil; IR (Nujol) 1752, 1433, 1369, 1224 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.00−2.15 (m, 14 H), 3.50−3.59 (m, 3 H), 3.87−3.92 (m, 1 H), 4.02−4.14 (m, 2 H), 4.23−4.29 (m, 1 H), 4.85−4.96 (m, 1 H), 5.01−5.07 (m, 2 H), 5.44 (t, J = 9.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.34, 20.40, 20.45, 29.95, 31.75, 61.60, 65.48, 67.10, 68.22, 69.75, 70.42, 95.61, 168.98, 169.47, 169.50, 169.95; ESI-HRMS m/z calcd for $C_{17}H_{25}BrNaO_{10}$ ($M + Na^+$): 491.0528; found: 491.0527.

3-Bromopropyl 2,3,4,6-tetra-*O*-acetyl-(α/β)-D-galactopyranoside (12(α-Gal-3) and 12(β-Gal-3)). Yields: **12(α-Gal-3)** 0.75 g (15%) and **12(β-Gal-3)**[3] 2.1 g (35%) from penta-*O*-acetyl-β-D-galactopyranose (5.0 g, 13 mmol) and 3-bromopropanol (2.1 g, 15 mmol). **12(α-Gal-3)**: a colorless oil; IR (Nujol) 1747, 1455, 1375, 1230 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.99−2.17 (m, 14 H), 3.51−3.60 (m, 3 H), 3.85−3.92 (m, 1 H), 4.09−4.12 (m, 2 H), 4.24 (t, J = 6.6 Hz, 1 H), 5.11−5.15 (m, 2 H), 5.30−5.34 (m, 1 H), 5.46 (d, J = 3.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.75, 20.83, 20.89, 30.20, 32.09, 61.83, 65.84, 66.42, 67.57, 68.07, 68.12, 96.42, 169.94, 170.10, 170.21, 170.30; ESI-HRMS m/z calcd for $C_{17}H_{25}BrNaO_{10}$ ($M + Na^+$): 491.0528; found: 491.0526.

12-Bromododecyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (12(β-Glc-12)).[7] A colorless oil (1.1 g, 25%) from penta-*O*-acetyl-β-D-glucopyranose (3.0 g, 7.7 mmol) and 12-bromododecanol (2.5 g, 9.2 mmol); IR (Nujol) 1746, 1468, 1371, 1232 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.22−1.28 (br m, 14 H), 1.38−1.48 (br m, 2 H), 1.52−1.59 (br m, 2 H), 1.80−1.94 (m, 2 H), 1.98−2.10 (m, 12 H), 3.38−3.52 (m, 3 H), 3.71−3.76 (m, 1 H), 3.82−3.89 (m, 1 H), 4.09−4.13 (m, 1 H), 4.25−4.31 (m, 1 H), 4.53 (d, J = 7.8 Hz, 1 H), 4.95 (t, J = 8.7 Hz, 1 H), 5.06 (t, J = 9.6 Hz, 1 H), 5.17−5.24 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.05, 20.33, 20.38, 20.46, 20.75, 25.59, 27.93, 28.53, 29.06, 29.19, 29.29, 29.34, 32.61, 33.68, 59.93, 61.73, 68.24, 69.72, 71.07, 72.55, 100.38, 168.53, 168.77, 169.50, 169.87; ESI-HRMS m/z calcd for $C_{26}H_{43}BrNaO_{10}$ ($M + Na^+ + 2$): 619.1916; found: 619.1919.

2-Iodo-6-[3-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)propoxy]pyridine (13(α-Glc-3)). **Typical procedure of Williamson synthesis.** To a suspension of K_2CO_3 (2.9 g, 21 mmol) in acetone (25 mL) were added **12(α-Glc-3)** (1.6 g, 3.5 mmol) and 6-iodo-2-pyridone[6] (0.92 g, 4.2 mmol) subsequently at

room temperature. The mixture was refluxed for 5 h, and the resulting mixture was filtered and evaporated. The residue was subjected to silica gel column chromatography (eluent; AcOEt/hexane = 1 : 4) to afford **13(α-Glc-3)** (1.5 g, 71%) as a colorless oil. IR (Nujol) 2952, 1751, 1581, 1550, 1458, 1375, 1222 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.00−2.18 (m, 14 H), 3.55−3.63 (m, 1 H), 3.84−3.89 (m, 1 H), 3.99−4.13 (m, 2 H), 4.21−4.27 (m, 1 H), 4.33−4.38 (m, 2 H), 4.40−4.88 (m, 1 H), 5.02−5.09 (m, 2 H), 5.48 (t, J = 9.6 Hz, 1 H), 6.68 (d, J = 8.1 Hz, 1 H), 7.19 (t, J = 7.8 Hz, 1 H), 7.30, (d, J = 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.83, 20.93, 28.82, 61.93, 63.28, 65.32, 67.30, 68.59, 70.27, 70.90, 95.87, 109.91, 113.60, 127.60, 139.73, 162.82, 169.49, 169.97, 170.12, 170.51; ESI-HRMS *m*/*z* calcd for $C_{22}H_{28}INNaO_{11}$ ($M + Na^+$): 632.0604; found: 632.0602.

2-Iodo-6-[3-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)propoxy]pyridine (13(β-Glc-3)). A colorless oil (2.0 g, 88%) from **12(β-Glc-3)** (1.8 g, 3.8 mmol); IR (Nujol) 2984, 1752, 1581, 1550, 1436, 1374, 1224 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.00−2.19 (m, 14 H), 3.63−3.74 (m, 2 H), 4.00−4.15 (m, 2 H), 4.24−4.29 (m, 3 H), 4.53 (d, J = 7.8 Hz, 1 H), 4.97−5.12 (m, 2 H), 5.21 (t, J = 9.3 Hz, 1 H), 6.67 (d, J = 7.8 Hz, 1 H), 7.19 (t, J = 7.5 Hz, 1 H), 7.30 (d, J = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.78, 20.94, 21.06, 29.02, 62.01, 63.33, 66.81, 68.48, 71.29, 71.84, 72.85, 100.89, 109.80, 113.63, 127.55, 139.67, 162.90, 169.29, 170.15, 170.54; ESI-HRMS *m*/*z* calcd for $C_{22}H_{28}INNaO_{11}$ ($M + Na^+$): 632.0604; found: 632.0605.

2-Iodo-6-[3-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)propoxy]pyridine (13(α-Gal-3)). A colorless oil (1.5 g, 83%) from **12(α-Gal-3)** (1.4 g, 3.0 mmol); IR (Nujol) 2979, 1756, 1581, 1550, 1436, 1374, 1226 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.99−2.15 (m, 14 H), 3.57−3.61 (m, 1 H), 3.86−3.89 (m, 1 H), 4.07−4.10 (m, 2 H), 4.24 (t, J = 6.6 Hz, 1 H), 4.33−4.39 (m, 2 H), 5.09−5.13 (m, 2 H), 5.33−5.37 (m, 1 H), 5.45 (s, 1 H), 6.68 (d, J = 8.4 Hz, 1 H), 7.19 (t, J = 7.5 Hz, 1 H), 7.29 (d, J = 5.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.83, 20.86, 20.91, 21.04, 28.89, 61.84, 63.35, 65.36, 66.34, 67.70, 68.17, 68.24, 96.36, 109.90, 113.62, 127.58, 139.73, 152.84, 169.87, 170.10, 170.26, 170.36; ESI-HRMS *m*/*z* calcd for $C_{22}H_{28}INNaO_{11}$ ($M + Na^+$): 632.0604; found: 632.0604.

2-Iodo-6-[3-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)propoxy]pyridine (13(β-Gal-3)). A colorless oil (1.4 g, 74%) from **12(β-Gal-3)** (1.5 g, 3.1 mmol); IR (Nujol) 2973, 1747, 1581, 1550, 1439, 1375, 1220 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.98−2.16 (m, 14 H), 3.66−3.70 (m, 1 H), 3.91−3.94 (m, 1 H), 3.96−4.19 (m, 3 H), 4.30 (t, J = 6.3 Hz, 2 H), 4.51 (d, J = 8.1 Hz, 1 H), 4.99−5.05 (m, 1 H), 5.18−5.24 (m, 1 H), 5.39 (d, J = 3.0 Hz, 1 H), 6.68 (d, J = 8.1 Hz, 1 H), 7.20 (t, J = 8.1 Hz, 1 H), 7.30 (d,

J = 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.80, 20.89, 29.06, 61.37, 63.40, 66.84, 67.15, 68.91, 70.71, 70.99, 101.44, 109.85, 113.67, 127.57, 139.68, 162.93, 169.44, 170.07, 170.18, 170.30; ESI-HRMS m/z calcd for $C_{22}H_{28}INNaO_{11}$ ($M + Na^+$): 632.0604; found: 632.0608.

2-Iodo-6-[3-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)propoxy]pyridine (13(α-Man-3)). A colorless oil (3.6 g, 82%) from **12(α-Man-3)** (3.3 g, 7.1 mmol); IR (Nujol) 2973, 1748, 1581, 1550, 1437, 1375, 1226 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.00−2.18 (m, 14 H), 3.62−3.67 (m, 1 H), 3.84−3.89 (m, 1 H), 3.91−4.00 (m, 1 H), 4.03−4.08 (m, 1 H), 4.23−4.28 (m, 1 H), 4.33−4.44 (m, 2 H), 4.84 (s, 1 H), 5.24−5.32 (m, 3 H), 6.69 (d, J = 8.1 Hz, 1 H), 7.20 (t, J = 8.1 Hz, 1 H), 7.30 (d, J = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.73, 20.80, 20.94, 28.77, 62.35, 63.32, 65.02, 66.05, 68.41, 69.04, 69.40, 69.51, 97.49, 109.74, 113.49, 127.45, 139.64, 162.66, 169.44, 169.55, 169.73, 170.30; ESI-HRMS m/z calcd for $C_{22}H_{28}INNaO_{11}$ ($M + Na^+$): 632.0604; found: 632.0605.

2-Iodo-6-[6-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)hexyloxy]pyridine (13(β-Glc-6)). A colorless oil (2.0 g, 85%) from **12(β-Glc-6)** (1.8 g, 3.6 mmol); IR (Nujol) 3022, 1755, 1582, 1549, 1436, 1368, 1224 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.41−1.46 (m, 4 H), 1.57−1.60 (m, 2 H), 1.62−1.78 (m, 2 H), 2.01−2.12 (m, 12 H), 3.46−3.52 (m, 1 H), 3.69−3.73 (m, 1 H), 3.86−3.92 (m, 1 H), 4.11−4.16 (m, 1 H), 4.22−4.30 (m, 3 H), 4.51 (d, J = 8.1 Hz, 1 H), 4.95−5.01 (m, 1 H), 5.05−5.08 (m, 1 H), 5.21 (t, J = 9.3 Hz, 1 H), 6.67 (d, J = 7.8 Hz, 1 H), 7,18 (t, J = 7.5 Hz, 1 H), 7.28 (d, J = 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.70, 20.76, 20.83, 25.60, 25.75, 25.84, 28.81, 29.36, 61.96, 66.57, 68.45, 69.97, 71.31, 71.70, 72.81, 100.69, 109.77, 113.59, 127.19, 139.52, 163.01, 169.00, 169.15, 170.00, 170.38; ESI-HRMS m/z calcd for $C_{25}H_{35}INO_{11}$ ($M + H^+$): 652.1254; found: 652.1254.

2-Iodo-6-[12-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)dodecyloxy]pyridine (13(β-Glc-12)). A colorless oil (1.7 g, 90%) from **12(β-Glc-12)**; IR (Nujol) 3078, 1758, 1579, 1550, 1457, 1375, 1220 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.27 (br s, 16 H), 1.56 (br s, 2 H), 1.71−1.76 (m, 2 H), 1.99−2.09 (m, 12 H), 3.40−3.49 (m, 1 H), 3.67−3.73 (m, 1 H), 3.85−3.88 (m, 1 H), 4.10−4.15 (m, 1 H), 4.23−4.30 (m, 3 H), 4.50 (d, J = 7.8 Hz, 1 H), 4.95−4.99 (m, 1 H), 5.01−5.12 (m, 1 H), 5.17−5.24 (m, 1 H), 6.66 (d, J = 8.1 Hz, 1 H), 7.17 (t, J = 7.5 Hz, 1 H), 7.27 (d, J = 6.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.75, 20.78, 20.88, 25.91, 26.10, 28.93, 29.40, 29.44, 29.49, 29.66, 62.04, 66.86, 68.51, 70.24, 71.37, 71.75, 72.89, 100.77, 109.82, 113.67, 127.16, 139.51, 163.16, 169.05, 169.21, 170.09, 170.44; ESI-HRMS m/z calcd for $C_{31}H_{46}INNaO_{11}$ ($M + Na^+$): 758.2013; found: 758.2013.

2-[3-(α-D-Glucopyranosyl)propoxy]-6-iodopyridine (14(α-Glc-3)). Typical procedure of

hydrolysis of acetyl groups. To a mixed solution of MeOH (20 mL), Et_3N (4.0 mL), and water (4.0 mL) was added **13(α-Glc-3)** (0.83 g, 1.4 mmol) at room temperature. The mixture was stirred for 5 h at room temperature and evaporated. The residue was subjected to silica gel column chromatography (eluent; CH_2Cl_2/MeOH = 30 : 1) to afford **14(α-Glc-3)** (0.42 g, 70%) as a colorless solid. Mp 57−59 °C; IR (Nujol) 3419 (br), 2951, 1715, 1579, 1549, 1460, 1376, 1217 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.05 (t, J = 5.7 Hz, 2 H), 2.52 (br s, 1 H), 3.58 (br s, 4 H), 3.74−3.85 (m, 4 H), 4.02 (br s, 1 H), 4.33−4.37 (m, 2 H), 4.79 (br s, 1 H), 4.87 (d, J = 3.3 Hz, 1 H), 5.04 (br s, 1 H), 6.66 (d, J = 8.4 Hz, 1 H), 7.16 (t, J = 7.5 Hz, 1 H), 7.26 (d, J = 6.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.13, 61.31, 63.92, 65.26, 69.56, 71.84, 72.07, 74.25, 98.81, 109.99, 113.81, 127.71, 139.96, 162.92; ESI-HRMS m/z calcd for $C_{14}H_{20}INNaO_7$ ($M + Na^+$): 464.0182; found: 464.0184.

2-[3-(β-D-Glucopyranosyl)propoxy]-6-iodopyridine (14(β-Glc-3)). A colorless solid (1.0 g, 99%) from **13(β-Glc-3)** (1.5 g, 2.4 mmol); Mp 45−47 °C; IR (Nujol) 3420 (br), 2951, 1715, 1576, 1548, 1460, 1376, 1300 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.05 (t, J = 8.4 Hz, 2 H), 3.30−3.42 (m, 2 H), 3.54−3.72 (m, 3 H), 3.85 (br s, 3 H), 3.98−4.01 (m, 1 H), 4.29−4.36 (m, 3 H), 4.80 (br s, 1 H), 5.11 (br s, 1 H), 5.42 (br s, 1 H), 6.66 (d, J = 7.8 Hz, 1 H), 7.15 (t, J = 7.5 Hz, 1 H), 7.25 (d, J = 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.41, 61.50, 63.98, 67.31, 69.48, 73.54, 75.76, 76.55, 103.02, 110.03, 113.83, 127.70, 139.93, 162.98; ESI-HRMS m/z calcd for $C_{14}H_{21}INO_7$ ($M + H^+$): 442.0362; found: 442.0362.

2-[3-(α-D-Galactopyranosyl)propoxy]-6-iodopyridine (14(α-Gal-3)). A colorless solid (0.87 g, 81%) from **13(α-Gal-3)** (1.5 g, 2.5 mmol); Mp 55−60 °C; IR (Nujol) 3418 (br), 2956, 1716, 1575, 1550, 1462, 1376, 1225 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.03 (t, J = 6.0 Hz, 2 H), 3.56−3.60 (m, 1 H), 3.78−3.85 (m, 8 H), 4.08 (s, 1 H), 4.30−4.34 (m, 2 H), 4.57 (br s, 1 H), 4.70 (br s, 1 H), 4.93 (s, 1 H), 6.67 (d, J = 7.5 Hz, 1 H), 7.16 (t, J = 7.5 Hz, 1 H), 7.26 (d, J = 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.93, 61.98, 63.67, 64.96, 69.02, 69.83, 70.03, 70.59, 98.70, 109.79, 113.58, 127.54, 139.79, 162.75; ESI-HRMS m/z calcd for $C_{14}H_{20}INNaO_7$ ($M + Na^+$): 464.0182; found: 464.0184.

2-[3-(β-D-Galactopyranosyl)propoxy]-6-iodopyridine (14(β-Gal-3)). A colorless solid (0.54 g, 83%) from **13(β-Gal-3)** (0.90 g, 1.5 mmol); Mp 113−114 °C; IR (Nujol) 3370 (br), 2959, 1715, 1578, 1547, 1457, 1376, 1218 cm^{-1}; ^1H NMR (DMSO-d_6, 300 MHz) δ 1.96 (t, J = 6.3 Hz, 2 H), 3.27−3.34 (m, 3 H), 3.44−3.62 (m, 4 H), 3.83−3.89 (m, 1 H), 4.09 (d, J = 6.9 Hz, 1 H), 4.25−4.34 (m, 3 H), 4.55 (t, J = 5.7 Hz, 1 H), 4.68 (d, J = 4.5 Hz, 1 H), 4.85 (d, J = 4.2 Hz, 1 H), 6.84 (d, J = 6.6 Hz, 1 H), 7.37−7.43 (m, 2 H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ 28.87, 60.32, 63.62, 65.18, 68.06, 70.47, 73.33, 75.09, 103.39,

109.68, 114.13, 127.39, 140.70, 162.51; ESI-HRMS *m*/*z* calcd for $C_{14}H_{20}INNaO_7$ (M + Na^+): 464.0182; found: 464.0184.

2-Iodo-6-[3-(α-D-mannopyranosyl)propoxy]pyridine (14(α-Man-3)). A colorless solid (0.73 g, 90%) from **13(α-Man-3)** (1.1 g, 1.9 mmol); Mp 50−54 °C; IR (Nujol) 3389 (br), 2982, 1716, 1645, 1574, 1556, 1446, 1375, 1259 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.99 (t, *J* = 6.0 Hz, 2 H), 3.49−3.57 (m, 2 H), 3.73−3.85 (m, 4 H), 3.94 (br s, 2 H), 4.27−4.33 (m, 2 H), 4.50 (br s, 1 H), 4.83 (s, 1 H), 4.98−5.06 (br m, 3 H), 6.65 (d, *J* = 8.4 Hz, 1 H), 7.16 (t, *J* = 7.5 Hz, 1 H), 7.27 (d, *J* = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 28.80, 60.85, 63.36, 64.25, 66.00, 70.85, 71.47, 72.15, 99.86, 109.67, 113.47, 127.34, 139.52, 162.61; ESI-HRMS *m*/*z* calcd for $C_{14}H_{20}INNaO_7$ (M + Na^+): 464.0182; found: 464.0184.

2-[6-(β-D-Glucopyranosyl)hexyloxy]-6-iodopyridine (14(β-Glc-6)). A colorless solid (0.92 g, 93%) form **13(β-Glc-6)** (1.3 g, 2.1 mmol); Mp 54−56 °C; IR (Nujol) 3390 (br), 2966, 1582, 1548, 1461, 1376, 1294 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.41 (br s, 4 H), 1.64−1.75 (m, 4 H), 3.29−3.32 (m, 1 H), 3.37−3.42 (m, 1 H), 3.46−3.62 (m, 3 H), 3.78−3.85 (m, 4 H), 4.21 (t, *J* = 6.3 Hz, 2 H), 4.31 (d, *J* = 7.5 Hz, 1 H), 4.63 (br s, 1 H), 5.10 (br s, 1 H), 5.41 (br s, 1 H), 6.65 (d, *J* = 8.4 Hz, 1 H), 7.15 (t, *J* = 7.8 Hz, 1 H), 7.26 (d, *J* = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.09, 26.15, 29.05, 29.73, 61.54, 66.89, 69.46, 70.50, 73.49, 75.71, 76.55, 102.92, 109.95, 113.85, 127.42, 139.73, 163.23; ESI-HRMS *m*/*z* calcd for $C_{17}H_{27}INO_7$ (M + H^+): 484.0832; found: 484.0831.

2-[12-(β-D-Glucopyranosyl)dodecyloxy]-6-iodopyridine (14(β-Glc-12)). A colorless solid (0.43 g, 93%) from **13(β-Glc-12)** (0.60 g, 0.82 mmol); Mp 68−71 °C; IR (Nujol) 3366 (br), 2938, 1716, 1579, 1548, 1464, 1376, 1217 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.21−1.40 (m, 16 H), 1.62 (br s, 2 H), 1.68−1.75 (m, 2 H), 3.29 (d, *J* = 9.0 Hz, 1 H), 3.39 (t, *J* = 6.6 Hz, 1 H), 3.37−3.62 (m, 4 H), 3.84 (br s, 3 H), 4.23 (t, *J* = 6.6 Hz, 2 H), 4.30 (d, *J* = 7.5 Hz, 1 H), 4.49 (br s, 1 H), 4.97 (br s, 1 H), 5.30 (br s, 1 H), 6.65 (d, *J* = 7.8 Hz, 1 H), 7.15 (t, *J* = 7.8 Hz, 1 H), 7.27 (d, *J* = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.18, 26.31, 28.47, 29.08, 29.13, 29.70, 29.76, 29.91, 33.09, 34.31, 61.59, 67.07, 69.48, 70.73, 73.49, 75.68, 76.54, 102.92, 109.98, 113.85, 127.34, 139.64, 163.34; ESI-HRMS *m*/*z* calcd for $C_{23}H_{39}INO_7$ (M + H^+): 568.1771; found: 568.1770.

α-Glucoside-linked dimer with a TBS terminal α-Glc-3-2-TBS. Typical procedure of Sonogashira reaction to prepare dimers Yyy-*m*-2-TBS. To an *i*-Pr_2NH (15 mL) and THF (15 mL) suspension of $Pd[P(t\text{-}Bu)_3]_2$ (22 mg, 0.044 mmol), CuI (8.4 mg, 0.044 mmol), and K_2CO_3 (0.24 g, 1.8 mmol) were

added **14(α-Glc-3)** (0.39 g, 0.88 mmol) and **8** (0.33 g, 1.1 mmol) at room temperature. The mixture was stirred for 3 h at room temperature, and then to the mixture was added 3-aminopropyl-functionalized silica gel (0.30 g). After strring for 1 h, the mixture was diluted with THF and filtered off the insoluble materials. The filtrate was concentrated and subjected to silica gel column chromatography (eluent; CH_2Cl_2/MeOH = 50 : 1) to afford **α-Glc-3-2-TBS** (0.44 g, 81%) as a brown solid. Mp 76−78 °C; IR (Nujol) 3366 (br), 3070, 2952, 1715, 1644, 1578, 1550, 1461, 1376, 1311, 1250 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.19 (s, 6 H), 0.99 (s, 9 H), 2.04 (br m, 2 H), 2.53 (q, J = 6.3 Hz, 2 H), 3.59 (br s, 4 H), 3.78−3.81 (br m, 5 H), 4.06 (t, J = 6.3 Hz, 2 H), 4.18 (br s, 1 H), 4.38 (br s, 2 H), 4.82 (br s, 1 H), 4.93 (br s, 1 H), 5.09−5.18 (m, 2 H), 5.26 (br s, 1 H), 5.79−5.88 (m, 1 H), 6.71 (d, J = 8.4 Hz, 1 H), 6.94 (d, J = 2.1 Hz, 1 H), 7.07 (d, J = 2.4 Hz, 1 H), 7.15 (d, J = 7.2 Hz, 1 H), 7.52 (t, J = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.52, 16.88, 26.35, 29.16, 33.29, 61.57, 63.24, 65.14, 67.73, 69.92, 71.73, 72.12, 74.29, 87.04, 88.17, 93.72, 98.77, 103.86, 112.11, 113.80, 114.35, 117.76, 121.58, 133.50, 138.78, 139.12, 143.94, 144.38, 163.34, 164.96; ESI-HRMS m/z calcd for $C_{33}H_{45}N_2O_8Si$ ($M + H^+$): 625.2945; found: 625.2949.

β-Glc-3-2-TBS. A brown solid (0.68 g, 90%) from **14(β-Glc-3)** (0.54 g, 1.2 mmol); Mp 76−78 °C; IR (Nujol) 3375 (br), 3076, 2953, 1715, 1644, 1575, 1550, 1461, 1250 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.18 (s, 6 H), 0.98 (s, 9 H), 2.05 (br s, 2 H), 2.53 (q, J = 6.6 Hz, 2 H), 3.29−3.32 (m, 1 H), 3.43−3.46 (m, 1 H), 3.53−3.84 (m, 7 H), 3.97−4.00 (m, 1 H), 4.05 (t, J = 6.6 Hz, 2 H), 4.32−4.39 (m, 3 H), 4.56 (br s, 1 H), 4.84 (d, J = 10.5 Hz, 1 H), 5.09−5.18 (m, 2 H), 5.79−5.88 (m, 1 H), 6.71 (d, J = 8.1 Hz, 1 H), 6.94 (d, J = 2.7 Hz, 1 H), 7.06 (d, J = 2.1 Hz, 1 H), 7.15 (d, J = 7.2 Hz, 1 H), 7.51 (t, J = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.46, 0.31, 16.96, 19.44, 26.41, 29.49, 29.81, 33.35, 61.83, 63.35, 67.28, 67.78, 69.77, 73.59, 75.63, 76.57, 87.10, 88.20, 93.78, 103.07, 103.89, 112.16, 113.88, 114.41, 117.84, 121.63, 114.77, 133.57, 138.79, 139.18, 144.00, 144.46, 163.45, 165.00; ESI-HRMS m/z calcd for $C_{33}H_{45}N_2O_8Si$ ($M + H^+$): 625.2945; found: 625.2947.

α-Gal-3-2-TBS. A brown solid (1.1 g, 93%) from **14(α-Gal-3)** (0.85 g, 1.9 mmol); Mp 78−81 °C; IR (Nujol) 3392 (br), 3077, 2952, 1716, 1645, 1576, 1542, 1457, 1376, 1250 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.20 (s, 6 H), 1.00 (s, 9 H), 2.05 (br s, 2 H), 2.53−2.60 (m, 2 H), 2.72−2.81 (br m, 2 H), 3.19 (br s, 1 H), 3.57−3.64 (m, 1 H), 3.73−3.98 (m, 7 H), 4.07−4.11 (m, 2 H), 4.20 (br s, 1 H), 4.45−4.51 (m, 1 H), 4.63−4.68 (m, 1 H), 5.00 (d, J = 3.6 Hz, 1 H), 5.12−5.22 (m, 2 H), 5.81−5.90 (m, 1 H), 6.74 (d, J = 8.4 Hz, 1 H), 6.96 (d, J = 2.1 Hz, 1 H), 7.07 (d, J = 2.4 Hz, 1 H), 7.17 (d, J = 7.2 Hz, 1 H), 7.56 (t, J = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.47, 16.98, 26.35, 26.39, 29.36, 33.37, 62.43, 63.56, 64.47, 67.86, 69.68, 70.69, 71.15, 86.86, 88.36, 94.51, 98.78, 103.51, 112.44, 114.06, 114.30, 117.94,

121.43, 133.47, 138.91, 139.04, 143.73, 144.47, 163.55, 165.22; ESI-HRMS *m*/*z* calcd for $C_{33}H_{45}N_2O_8Si$ (M + H^+): 625.2945; found: 625.2946.

β-Gal-3-2-TBS. A brown solid (0.22 g, 48%) from **14(β-Gal-3)** (0.32 g, 0.73 mmol); Mp 75−77 °C; IR (Nujol) 3366 (br), 3073, 2974, 1715, 1643, 1577, 1549, 1455, 1376, 1236 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.19 (s, 6 H), 0.99 (s, 9 H), 2.06 (t, *J* = 6.6 Hz, 2 H), 2.53 (q, *J* = 6.6 Hz, 2 H), 3.52 (br s, 1 H), 3.58−3.73 (br m, 3 H), 3.83 (br s, 2 H), 3.99−4.08 (m, 5 H), 4.26 (d, *J* = 6.9 Hz, 1 H), 4.37 (br s, 2 H), 4.48 (br s, 2 H), 4.83 (br s, 1 H), 5.09−5.18 (m, 2 H), 5.79−5.88 (m, 1 H), 6.72 (d, *J* = 8.4 Hz, 1 H), 6.94 (d, *J* = 2.1 Hz, 1 H), 7.07 (d, *J* = 2.4 Hz, 1 H), 7.15 (d, *J* = 7.2 Hz, 1 H), 7.52 (t, *J* = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.44, 0.31, 16.96, 26.45, 29.50, 29.95, 33.37, 61.73, 63.46, 67.20, 67.81, 69.22, 71.54, 73.75, 74.48, 87.18, 88.23, 93.91, 103.57, 103.89, 109.98, 112.24, 113.91, 114.45, 117.84, 121.61, 133.57, 133.84, 139.17, 143.97, 144.47, 163.53, 165.07; ESI-HRMS *m*/*z* calcd for $C_{33}H_{45}N_2O_8Si$ (M + H^+): 625.2945; found: 625.2945.

α-Man-3-2-TBS. A brown solid (1.2 g, 82%) from **14(α-Man-3)** (1.0 g, 2.3 mmol); Mp 73−76 °C; IR (Nujol) 3383 (br), 3076, 2952, 1716, 1652, 1577, 1549, 1459, 1376, 1250 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.19 (s, 6 H), 0.99 (s, 9 H), 2.00 (t, *J* = 6.0 Hz, 2 H), 2.54 (q, *J* = 6.6 Hz, 2 H), 3.52 (d, *J* = 9.3 Hz, 2 H), 3.73−3.95 (m, 6 H), 4.07 (t, *J* = 6.6 Hz, 2 H), 4.31−4.45 (m, 3 H), 4.79 (br s, 2 H), 4.84 (s, 1 H), 5.09 (br s, 1 H), 5.10−5.19 (m, 2 H), 5.79−5.89 (m, 1 H), 6.70 (d, *J* = 8.4 Hz, 1 H), 6.95 (d, *J* = 2.1 Hz, 1 H), 7.06 (d, *J* = 2.4 Hz, 1 H), 7.17 (d, *J* = 7.5 Hz, 1 H), 7.53 (t, *J* = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.46, 16.95, 26.41, 29.27, 33.35, 61.39, 62.91, 64.40, 66.76, 67.78, 71.08, 71.84, 72.33, 86.91, 88.31, 93.86, 100.19, 103.88, 112.11, 113.86, 114.41, 117.84, 121.56, 133.52, 138.73, 139.21, 144.02, 144.46, 163.47, 165.04; ESI-HRMS *m*/*z* calcd for $C_{33}H_{45}N_2O_8Si$ (M + H^+): 625.2945; found: 625.2945.

β-Glc-6-2-TBS. A brown solid (0.41 g, 75%) from **14(β-Glc-6)** (0.39 g, 0.81 mmol); Mp 69−72 °C; IR (Nujol) 3392 (br), 3068, 2951, 1716, 1644, 1578, 1549, 1460, 1376, 1250 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.20 (s, 6 H), 1.00 (s, 9 H), 1.49 (br s, 4 H), 1.62−1.67 (m, 2 H), 1.77−1.82 (m, 2 H), 2.22−2.29 (m, 1 H), 2.53−2.59 (m, 2 H), 2.88 (br s,1 H), 2.98 (br s, 1 H), 3.37−3.41 (m, 2 H), 3.50−3.59 (m, 4 H), 3.80−3.95 (m, 3 H), 4.08 (t, *J* = 6.6 Hz, 2 H), 4.30−4.36 (m, 3 H), 5.12−5.21 (m, 2 H), 5.81−5.91 (m, 1 H), 6.73 (d, *J* = 8.4 Hz, 1 H), 6.96 (d, *J* = 2.7 Hz, 1 H), 7.08 (d, *J* = 2.7 Hz, 1 H), 7.17 (d, *J* = 6.9 Hz, 1 H), 7.54 (t, *J* = 6.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.46, 16.93, 25.91, 26.17, 26.39, 29.15, 29.68, 33.34, 61.67, 66.37, 67.72, 69.63, 70.47, 73.53, 75.65, 76.58, 86.95, 88.27, 93.60, 102.92, 103.98, 112.03, 113.78, 114.31, 117.81, 121.42, 133.52, 138.57, 139.28, 144.12, 144.49, 163.69, 164.92; ESI-

HRMS *m*/*z* calcd for $C_{36}H_{51}N_2O_8Si$ (M + H^+): 667.3414; found: 667.3413.

β-Glc-12-2-TBS. A brown foam (0.38 g, 94%) from **14(β-Glc-12)** (0.31 g, 0.54 mmol); IR (Nujol) 3390 (br), 3077, 2983, 1716, 1644, 1582, 1557, 1442, 1372, 1236 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.20 (s, 6 H), 1.00 (s, 9 H), 1.28 (br s, 16 H), 1.62 (t, *J* = 7.8 Hz, 2 H), 1.75 (t, *J* = 7.2 Hz, 2 H), 2.55 (q, *J* = 6.3 Hz, 2 H), 3.28−3.34 (br m, 1 H), 3.36−3.41 (m, 1 H), 3.51−3.68 (br m, 4 H), 3.84 (br s, 3 H), 4.07 (t, *J* = 6.6 Hz, 2 H), 4.27−4.32 (m, 3 H), 4.54 (br s, 1 H), 5.07 (br s, 1 H), 5.11−5.20 (m, 2 H), 5.38 (br s, 1 H), 5.81−5.90 (m, 1 H), 6.71 (d, *J* = 8.1 Hz, 1 H), 6.96 (d, *J* = 2.1 Hz, 1 H), 7.07 (d, *J* = 2.1 Hz, 1 H), 7.17 (d, *J* = 7.2 Hz, 1 H), 7.52 (t, *J* = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.52, 16.87, 26.10, 26.35, 28.97, 29.23, 29.73, 29.79, 29.87, 29.92, 33.29, 33.71, 66.46, 67.64, 69.46, 70.58, 73.38, 75.58, 86.86, 88.23, 93.46, 102.83, 103.96, 111.97, 113.68, 114.22, 117.74, 121.26, 133.44, 138.39, 139.26, 144.13, 144.47, 163.71, 164.83; ESI-HRMS *m*/*z* calcd for $C_{42}H_{63}N_2O_8Si$ (M + H^+): 751.4353; found: 751.4353.

α-Glucoside-linked desilylated dimer α-Glc-3-2-H. Typical procedure of desilylation to prepare YYY-*m*-2-H. To a THF (30 mL) solution of **α-Glc-3-2-TBS** (0.42 g, 0.67 mmol) were added *n*-Bu_4NF (1.0 M THF solution, 1.0 mL, 1.0 mmol) and a few drops of water at room temperature. The mixture was stirred for 30 min and concentrated. The residue was purified by silica gel column chromatography (eluent; CH_2Cl_2/MeOH = 50 : 1) to afford **α-Glc-3-2-H** (0.24 g, 70%) as a brown solid. Mp 66−68 °C; IR (Nujol) 3366 (br), 3073, 2965, 1715, 1643, 1581, 1551, 1456, 1376, 1235 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.02 (br s, 2 H), 2.52 (q, *J* = 6.3 Hz, 2 H), 3.28 (s, 1 H), 3.57 (br s, 4 H), 3.73−3.82 (m, 4 H), 3.97−4.05 (m, 3 H), 4.35 (br s, 2 H), 4.59 (br s, 1 H), 4.85 (br s, 1 H), 5.08−5.16 (m, 2 H), 5.46 (br s, 2 H), 5.75−5.88 (m, 1 H), 6.70 (d, *J* = 8.4 Hz, 1 H), 6.93 (d, *J* = 2.4 Hz, 1 H), 7.07 (d, *J* = 2.1 Hz, 1 H), 7.13 (d, *J* = 6.9 Hz, 1 H), 7.51 (t, *J* = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.11, 33.21, 61.36, 63.41, 67.80, 69.80, 71.84, 72.04, 74.08, 78.19, 82.08, 86.73, 88.36, 98.80, 112.26, 114.01, 114.20, 117.78, 121.47, 133.42, 138.78, 138.89, 143.45, 143.87, 163.40, 165.09; ESI-HRMS *m*/*z* calcd for $C_{27}H_{31}N_2O_8$ (M + H^+): 511.2080; found: 511.2083.

β-Glc-3-2-H. A brown solid (0.36 g, 91%) from **β-Glc-3-2-TBS** (0.48 g, 0.77 mmol); Mp 63−66 °C; IR (Nujol) 3291 (br), 3075, 2957, 1716, 1642, 1579, 1550, 1456, 1376, 1234 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.03 (br s, 2 H), 2.53 (q, *J* = 6.6 Hz, 2 H), 3.23 (s, 1 H), 3.30−3.33 (m, 1 H), 3.44−3.47 (m, 1 H), 3.59−3.71 (m, 4 H), 3.85 (br s, 2 H), 3.95−4.06 (m, 3 H), 4.32−4.38 (m, 3 H), 4.70 (br s, 1 H), 4.86−4.93 (br m, 1 H), 5.09−5.18 (m, 2 H), 5.32 (br s, 1 H), 5.76−5.89 (m, 1 H), 6,71 (d, *J* = 8.4 Hz, 1 H), 6.95 (d, *J* = 2.1 Hz, 1 H), 7.08 (d, *J* = 2.1 Hz, 1 H), 7.14 (d, *J* = 7.2 Hz, 1 H), 7.51 (t, *J* = 7.5 Hz, 1

H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.52, 33.29, 61.89, 63.58, 67.15, 67.86, 70.03, 73.61, 75.73, 78.07, 82.21, 86.81, 88.44, 103.09, 112.31, 114.12, 114.28, 117.86, 121.53, 133.47, 138.75, 139.04, 143.58, 144.04, 163.53, 165.15; ESI-HRMS *m*/*z* calcd for $C_{27}H_{31}N_2O_8$ ($M + H^+$): 511.2080; found: 511.2080.

α-Gal-3-2-H. A brown solid (0.77 g, 86%) from **α-Gal-3-2-TBS** (1.1 g, 1.8 mmol); Mp 63−64 °C; IR (Nujol) 3365 (br), 3072, 2952, 1716, 1644, 1577, 1550, 1456, 1376, 1234 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.02 (t, *J* = 5.7 Hz, 2 H), 2.54 (q, *J* = 6.6 Hz, 2 H), 3.25 (s, 1 H), 3.56−3.91 (m, 10 H), 4.06 (t, *J* = 6.6 Hz, 2 H), 4.20 (br s, 1 H), 4.37−4.46 (m, 2 H), 4.70 (br s, 1 H), 4.94 (s, 1 H), 5.09−5.19 (m, 2 H), 5.79−5.88 (m, 1 H), 6.72 (d, *J* = 8.4 Hz, 1 H), 6.96 (d, *J* = 1.8 Hz, 1 H), 7.08 (d, *J* = 1.5 Hz, 1 H), 7.15 (d, *J* = 7.2 Hz, 1 H), 7.53 (t, *J* = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.26, 33.25, 62.52, 63.09, 64.84, 67.86, 69.27, 69.95, 70.52, 70.66, 78.19, 82.04, 86.65, 88.44, 98.96, 112.34, 114.14, 114.28, 117.87, 121.47, 133.39, 138.81, 138.92, 143.55, 143.89, 163.48, 165.20; ESI-HRMS *m*/*z* calcd for $C_{27}H_{31}N_2O_8$ ($M + H^+$): 511.2080; found: 511.2080.

β-Gal-3-2-H. A brown solid (0.22 g, 83%) from **β-Gal-3-2-TBS** (0.32 g, 0.52 mmol); Mp 66−69 °C; IR (Nujol) 3375 (br), 3074, 2954, 1716, 1644, 1579, 1551, 1450, 1376, 1235 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.04 (br s, 2 H), 2.52 (q, *J* = 6.3 Hz, 2 H), 3.27 (s, 1 H), 3.53 (br s, 1 H), 3.64−3.70 (m, 3 H), 3.82 (br s, 2 H), 3.99−4.06 (m, 4 H), 4.25 (d, *J* = 5.7 Hz, 2 H), 4.35 (br s, 2 H), 4.59 (br s, 1 H), 4.72 (br s, 1 H), 5.02 (br s, 1 H), 5.08−5.17 (m, 2 H), 5.75−5.86 (m, 1 H), 6.70 (d, *J* = 8.1 Hz, 1 H), 6.95 (d, *J* = 2.1 Hz, 1 H), 7.07 (d, *J* = 2.4 Hz, 1 H), 7.12 (d, *J* = 7.2 Hz, 1 H), 7.50 (t, *J* = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.44, 33.25, 61.28, 63.62, 67.05, 67.83, 68.96, 71.36, 73.74, 74.55, 78.19, 82.13, 86.73, 88.41, 103.55, 112.29, 114.06, 114.27, 117.81, 121.48, 133.45, 138.75, 138.94, 143.53, 143.97, 163.52, 165.13; ESI-HRMS *m*/*z* calcd for $C_{27}H_{31}N_2O_8$ ($M + H^+$): 511.2080; found: 511.2080.

α-Man-3-2-H. A brown solid (0.094 g, 96%) from **α-Man-3-2-TBS** (0.12 g, 0.19 mmol); Mp 62−64 °C; IR (Nujol) 3361 (br), 3072, 2951, 1716, 1642, 1578, 1551, 1457, 1376, 1235 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.98 (t, *J* = 5.7 Hz, 2 H), 2.54 (q, *J* = 6.6 Hz, 2 H), 3.22 (s, 1 H), 3.49−3.52 (m, 2 H), 3.72−3.95 (m, 7 H), 4.05 (t, *J* = 6.6 Hz, 2 H), 4.29−4.45 (m, 3 H), 4.83 (s, 1 H), 4.93 (br s, 1 H), 5.09−5.19 (m, 2 H), 5.25 (br s, 1 H), 5.79−5.88 (m, 1 H), 6.71 (d, *J* = 8.1 Hz, 1 H), 6.96 (d, *J* = 2.7 Hz, 1 H), 7.09 (d, *J* = 2.1 Hz, 1 H), 7.16 (d, *J* = 7.2 Hz, 1 H), 7.53 (t, *J* = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.34, 33.32, 61.49, 62.96, 64.25, 66.92, 67.91, 71.02, 71.84, 72.38, 78.07, 82.20, 86.57, 88.56, 100.27, 112.28, 114.15, 114.31, 117.92, 121.53, 133.44, 138.76, 139.09, 143.57, 144.08, 163.55, 165.25; ESI-HRMS *m*/*z* calcd for $C_{27}H_{31}N_2O_8$ ($M + H^+$): 511.2080; found: 511.2078.

β-Glc-6-2-H. A brown solid (0.26 g, 99%) from **β-Glc-6-2-TBS** (0.30 g, 0.46 mmol); Mp 68−70 °C; IR (Nujol) 3411 (br), 3070, 2965, 1715, 1644, 1577, 1551, 1459, 1376, 1235 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.41 (br s, 4 H), 1.63 (br s, 2 H), 1.74 (br s, 2 H), 2.53 (q, J = 6.3 Hz, 2 H), 3.22 (s, 1 H), 3.31−3.40 (br m, 1 H), 3.42 (br s, 1 H), 3.53−3.62 (br m, 4 H), 3.86 (br s, 4 H), 4.05 (t, J = 6.3 Hz, 2 H), 4.24−4.29 (m, J = 6.0 Hz, 3 H), 4.63 (br s, 1 H), 5.09−5.18 (m, 2 H), 5.41 (br s, 1 H), 5.76−5.88 (m, 1 H), 6.72 (d, J = 8.4 Hz, 1 H), 6.97 (d, J = 2.4 Hz, 1 H), 7.10 (d, J = 2.1 Hz, 1 H), 7.16 (d, J = 7.2 Hz, 1 H), 7.53 (t, J = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.86, 26.10, 29.08, 29.68, 33.27, 61.67, 66.37, 67.80, 69.69, 70.37, 73.48, 75.63, 77.81, 82.26, 86.68, 88.41, 102.89, 112.15, 114.06, 114.17, 117.86, 121.40, 133.42, 138.60, 139.13, 143.60, 144.13, 163.69, 165.07; ESI-HRMS m/z calcd for $C_{30}H_{37}N_2O_8$ ($M + H^+$): 553.2549; found: 553.2547.

β-Glc-12-2-H. A brown foam (0.26 g, 99%) from **β-Glc-12-2-TBS** (0.31 g, 0.41 mmol); IR (Nujol) 3391 (br), 1717, 1644, 1579, 1558, 1457, 1376, 1226 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.27 (br s, 16 H), 1.61 (br s, 2 H), 1.70−1.80 (m, 2 H), 2.55 (q, J = 6.6 Hz, 2 H), 3.18 (s, 1 H), 3.29−3.32 (m, 1 H), 3.36−3.41 (m, 1 H), 3.46−3.65 (m, 4 H), 3.85 (br m, 4 H), 4.07 (t, J = 6.6 Hz, 2 H), 4.23−4.32 (m, 2 H), 4.60 (br s, 1 H), 5.11−5.19 (m, 3 H), 5.40 (br s, 1 H), 5.80−5.89 (m, 1 H), 6.72 (d, J = 8.1 Hz, 1 H), 6.97 (d, J = 2.4 Hz, 1 H), 7.10 (d, J = 2.1 Hz, 1 H), 7.18 (d, J = 7.2 Hz, 1 H), 7.53 (t, J = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 26.09, 26.31, 29.19, 29.66, 29.76, 29.89, 33.24, 50.66, 61.52, 66.46, 67.73, 69.48, 70.58, 73.36, 75.60, 76.47, 82.28, 86.61, 88.38, 102.83, 112.07, 113.96, 114.10, 117.79, 121.30, 133.36, 138.44, 139.15, 143.60, 144.20, 163.73, 164.99; ESI-HRMS m/z calcd for $C_{36}H_{49}N_2O_8$ ($M + H^+$): 637.3488; found: 637.3487.

β-Glc-3-3-TBS. To an i-Pr_2NH (10 mL) and THF (10 mL) suspension of $Pd[P(t\text{-}Bu)_3]_2$ (3.5 mg, 0.0068 mmol), CuI (1.3 mg, 0.0068 mmol), and K_2CO_3 (38 mg, 0.27 mmol) were added **β-Glc-3-2-H** (89 mg, 0.14 mmol) and **4** (0.10 g, 0.25 mmol) at room temperature. The mixture was stirred for 2 h at room temperature, and then to the mixture was added 3-aminopropyl-functionalized silica gel (0.10 g). After stirring for 1 h, the mixture was diluted with THF and filtered off the insoluble materials. The filtrate was concentrated and subjected to silica gel column chromatography (eluent; CH_2Cl_2/MeOH = 50 : 1) to afford **β-Glc-3-3-TBS**

α-Gal-3-6-TBS. A brown solid (0.27 g, 64%) from **α-Gal-3-2-H** (0.16 g, 0.33 mmol); Mp 106−108 °C; IR (Nujol) 3366 (br), 3073, 2971, 1715, 1643, 1576, 1540, 1462, 1376, 1250 cm^{-1}; ^1H NMR ($CDCl_3/CD_3OD$ = 1:1, 500 MHz) δ 0.23 (s, 6 H), 1.03 (s, 9 H), 2.12−2.16 (m, 2 H), 2.57−2.64 (m, 10 H), 3.62−3.84 (m, 6 H), 3.93−3.97 (m, 2 H), 4.15−4.21 (m, 10 H), 4.47 (t, *J* = 6.3 Hz, 2 H), 4.91 (d, *J* = 3.0 Hz, 1 H), 5.14−5.24 (m, 10 H), 5.87−5.95 (m, 5 H), 6.83 (d, *J* = 8.5 Hz, 1 H), 7.05 (d, *J* = 2.5 Hz, 1 H), 7.23−7.32 (m, 10 H), 7.66 (t, *J* = 8.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.52, 0.25, 16.89, 19.36, 26.35, 29.31, 33.22, 62.93, 64.55, 67.77, 68.01, 69.40, 69.97, 70.56, 71.00, 86.57, 87.18, 87.38, 87.57, 87.73, 88.67, 93.72, 99.07, 103.85, 112.40, 113.88, 114.22, 114.77, 117.84, 121.30, 133.33, 133.42, 138.81, 143.52, 143.66, 144.47, 163.47, 164.96, 165.10, 165.13, 165.20; ESI-HRMS *m*/*z* calcd for $C_{77}H_{81}N_6O_{12}Si$ ($M + H^+$): 1309.5681; found: 1309.5679.

β-Gal-3-6-TBS. A brown solid (0.32 g, 56%) from **β-Gal-3-2-H** (0.22 g, 0.43 mmol); Mp 112−114 °C; IR (Nujol) 3366 (br), 3071, 2978, 1716, 1642, 1577, 1541, 1455, 1376, 1250 cm^{-1}; ^1H NMR ($CDCl_3/CD_3OD$ = 1:1, 500 MHz) δ 0.22 (s, 6 H), 1.02 (s, 9 H), 2.11−2.16 (m, 2 H), 2.57−2.63 (m, 10 H), 3.50−3.60 (m, 3 H), 3.76−3.83 (m, 3 H), 3.90 (d, *J* = 3.8 Hz, 1 H), 4.08−4.20 (m, 11 H), 4.28 (d, *J* = 7.0 Hz, 1 H), 4.45−4.49 (m, 2 H), 5.14−5.24 (m, 10 H), 5.87−5.94 (m, 5 H), 6.80 (d, *J* = 8.0 Hz, 1 H), 7.04 (d, *J* = 2.0 Hz, 1 H), 7.21−7.29 (m, 10 H), 7.64 (t, *J* = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.52, 16.88, 26.35, 29.47, 33.17, 62.10, 63.64, 66.86, 67.73, 67.93, 69.45, 71.60, 73.69, 74.58, 86.75, 87.21, 87.38, 87.55, 88.52, 93.67, 103.46, 103.86, 112.29, 113.84, 114.28, 114.61, 114.74, 117.78, 117.83, 121.47, 133.31, 133.36, 133.41, 138.66, 138.97, 143.71, 143.76, 143.91, 144.02, 144.51, 163.50, 164.94, 165.10; ESI-HRMS *m*/*z* calcd for $C_{77}H_{81}N_6O_{12}Si$ ($M + H^+$): 1309.5681; found: 1309.5679.

α-Man-3-6-TBS. A brown solid (0.50 g, 74%) from **α-Man-3-2-H** (0.26 g, 0.51 mmol); Mp 106−108 °C; IR (Nujol) 3375 (br), 3068, 2971, 1715, 1642, 1582, 1545, 1462, 1376, 1221 cm^{-1}; ^1H NMR ($CDCl_3/CD_3OD$ = 2:1, 500 MHz) δ 0.21 (s, 6 H), 1.01 (s, 9 H), 2.05 (br m, 2 H), 2.55−2.62 (m, 10 H), 3.52−3.58 (m, 4 H), 3.74−3.78 (m, 2 H), 3.94 (d, *J* = 2.0 Hz, 1 H), 4.10−4.15 (m, 11 H), 4.35−4.40 (m, 1 H), 4.53−4.57 (m, 1 H), 4.83 (s, 1 H), 5.14−5.23 (m, 10 H), 5.85−5.93 (m, 5 H), 6.76−6.78 (d, *J* = 8.5 Hz, 1 H), 7.01 (d, *J* = 2.5 Hz, 1 H), 7.16−7.24 (m, 10 H), 7.61 (t, *J* = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3/CD_3OD$ = 3:1, 75 MHz) δ −5.01, 16.54, 25.91, 28.98, 29.57, 32.93, 61.12, 62.75, 64.08, 66.81, 67.68, 67.85, 70.53, 71.18, 72.22, 85.98, 86.84, 86.95, 87.07, 88.38, 94.01, 99.77, 100.59, 103.20, 112.00, 113.93, 114.43, 114.70, 117.47, 121.32, 133.10, 133.15, 138.60, 143.00, 143.13, 143.21, 143.39, 143.62, 144.05, 163.26, 165.05, 165.25; ESI-HRMS *m*/*z* calcd for $C_{77}H_{81}N_6O_{12}Si$ ($M + H^+$):

1309.5681; found: 1309.5688.

β-Glc-6-6-TBS. A brown solid (0.26 g, 62%) from **β-Glc-6-2-H** (0.17 g, 0.31 mmol); Mp 89−92 °C; IR (Nujol) 3391 (br), 3071, 2951, 1715, 1644, 1577, 1541, 1461, 1376, 1250 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.20 (s, 6 H), 1.00 (s, 9 H), 1.42 (br s, 4 H), 1.59−1.64 (m, 2 H), 1.71−1.77 (m, 2 H), 2.56−2.59 (m, 10 H), 3.33−3.38 (br m, 1 H), 3.48−3.69 (br m, 5 H), 3.85−3.92 (br m, 3 H), 4.09 (q, J = 6.0 Hz, 10 H), 4.30 (br s, 4 H), 4.53−4.55 (m, 1 H), 4.85 (br s, 1 H), 5.13−5.22 (m, 10 H), 5.80−5.93 (m, 5 H), 6.73 (d, J = 8.1 Hz, 1 H), 6.98 (d, J = 2.4 Hz, 1 H), 7.13−7.20 (m, 10 H), 7.54 (t, J = 8.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.54, 16.87, 25.65, 25.80, 26.33, 28.81, 29.50, 33.16, 62.43, 66.26, 67.72, 67.90, 70.11, 70.60, 73.78, 75.84, 86.55, 87.18, 87.38, 87.42, 87.59, 87.73, 88.64, 93.69, 103.07, 103.81, 112.15, 113.83, 114.28, 114.74, 117.78, 117.84, 121.40, 133.28, 133.39, 138.54, 139.07, 143.70, 143.87, 144.12, 144.47, 163.69, 164.92, 165.07; ESI-HRMS m/z calcd for $C_{80}H_{87}N_6O_{12}Si$ (M + H^+ + 1): 1352.6184; found: 1352.6180.

β-Glc-12-6-TBS. A brown solid (0.25 g, 63%) from **β-Glc-12-2-H** (0.17 g, 0.27 mmol); Mp 102−104 °C; IR (Nujol) 3383 (br), 3072, 2964, 1716, 1645, 1576, 1540, 1461, 1376, 1251 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.20 (s, 6 H), 1.00 (s, 9 H), 1.24 (br s, 16 H), 1.54−1.62 (m, 2 H), 1.74−1.76 (m, 2 H), 2.57 (t, J = 6.0 Hz, 10 H), 3.32−3.38 (br m, 1 H), 3.40−3.51 (br m, 2 H), 3.60−3.69 (m, 4 H), 3.82−3.86 (m, 4 H), 4.09 (q, J = 6.6 Hz, 10 H), 4.29−4.31 (m, 4 H), 5.13−5.22 (m, 10 H), 5.80−5.94 (m, 5 H), 6.73 (d, J = 8.4 Hz, 1 H), 6.98 (d, J = 1.8 Hz, 1 H), 7.13−7.21 (m, 10 H), 7.54 (t, J = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.51, 16.91, 19.36, 26.09, 26.22, 26.36, 29.15, 29.63, 29.74, 33.21, 48.50. 66.47, 67.80, 67.99, 70.47, 73.78, 75.79, 77.62, 86.58, 87.20, 87.41, 87.52, 87.70, 87.84, 88.64, 93.80, 103.00, 103.83, 112.16, 113.91, 114.80, 117.83, 117.89, 121.37, 133.31, 133.37, 133.42, 138.50, 139.15, 143.66, 143.73, 143.91, 144.25, 144.52, 163.78, 164.99, 165.12, 165.20; ESI-HRMS m/z calcd for $C_{86}H_{99}N_6O_{12}Si$ (M + H^+ + 1): 1436.7123; found: 1436.7126.

α-Glucoside-linked desilylated hexamer α-Glc-3-6-H. Typical procedure of desilylation of Yyy-*m*-6-TBS to prepare Yyy-*m*-6-H. To a THF (20 mL) solution of **α-Glc-3-6-TBS** (0.18 g, 0.14 mmol) were added *n*-Bu_4NF (1.0 M THF solution, 0.21 mL, 0.21 mmol) and a few drops of water at room temperature. The mixture was stirred for 30 min and concentrated. The residue was purified by silica gel column chromatography (eluent; CH_2Cl_2/MeOH = 50 : 1) to afford **α-Glc-3-6-H** (0.15 g, 90%) as a brown solid. Mp 99−102 °C; IR (Nujol) 3335 (br), 3073, 2982, 1716, 1642, 1580, 1542, 1444, 1375, 1198 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.02 (br s, 2 H), 2.55−2.58 (m, 10 H), 3.17 (s, 1 H), 3.37 (br s, 1 H), 3.59−3.71 (m, 5 H), 3.85−3.98 (m, 5 H), 4.05−4.11 (m, 10 H), 4.38−4.42 (m, 1 H), 4.49−4.53 (m,

1 H), 4.79 (br s, 1 H), 4.89 (d, J = 2.4 Hz, 1 H), 5.12−5.22 (m, 10 H), 3.78−5.94 (m, 5 H), 6.71 (d, J = 8.1 Hz, 1 H), 6.99 (d, J = 2.4 Hz, 1 H), 7.11−7.21 (m, 10 H), 7.53 (t, J = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.47, 29.23, 33.19, 62.52, 63.07, 64.66, 65.95, 67.80, 67.91, 71.11, 71.91, 72.52, 74.40, 82.21, 86.65, 87.31, 87.36, 87.47, 87.54, 87.62, 88.64, 98.88, 112.34, 114.10, 114.51, 114.62, 114.75, 117.84, 121.37, 133.33, 138.71, 138.92, 143.57, 143.62, 143.78, 143.99, 163.44, 165.05, 165.12; ESI-HRMS m/z calcd for $C_{71}H_{66}N_6NaO_{12}$ ($M + Na^+$): 1217.4636; found: 1217.4636.

β-Glc-3-6-H. A brown solid (0.52 g, 88%) from **β-Glc-3-6-TBS** (0.64 g, 0.49 mmol); Mp 80−82 °C; IR (Nujol) 3364 (br), 3071, 2958, 1716, 1642, 1578, 1544, 1461, 1376, 1196 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.03 (br s, 2 H), 2.55−2.58 (m, 10 H), 3.16 (s, 1 H), 3.39 (br s, 1 H), 3.52−3.73 (m, 5 H), 3.84−3.99 (m, 4 H), 4.05−4.11 (m, 10 H), 4.35−4.51 (m, 4 H), 4.83−5.01 (br m, 1 H), 5.12−5.21 (m, 10 H), 5.79−5.94 (m, 5 H), 6.71 (d, J = 8.7 Hz, 1 H), 6.99 (d, J = 2.4 Hz, 1 H), 7.11−7.18 (m, 10 H), 7.53 (t, J = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.60, 33.21, 62.69, 63.54, 67.07, 67.83, 67.93, 70.94, 73.91, 75.94, 82.25, 86.81, 87.34, 87.41, 87.52, 87.57, 87.65, 88.56, 103.41, 112.39, 114.14, 114.67, 114.77, 117.86, 121.50, 133.34, 138.71, 139.00, 143.65, 143.81, 143.84, 144.07, 163.52, 165.09, 165.13; ESI-HRMS m/z calcd for $C_{71}H_{66}N_6NaO_{12}$ ($M + Na^+$): 1217.4636; found: 1217.4634.

α-Gal-3-6-H. A brown solid (0.10 g, 73%) from **α-Gal-3-6-TBS** (0.16 g, 0.12 mmol); Mp 105−107 °C; IR (Nujol) 3393 (br), 3070, 2952, 1716, 1652, 1575, 1540, 1458, 1376, 1255 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.06 (br s, 2 H), 2.58 (q, J = 6.6 Hz, 10 H), 2.85−3.07 (br m, 2 H), 3.13 (s, 1 H), 3.58−3.65 (m, 1 H), 3.74 (br s, 1 H), 3.82−3.97 (m, 5 H), 4.05−4.12 (m, 11 H), 4.20 (br s, 1 H), 4.41 (br s, 1 H), 4.53−4.59 (m, 1 H), 4.61−4.68 (m, 1 H), 5.02 (d, J = 3.9 Hz, 1 H), 5.14−5.22 (m, 10 H), 5.81−5.94 (m, 5 H), 6.74 (d, J = 8.7 Hz, 1 H), 7.00 (d, J = 2.4 Hz, 1 H), 7.11−7.21 (m, 10 H), 7.57 (t, J = 8.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.32, 29.87, 33.21, 62.83, 63.24, 64.55, 67.81, 67.93, 69.45, 70.00, 70.58, 71.05, 82.23, 86.58, 87.33, 87.42, 87.49, 87.67, 87.75, 88.61, 99.09, 112.39, 114.10, 114.49, 114.64, 114.74, 117.84, 121.27, 133.33, 138.75, 138.87, 143.62, 143.78, 143.81, 143.89, 163.47, 165.07, 165.10, 165.18, 165.23; ESI-HRMS m/z calcd for $C_{71}H_{66}N_6NaO_{12}$ ($M + Na^+$): 1217.4636; found: 1217.4634.

β-Gal-3-6-H. A brown solid (0.11 g, 64%) from **β-Gal-3-6-TBS** (0.19 g, 0.14 mmol); Mp 103−105 °C; IR (Nujol) 3364 (br), 3070, 2969, 1716, 1644, 1575, 1540, 1455, 1376, 1221 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.04 (br s, 2 H), 2.57 (br s, 10 H), 3.16 (s, 1 H), 3.59 (br s, 1 H), 3.70−3.77 (m, 4 H), 3.90−4.05 (m, 4 H), 4.07−4.11 (m, 12 H), 4.20−4.28 (m, 1 H), 4.30 (d, J = 7.8 Hz, 1 H), 4.38−4.44 (m, 2 H), 5.12−5.21 (m, 10 H), 5.80−5.92 (m, 5 H), 6.70 (d, J = 8.4 Hz, 1 H), 6.99 (d, J = 2.4 Hz, 1 H),

7.11−7.17 (m, 10 H), 7.53 (t, J = 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.10, 29.49, 29.87, 33.19, 62.14, 63.67, 66.83, 67.81, 67.91, 69.42, 71.63, 73.74, 74.69, 82.23, 86.76, 87.33, 87.41, 87.49, 87.55, 88.52, 103.49, 112.31, 114.12, 114.28, 114.64, 114.72, 117.83, 121.43, 133.34, 138.66, 138.97, 143.63, 143.71, 143.78, 144.04, 163.52, 165.07, 165.12; ESI-HRMS m/z calcd for $C_{71}H_{66}N_6NaO_{12}$ (M + Na^+): 1217.4636; found: 1217.4640.

α-Man-3-6-H. A brown solid (0.29 g, 80%) from **α-Man-3-6-TBS** (0.40 g, 0.31 mmol); Mp 102−106 °C; IR (Nujol) 3374 (br), 3069, 2953, 1715, 1642, 1580, 1541, 1461, 1376, 1254 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.98 (br s, 2 H), 2.57 (br s, 10 H), 3.19 (s, 1 H), 3.35−3.59 (br m, 3 H), 3.78 (br s, 2 H), 3.88−4.17 (br m, 14 H), 4.34 (br s, 2 H), 4.47 (br s, 1 H), 4.87 (br s, 1 H), 5.02 (br s, 2 H), 5.14−5.21 (m, 10 H), 5.81−5.88 (m, 5 H), 6.72 (d, J = 7.8 Hz, 1 H), 6.99 (br s, 1 H), 7.16 (br s, 10 H), 7.54 (t, J = 7.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.81, 19.79, 24.21, 29.19, 29.76, 33.08, 59.03, 61.55, 62.77, 63.96, 66.94, 67.72, 67.81, 70.92, 71.68, 72.49, 77.49, 82.13, 86.42, 87.20, 87.28, 87.39, 88.46, 100.16, 112.07, 114.01, 114.59, 117.73, 121.34, 133.21, 138.54, 138.91, 143.53, 143.68, 143.99, 163.34, 164.94, 165.00; ESI-HRMS m/z calcd for $C_{71}H_{66}N_6NaO_{12}$ (M + Na^+): 1217.4636; found: 1217.4639.

β-Glc-6-6-H. A brown solid (0.17 g, 86%) from **β-Glc-6-6-TBS** (0.22 g, 0.16 mmol); Mp 82−85 °C; IR (Nujol) 3365 (br), 3073, 2963, 1716, 1643, 1578, 1543, 1458, 1376, 1194 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.42 (br s, 4 H), 1.61 (br s, 2 H), 1.75 (br s, 2 H), 2.57 (br s, 10 H), 3.17 (s, 1 H), 3.36 (br s, 1 H), 3.46−3.71 (br m, 5 H), 3.87 (br s, 4 H), 4.10 (br s, 10 H), 4.30 (br s, 3 H), 4.53 (br s, 1 H), 4.86 (br s, 1 H), 5.13−5.21 (m, 10 H), 5.81−5.92 (m, 5 H), 6.73 (d, J = 8.4 Hz, 1 H), 7.00 (d, J = 1.5 Hz, 1 H), 7.12−7.21 (m, 10 H), 7.55 (t, J = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.68, 25.86, 28.85, 29.52, 33.11, 62.23, 66.24, 67.75, 67.85, 70.10, 70.40, 73.67, 75.82, 82.13, 86.57, 87.25, 87.38, 87.44, 88.51, 103.02, 112.08, 114.06, 114.22, 114.57, 114.64, 117.79, 121.35, 133.24, 138.49, 139.04, 143.57, 143.62, 143.71, 144.08, 163.63, 164.99, 165.04; ESI-HRMS m/z calcd for $C_{74}H_{72}N_6NaO_{12}$ (M + Na^+): 1259.5105; found: 1259.5106.

β-Glc-12-6-H. A brown solid (0.18 g, 80%) from **β-Glc-12-6-TBS** (0.25 g, 0.17 mmol); Mp 88−91 °C; IR (Nujol) 3390 (br), 3071, 2960, 1716, 1643, 1576, 1541, 1457, 1376, 1194 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.24−1.45 (m, 16 H), 1.56 (br s, 2 H), 1.66−1.79 (m, 2 H), 2.57−2.61 (m, 10 H), 3.16 (s, 1 H), 3.33−3.38 (m, 2 H), 3.45−3.48 (m, 2 H), 3.60−3.65 (m, 2 H), 3.80−3.87 (m, 3 H), 4.06−4.12 (m, 11 H), 4.31 (t, J = 6.6 Hz, 3 H), 4.76−4.92 (br m, 2 H), 5.13−5.22 (m, 10 H), 5.81−5.94 (m, 5 H), 6.73 (d, J = 8.4 Hz, 1 H), 7.00 (d, J = 2.4 Hz, 1 H), 7.13−7.21 (m, 10 H), 7.54 (t, J = 7.8 Hz, 1 H); ^{13}C NMR

($CDCl_3$, 75 MHz) δ 13.92, 19.92, 24.37, 26.07, 26.25, 29.15, 29.57, 29.66, 29.78, 33.17, 59.21, 62.22, 66.46, 67.81, 67.90, 70.42, 73.67, 75.76, 82.18, 86.60, 87.29, 87.42, 87.50, 87.62, 88.52, 102.97, 112.10, 114.12, 114.22, 114.62, 117.86, 121.32, 133.26, 133.34, 138.44, 139.15, 143.63, 143.76, 144.23, 163.73, 165.02, 165.05, 165.10; ESI-HRMS *m*/*z* calcd for $C_{80}H_{85}N_6O_{12}$ (M + H^+ + 1): 1322.6259; found: 1322.6253.

α-Glucoside-linked decamer α-Glc-3-10-TBS. Typical procedure of Sonogashira reaction of Yyy-*m*-6-H with 11 to prepare decamers Yyy-*m*-10-TBS. To an *i*-Pr_2NH (10 mL) and THF (10mL) suspension of Pd[P(*t*-Bu)$_3$]$_2$ (4.3 mg, 0.0084 mmol), CuI (1.6 mg, 0.0084 mmol), and K_2CO_3 (46 mg, 0.33 mmol) were added **α-Glc-3-6-H** (0.20 g, 0.17 mmol) and **11** (0.19 g, 0.20 mmol) at room temperature. The mixture was stirred for 3 h at room temperature, and then to the mixture was added 3-aminopropyl-functionalized silica gel (0.10 g). After stirring for 1 h, the mixture was diluted with THF and filtered off the insoluble materials. The filtrate was concentrated and purified by silica gel column chromatography (eluent; CH_2Cl_2/MeOH = 50 : 1) to afford **α-Glc-3-10-TBS** (0.20 g, 62%) as a yellow solid. Mp 160−161 °C; IR (Nujol), 3391 (br), 3069, 2967, 1715, 1641, 1581, 1542, 1462, 1376, 1214 cm^{-1}; ^{1}H NMR ($CDCl_3$/CD_3OD = 1:1, 500 MHz) δ 0.23 (s, 6 H), 1.03 (s, 9 H), 2.12−2.15 (m, 2 H), 2.57−2.64 (m, 18 H), 3.39−3.49 (m, 1 H), 3.63−3.82 (m, 6 H), 3.92−3.97 (m, 1 H), 4.14−4.22 (m, 18 H), 4.42−4.50 (m, 2 H), 4.87 (d, *J* = 3.5 Hz, 1 H), 5.14−5.24 (m, 18 H), 5.87−5.96 (m, 9 H), 6.82 (d, *J* = 9.0 Hz, 1 H), 7.05 (d, *J* = 2.5 Hz, 1 H), 7.22−7.30 (m, 18 H), 7.65 (t, *J* = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$/CD_3OD = 3:1, 75 MHz) δ −5.01, 14.86, 16.54, 25.91, 28.74, 32.95, 61.76, 65.76, 67.67, 67.85, 68.06, 69.87, 72.00, 86.16, 86.84, 86.95, 87.23, 87.29, 94.03, 103.20, 112.15, 113.94, 114.33, 114.48, 114.80, 117.45, 117.52, 117.57, 133.03, 133.08, 138.54, 142.97, 143.07, 144.08, 162.87, 165.04, 165.12, 165.17; ESI-HRMS *m*/*z* calcd for $C_{121}H_{116}N_{10}NaO_{16}Si$ (M + Na^+ + 1): 2016.8271; found: 2016.8266.

β-Glc-3-10-TBS. A yellow solid (0.34 g, 68%) from **β-Glc-3-6-H** (0.30 g, 0.25 mmol); Mp 139−142 °C; IR (Nujol) 3373 (br), 3069, 2966, 1715, 1641, 1577, 1540, 1462, 1376, 1157 cm^{-1}; ^{1}H NMR ($CDCl_3$/CD_3OD = 1:1, 500 MHz) δ 0.22 (s, 6 H), 1.03 (s, 9 H), 2.11−2.17 (m, 2 H), 2.57−2.64 (m, 18 H), 3.27−3.48 (m, 3 H), 3.72−3.90 (m, 3 H), 4.08−4.23 (m, 20 H), 4.33 (d, *J* = 7.5 Hz, 1 H), 4.43−4.48 (m, 2 H), 5.15−5.24 (m, 18 H), 5.87−5.95 (m, 9 H), 6.81 (d, *J* = 8.8 Hz, 1 H), 7.04 (d, *J* = 2.0 Hz, 1 H), 7.22−7.30 (m, 18 H), 7.65 (t, *J* = 8.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.57, 16.83, 23.11, 23.87, 25.73, 26.30, 29.03, 29.10, 29.55, 29.81, 30.46, 30.88, 33.13, 38.80, 62.90, 63.35, 66.94, 67.67, 67.83, 67.99, 68.17, 71.23, 73.98, 86.66, 87.17, 87.41, 87.65, 88.43, 93.60, 103.81, 113.76, 114.22, 114.62, 117.79, 118.20, 121.37, 128.71, 130.82, 133.23, 133.33, 138.57, 138.94, 143.68, 143.79, 143.89, 144.02, 144.46, 163.37, 164.86, 165.02; ESI-HRMS *m*/*z* calcd for $C_{121}H_{116}N_{10}NaO_{16}Si$ (M +

Na^+ + 1): 2016.8271; found: 2016.8266.

α-Gal-3-10-TBS. A yellow solid (0.091 g, 55%) from **α-Gal-3-6-H** (0.098 g, 0.082 mmol); Mp 135−140 °C; IR (Nujol) 3392 (br), 3070, 2968, 1715, 1643, 1575, 1540, 1462, 1376, 1217 cm^{-1}; ^1H NMR ($CDCl_3/CD_3OD$ = 1:1, 500 MHz) δ0.22 (s, 6 H), 1.03 (s, 9 H), 2.11−2.15 (m, 2 H), 2.57−2.64 (m, 18 H), 3.63−3.68 (m, 1 H), 3.73−3.84 (m, 5 H), 3.93−3.98 (m, 2 H), 4.14−4.20 (m, 18 H), 4.45−4.48 (m, 2 H), 4.92 (d, *J* = 2.5 Hz, 1 H), 5.15−5.25 (m, 18 H), 5.87−5.96 (m, 9 H), 6.82 (d, *J* = 8.5 Hz, 1 H), 7.04 (d, *J* = 2.5 Hz, 1 H), 7.21−7.30 (m, 18 H), 7.65 (t, *J* = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3/CD_3OD$ = 3:1, 75 MHz) δ−5.02, 16.56, 25.91, 28.92, 29.58, 32.96, 62.09, 64.77, 67.70, 67.91, 68.91, 69.77, 70.23, 86.11, 86.89, 87.12, 87.25, 91.03, 94.06, 98.80, 112.03, 113.96, 114.67, 117.50, 121.34, 133.10, 133.16, 138.60, 143.02, 143.21, 144.10, 163.26, 165.10, 165.23; ESI-HRMS *m*/*z* calcd for $C_{121}H_{116}N_{10}NaO_{16}Si$ (M + Na^+ + 1): 2016.8271; found: 2016.8265.

β-Gal-3-10-TBS. A yellow solid (0.11 g, 62%) from **β-Gal-3-6-H** (0.11 g, 0.092 mmol); Mp 157−159 °C; IR (Nujol) 3389 (br), 3072, 2976, 1715, 1642, 1581, 1546, 1455, 1376, 1204 cm^{-1}; ^1H NMR ($CDCl_3/CD_3OD$ = 1:1, 500 MHz) δ0.22 (s, 6 H), 1.03 (s, 9 H), 2.11−2.15 (m, 2 H), 2.57−2.64 (m, 18 H), 3.49−3.61 (m, 4 H), 3.76−3.84 (m, 3 H), 3.90 (d, *J* = 2.5 Hz, 1 H), 4.18−4.22 (m, 18 H), 4.28 (d, *J* = 8.0 Hz, 1 H), 4.44−4.47 (m, 2 H), 5.14−5.24 (m, 18 H), 5.87−5.96 (m, 9 H), 6.81 (d, *J* = 9.0 Hz, 1 H), 7.05 (d, *J* = 2.0 Hz, 1 H), 7.22−7.31 (m, 18 H), 7.65 (t, *J* = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3/CD_3OD$ = 3:1, 75 MHz) δ −5.01, 16.54, 26.56, 29.55, 32.93, 58.66, 61.29, 63.38, 67.65, 67.83, 68.91, 71.16, 73.28, 74.42, 86.08, 86.86, 87.08, 87.70, 88.25, 93.98, 103.20, 111.94, 113.88, 114.61, 117.49, 121.26, 133.07, 142.15, 142.56, 143.19, 143.64, 144.04, 163.29, 165.04, 165.15; ESI-HRMS *m*/*z* calcd for $C_{121}H_{116}N_{10}NaO_{16}Si$ (M + Na^+ + 1): 2016.8271; found: 2016.8268.

α-Man-3-10-TBS. A yellow solid (0.26 g, 76%) from **α-Man-3-6-H** (0.10 g, 0.17 mmol); Mp 165−168 °C; IR (Nujol) 3389 (br), 3070, 2964, 1715, 1642, 1581, 1542, 1462, 1376, 1223 cm^{-1}; ^1H NMR ($CDCl_3/CD_3OD$ = 2:1, 500 MHz) δ0.23 (s, 6 H), 1.03 (s, 9 H), 2.05−2.09 (m, 2 H), 2.58−2.64 (m, 18 H), 3.58−3.61 (m, 2 H), 3.72−3.92 (m, 6 H), 4.14−4.21 (m, 18 H), 4.37−4.52 (m, 2 H), 4.83 (s, 1 H), 5.14−5.24 (m, 18 H), 5.87−5.95 (m, 9 H), 6.81 (d, *J* = 8.0 Hz, 1 H), 7.04 (d, *J* = 2.0 Hz, 1 H), 7.21−7.29 (m, 18 H), 7.65 (t, *J* = 8.0 Hz, 1 H); ^{13}C NMR ($CDCl_3/CD_3OD$ = 3:1, 75 MHz) δ−5.01, 16.56, 25.91, 29.21, 29.57, 32.93, 58.67, 61.08, 62.78, 67.67, 67.85, 70.23, 72.30, 86.86, 87.08, 88.02, 90.48, 94.03, 99.93, 100.58, 103.22, 104.35, 111.98, 113.94, 114.64, 117.49, 121.19, 133.07, 138.60, 143.18, 144.12, 163.23, 165.05, 165.20; ESI-HRMS *m*/*z* calcd for $C_{121}H_{116}N_{10}NaO_{16}Si$ (M + Na^+ + 1): 2016.8271; found: 2016.8265.

β-Glc-6-10-TBS. A yellow solid (0.17 g, 65%) from **β-Glc-6-6-H** (0.16 g, 0.13 mmol); Mp 145−147 °C; IR (Nujol) 3391 (br), 3070, 2964, 1715, 1642, 1576, 1540, 1461, 1376, 1251 cm^{-1}; ^1H NMR ($CDCl_3/CD_3OD$ = 1:1, 500 MHz) δ 0.22 (s, 6 H), 1.03 (s, 9 H), 1.3−1.4 (br m, 2 H), 1.45−1.50 (m, 2 H), 1.60−1.66 (m, 2 H), 1.77−1.82 (m, 2 H), 2.57−2.64 (m, 18 H), 3.40−3.92 (m, 8 H), 4.14−4.22 (m, 19 H), 4.28−4.33 (m, 2 H), 5.14−5.24 (m, 18 H), 5.87−5.95 (m, 9 H), 6.80 (d, J = 8.0 Hz, 1 H), 7.04 (d, J = 2.5 Hz, 1 H), 7.21−7.33 (m, 18 H), 7.64 (t, J = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.55, 16.85, 25.57, 25.68, 26.31, 28.68, 29.47, 30.91, 33.14, 62.88, 66.20, 67.70, 67.86, 69.97, 71.16, 73.98, 76.05, 86.53, 87.18, 87.42, 87.68, 88.61, 93.65, 103.23, 103.81, 112.13, 113.80, 114.65, 117.76, 117.83, 121.35, 133.24, 133.36, 138.50, 139.05, 143.79, 144.12, 144.47, 163.69, 164.89, 165.05; ESI-HRMS m/z calcd for $C_{124}H_{122}N_{10}NaO_{16}Si$ ($M + Na^+ + 1$): 2058.8740; found: 2058.8735.

β-Glc-12-10-TBS. A yellow solid (0.15 g, 51%) from **β-Glc-12-6-H** (0.18 g, 0.14 mmol); Mp 138−140 °C; IR (Nujol) 3392 (br), 3070, 2975, 1715, 1643, 1575, 1540, 1455, 1376, 1251 cm^{-1}; ^1H NMR ($CDCl_3/CD_3OD$ = 1:1, 500 MHz) δ 0.23 (s, 6 H), 1.03 (s, 9 H), 1.25−1.55 (m, 16 H), 1.67−1.72 (m, 2 H), 1.80−1.83 (m, 2 H), 2.58−2.64 (m, 18 H), 3.40−3.96 (m, 8 H), 4.16−4.22 (m, 19 H), 4.32 (t, J = 6.8 Hz, 2 H), 5.15−5.24 (m, 18 H), 5.87−5.95 (m, 9 H), 6.81 (d, J = 8.5 Hz, 1 H), 7.05 (d, J = 2.5 Hz, 1 H), 7.22−7.32 (m, 18 H), 7.65 (t, J = 7.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.55, 13.92, 16.88, 19.31, 19.92, 26.04, 26.17, 26.31, 29.10, 28.49, 29.57, 29.68, 30.23, 30.93, 33.14, 43.12, 43.22, 48.14, 62.31, 66.41, 67.70, 67.88, 68.25, 70.27, 70.84, 71.68, 72.41, 74.50, 86.55, 87.17, 87.29, 87.41, 87.59, 87.68, 88.51, 93.65, 98.56, 103.80, 112.08, 113.80, 114.20, 114.67, 117.76, 117.83, 121.29, 133.24, 133.31, 133.36, 138.42, 139.10, 143.78, 143.89, 144.18, 144.47, 163.71, 164.89, 165.07; ESI-HRMS m/z calcd for $C_{130}H_{135}N_{10}O_{16}Si$ ($M + H^+$): 2119.9826; found: 2119.9816.

Deglycosidated decamer HO-3-10-TBS. To a CH_2Cl_2 and MeOH mixed solution (10 + 10 mL) of **α-Man-3-10-TBS** (0.10 g, 0.050 mmol) was added trifluoroacetic acid (TFA) (10 mL) at room temperature. The mixture was stirred for 48 h at room temperature, and to the mixture was added a saturated aqueous $NaHCO_3$ solution. The organic layer was washed with additional water followed by brine, dried over anhydrous sodium sulfate, concentrated. The resulting residue was purified by column chromatography on silica gel (eluent; CH_2Cl_2/MeOH = 50 : 1) to afford **HO-3-10-TBS** as a brown solid (0.096 g, 99%). Mp 104−107 °C; IR (Nujol) 3401 (br), 3072, 2954, 1715, 1642, 1576, 1540, 1461, 1376, 1252 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.20 (s, 6 H), 1.00 (s, 9 H), 1.97−2.05 (m, 2 H), 2.58 (q, J = 6.3 Hz, 18 H), 3.17 (br s, 1 H), 3.75 (t, J = 5.7 Hz, 2 H), 4.09 (t, J = 6.3 Hz, 18 H), 4.55 (t, J = 6.0 Hz, 2 H), 5.14−5.23 (m, 18 H), 5.81−5.95 (m, 9 H), 6.75 (d, J = 8.4 Hz, 1 H), 6.98 (d, J = 2.4 Hz, 1 H),

7.11−7.23 (m, 18 H), 7.58 (t, J = 8.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.47, 16.93, 26.39, 29.92, 32.70, 33.22, 33.29, 59.24, 63.40, 67.75, 67.91, 87.31, 87.47, 87.70, 87.78, 93.69, 103.89, 112.26, 113.83, 114.25, 114.69, 117.84, 117.91, 121.50, 133.33, 133.39, 133.44, 138.99, 139.04, 143.79, 143.94, 144.08, 144.57, 163.78, 164.96, 165.10; ESI-HRMS m/z calcd for $C_{115}H_{107}N_{10}O_{11}Si$ (M + H^+ + 1): 1832.7923; found: 1832.7914.

α-Glucoside-linked desilylated decamer α-Glc-3-10-H. Typical procedure of desilylation of Yyy-3-10-TBS. To a THF (20 mL) solution of **α-Glc-3-10-TBS** (0.22 g, 0.11 mmol) were added n-Bu_4NF (1.0 M THF solution, 0.17 mL, 0.17 mmol) and a few drops of water at room temperature. The mixture was stirred for 10 min and concentrated. The residue was purified by silica gel column chromatography (eluent; CH_2Cl_2/MeOH = 50 : 1) to afford **α-Glc-3-10-H** (0.16 g, 78%) as a yellow solid. Mp 116−120 °C; IR (Nujol) 3365 (br), 3069, 2939, 1716, 1644, 1576, 1540, 1461, 1376, 1254 cm^{-1}; ^{1}H NMR ($CDCl_3$/CD_3OD = 1:1, 500 MHz) δ 2.11−2.16 (m, 2 H), 2.58−2.64 (m, 18 H), 3.45−3.48 (m, 1 H), 3.61−3.82 (m, 6 H), 3.92−3.98 (m, 1 H), 4.15−4.22 (m, 18 H), 4.42−4.52 (m, 2 H), 4.87 (d, J = 3.5 Hz, 1 H), 5.14−5.24 (m, 18 H), 5.87−5.96 (m, 9 H), 6.82 (d, J = 8.5 Hz, 1 H), 7.09 (d, J = 2.5 Hz, 1 H), 7.23−7.31 (m, 18 H), 7.65 (t, J = 8.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.31, 29.91, 33.21, 62.91, 62.86, 64.60, 67.81, 67.91, 71.54, 71.88, 72.72, 74.53, 82.26, 86.65, 87.41, 87.47, 87.57, 87.70, 87.75, 88.75, 98.96, 112.44, 114.11, 114.69, 117.89, 121.34, 133.31, 138.75, 138.96, 143.60, 143.68, 143.89, 144.04, 163.48, 165.10, 165.15, 165.23; ESI-HRMS m/z calcd for $C_{115}H_{103}N_{10}O_{16}$ (M + H^+ + 2): 1881.7616; found: 1881.7633.

β-Glc-3-10-H. A brown solid (0.18 g, 86%) from **β-Glc-3-10-TBS** (0.22 g, 0.11 mmol); Mp 119−121 °C; IR (Nujol) 3364 (br), 3072, 2969, 1715, 1642, 1582, 1544, 1462, 1376, 1254 cm^{-1}; ^{1}H NMR ($CDCl_3$/CD_3OD = 1:1, 500 MHz) δ 2.11−2.16 (m, 2 H), 2.58−2.64 (m, 18 H), 3.27−3.44 (m, 2 H), 3.57−3.82 (m, 4 H), 3.88−3.90 (m, 1 H), 4.08−4.33 (m, 19 H), 4.33 (d, J = 7.5 Hz, 1 H), 4.44−4.48 (m, 2 H), 5.14−5.24 (m, 18 H), 5.88−5.96 (m, 9 H), 6.82 (d, J = 8.5 Hz, 1 H), 7.10 (d, J = 2.0 Hz, 1 H), 7.24−7.31 (m, 18 H), 7.66 (t, J = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 29.53, 33.11, 38.80, 62.77, 63.43, 66.67, 66.91, 67.75, 67.85, 68.17, 71.11, 73.93, 75.99, 82.17, 86.70, 87.26, 87.41, 87.55, 88.46, 103.41, 112.24, 114.04, 114.25, 114.62, 117.78, 121.38, 124.20, 128.71, 130.80, 132.00, 132.34, 133.23, 138.58, 138.92, 143.58, 143.76, 143.99, 163.40, 165.02, 167.58; ESI-HRMS m/z calcd for $C_{115}H_{102}N_{10}NaO_{16}$ (M + Na^+ + 1): 1902.7406; found: 1902.7400.

α-Gal-3-10-H. A yellow solid (0.43 g, 86%) from **α-Gal-3-10-TBS** (0.53 g, 0.26 mmol); Mp 122−124 °C; IR (Nujol) 3365 (br), 3071, 2970, 1715, 1641, 1576, 1540, 1462, 1376, 1254 cm^{-1}; ^{1}H

NMR ($CDCl_3/CD_3OD$ = 1:1, 500 MHz) δ2.12−2.15 (m, 2 H), 2.58−2.64 (m, 18 H), 3.62−3.68 (m, 1 H), 3.72−3.85 (m, 5 H), 3.93−3.97 (m, 2 H), 4.15−4.22 (m, 18 H), 4.47 (t, J = 6.3 Hz, 2 H), 4.92 (d, J = 3.0 Hz, 1 H), 5.14−5.24 (m, 18 H), 5.87−5.96 (m, 9 H), 6.82 (d, J = 8.5 Hz, 1 H), 7.09 (d, J = 2.5 Hz, 1 H), 7.23−7.31 (m, 18 H), 7.65 (t, J = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ29.26, 29.83, 33.14, 62.83, 63.16, 64.50, 67.77, 67.85, 69.37, 69.98, 70.50, 71.02, 82.18, 86.55, 87.28, 87.41, 87.57, 87.64, 88.49, 99.11, 112.25, 114.04, 114.62, 117.81, 121.23, 133.25, 138.65, 138.84, 143.60, 143.78, 163.37, 165.02; ESI-HRMS m/z calcd for $C_{115}H_{103}N_{10}O_{16}$ (M + H^+ + 2): 1881.7616; found: 1881.7625.

β-Gal-3-10-H. A yellow solid (0.27 g, 91%) from **β-Gal-3-10-TBS** (0.32 g, 0.16 mmol); Mp 120−123 °C; IR (Nujol) 3374 (br), 3072, 2978, 1716, 1641, 1576, 1540, 1446, 1375, 1253 cm^{-1}; ^{1}H NMR ($CDCl_3/CD_3OD$ = 1:1, 500 MHz) δ2.11−2.16 (m, 2 H), 2.58−2.64 (m, 18 H), 3.48−3.60 (m, 4 H), 3.76−3.83 (m, 3 H), 3.90 (d, J = 3.5 Hz, 1 H), 4.18−4.23 (m, 18 H), 4.28 (d, J = 7.0 Hz, 1 H), 4.43−4.49 (m, 2 H), 5.14−5.24 (m, 18 H), 5.87−5.96 (m, 9 H), 6.81 (d, J = 8.5 Hz, 1 H), 7.09 (d, J = 3.0 Hz, 1 H), 7.24−7.31 (m, 18 H), 7.65 (t, J = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ29.55, 29.87, 33.19, 62.48, 63.64, 66.75, 67.80, 67.88, 69.56, 71.88, 73.74, 74.76, 82.23, 86.71, 87.33, 87.46, 88.51, 103.44, 112.26, 114.09, 114.19, 114.67, 117.86, 121.43, 133.29, 133.36, 138.61, 139.02, 143.65, 143.75, 143.85, 144.10, 163.48, 165.07; ESI-HRMS m/z calcd for $C_{115}H_{103}N_{10}O_{16}$ (M + H^+ + 2): 1881.7616; found: 1881.7578.

α-Man-3-10-H. A yellow solid (0.46 g, 93%) from **α-Man-3-10-TBS** (0.52 g, 0.26 mmol); Mp 116−119 °C; IR (Nujol) 3365 (br), 3072, 2979, 1716, 1642, 1576, 1540, 1445, 1375, 1253 cm^{-1}; ^{1}H NMR ($CDCl_3/CD_3OD$ = 2:1, 500 MHz) δ2.02−2.06 (m, 2 H), 2.56−2.63 (m, 18 H), 3.50−3.59 (m, 3 H), 3.75−3.93 (m, 5 H), 4.11−4.15 (m, 18 H), 4.34−4.38 (m, 1 H), 4.51−4.57 (m, 1 H), 4.83 (d, J = 1.5 Hz, 1 H), 5.14−5.23 (m, 18 H), 5.85−5.94 (m, 9 H), 6.77 (d, J = 8.5 Hz, 1 H), 7.04 (d, J = 3.0 Hz, 1 H), 7.16−7.25 (m, 18 H), 7.61 (t, J = 8.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ29.57, 29.91, 33.21, 62.30, 62.67, 63.79, 67.83, 67.91, 70.74, 71.89, 72.67, 82.26, 86.21, 87.25, 87.34, 87.46, 87.64, 87.80, 88.75, 100.42, 100.71, 112.26, 114.09, 114.19, 114.70, 117.89, 121.29, 124.27, 132.16, 133.33, 138.65, 138.91, 143.54, 143.68, 143.78, 143.88, 144.02, 163.57, 165.10, 165.17, 165.25; ESI-HRMS m/z calcd for $C_{115}H_{103}N_{10}O_{16}$ (M + H^+ + 2): 1881.7616; found: 1881.7625.

α-Glucoside-linked tetradecamer α-Glc-3-14-TBS. Typical procedure of Sonogashira reaction of Yyy-3-10-H with 11 to prepare tetradecamers Yyy-3-14-TBS. To an i-Pr_2NH (10 mL) and DMF (10 mL) suspension of Pd[P(t-Bu)$_3$]$_2$ (12.0 mg, 0.0040 mmol), CuI (0.76 mg, 0.0040 mmol), and K_2CO_3 (22 mg, 0.16 mmol) were added **α-Glc-3-10-H** (0.15 g, 0.080 mmol) and **11** (89 mg, 0.096 mmol) at room temperature. The mixture was stirred for 2 h at room temperature, and then to the mixture was added 3-

aminopropyl-functionalized silica gel (0.10 g). After stirring for 1 h, the mixture was diluted with THF and filtered off the insoluble materials. The filtrate was concentrated and purified by silica gel column chromatography (eluent; CH_2Cl_2/MeOH = 50 : 1) to afford **α-Glc-3-14-TBS** (0.15 g, 71%) as a brown solid. Mp 156−159 °C; IR (Nujol) 3375 (br), 3065, 2944, 1716, 1645, 1576, 1540, 1456, 1376, 1251 cm^{-1}; ^1H NMR ($CDCl_3/CD_3OD$ = 1:1, 500 MHz) δ 0.22 (s, 6 H), 1.03 (s, 9 H), 2.10−2.16 (m, 2 H), 2.57−2.64 (m, 26 H), 3.45−3.50 (m, 1 H), 3.61−3.82 (m, 5 H), 3.92−3.97 (m, 1 H), 4.14−4.21 (m, 26 H), 4.42−4.48 (m, 2 H), 4.87 (d, *J* = 4.0 Hz, 1 H), 5.14−5.24 (m, 26 H), 5.87−5.96 (m, 13 H), 6.82 (d, *J* = 8.5 Hz, 1 H), 7.05 (d, *J* = 2.5 Hz, 1 H), 7.22−7.31 (m, 26 H), 7.65 (t, *J* = 8.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.99, 16.59, 25.94, 28.73, 28.90, 29.60, 32.98, 61.59, 63.32, 64.30, 64.89, 67.70, 67.85, 67.96, 70.18, 72.02, 86.15, 86.91, 87.18, 94.06, 98.62, 98.82, 103.23, 112.07, 113.94, 114.66, 117.10, 117.54, 121.35, 123.96, 133.12, 138.63, 143.20, 144.12, 163.18, 165.10, 165.23; ESI-HRMS *m*/*z* calcd for $C_{165}H_{153}N_{14}O_{20}Si$ ($M + H^+ + 1$): 2679.1185; found: 2679.1195.

β-Glc-3-14-TBS. A brown solid (0.13 g, 60%) from **β-Glc-3-10-H** (0.15 g, 0.082 mmol); Mp 151−153 °C; IR (Nujol) 3390 (br), 3072, 2965, 1715, 1643, 1583, 1542, 1461, 1376, 1254 cm^{-1}; ^1H NMR ($CDCl_3/CD_3OD$ = 1:1, 500 MHz) δ 0.22 (s, 6 H), 1.03 (s, 9 H), 2.11−2.16 (m, 2 H), 2.57−2.64 (m, 26 H), 3.27−3.43 (m, 2 H), 3.57−3.81 (m, 4 H), 3.87−3.90 (m, 1 H), 4.08−4.22 (m, 27 H), 4.33 (d, *J* = 8.5 Hz, 1 H), 4.43−4.48 (m, 2 H), 5.14−5.24 (m, 26 H), 5.87−5.96 (m, 13 H), 6.82 (d, *J* = 8.4 Hz, 1 H), 7.05 (d, *J* = 2.5 Hz, 1 H), 7.22−7.31 (m, 26 H), 7.65 (t, *J* = 8.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.54, 16.87, 18.08, 26.33, 29.65, 29.86, 33.16, 63.06, 63.38, 67.70, 67.86, 69.25, 70.63, 86.71, 87.21, 87.42, 87.67, 88.46, 93.64, 103.85, 112.29, 113.78, 114.20, 114.64, 117.84, 121.38, 124.23, 133.26, 133.37, 138.58, 138.99, 142.63, 143.73, 143.86, 143.96, 144.52, 163.40, 164.89, 165.05; ESI-HRMS *m*/*z* calcd for $C_{165}H_{153}N_{14}O_{20}Si$ ($M + H^+ + 1$): 2679.1185; found: 2679.1183.

α-Gal-3-14-TBS. A brown solid (0.20 g, 56%) from **α-Gal-3-10-H** (0.25 g, 0.13 mmol); Mp 154−157 °C; IR (Nujol) 3384 (br), 3065, 2970, 1715, 1641, 1575, 1540, 1462, 1376, 1253 cm^{-1}; ^1H NMR ($CDCl_3/CD_3OD$ = 1:1, 500 MHz) δ 0.23 (s, 6 H), 1.03 (s, 9 H), 2.11−2.16 (br m, 2 H), 2.58−2.64 (m, 26 H), 3.64−3.98 (m, 7 H), 4.15−4.22 (br m, 27 H), 4.46 (t, *J* = 6.0 Hz, 1 H), 5.14−5.24 (m, 26 H), 5.88−5.96 (m, 13 H), 6.82 (d, *J* = 8.5 Hz, 1 H), 7.05 (d, *J* = 2.5 Hz, 1 H), 7.22−7.31 (m, 26 H), 7.65 (t, *J* = 7.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −4.99, 16.56, 25.93, 28.89, 29.57, 32.96, 63.21, 64.66, 65.92, 67.86, 68.93, 70.26, 86.12, 87.12, 88.43, 91.42, 94.03, 98.96, 103.23, 111.94, 113.93, 114.20, 114.61, 117.50, 121.21, 123.94, 133.08, 138.59, 143.23, 144.10, 163.19, 165.18; ESI-HRMS *m*/*z* calcd for $C_{165}H_{153}N_{14}O_{20}Si$ ($M + H^+ + 2$): 2680.1215; found: 2680.1221.

β-Gal-3-14-TBS. A yellow solid (0.21 g, 78%) from **β-Gal-3-10-H** (0.19 g, 0.103 mmol); Mp 154−156 °C; IR (Nujol) 3375 (br), 3070, 2943, 1716, 1642, 1576, 1540, 1462, 1376, 1252 cm^{-1}; ^1H NMR ($CDCl_3/CD_3OD$ = 1:1, 500 MHz) δ 0.22 (s, 6 H), 1.03 (s, 9 H), 2.10−2.14 (m, 2 H), 2.58−2.64 (m, 26 H), 3.57−4.00 (br m, 7 H), 4.08−4.22 (m, 27 H), 4.32 (br s, 1 H), 4.39−4.48 (m, 3 H), 5.14−5.24 (m, 26 H), 5.86−5.96 (m, 13 H), 6.79 (d, *J* = 8.5 Hz, 1 H), 7.05 (d, *J* = 2.5 Hz, 1 H), 7.21−7.30 (m, 26 H), 7.64 (t, *J* = 7.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ −5.04, 16.53, 17.69, 18.84, 19.41, 25.89, 28.66, 29.53, 32.92, 62.49, 65.39, 67.82, 71.34, 73.22, 74.37, 87.07, 93.98, 103.18, 111.94, 113.89, 114.59, 117.47, 123.91, 126.24, 133.07, 138.46, 142.97, 143.24, 144.04, 163.12, 165.04; ESI-HRMS *m*/*z* calcd for $C_{165}H_{153}N_{14}O_{20}Si$ ($M + H^+ + 1$): 2679.1185; found: 2679.1191.

α-Man-3-14-TBS. A brown solid (0.16 g, 32%) from **α-Man-3-10-H** (0.34 g, 0.18 mmol); Mp 189−194 °C (dec); IR (Nujol) 3364 (br), 3077, 2962, 1716, 1644, 1576, 1540, 1461, 1376, 1255 cm^{-1}; ^1H NMR ($CDCl_3/CD_3OD$ = 2:1, 500 MHz) δ 0.23 (s, 6 H), 1.03 (s, 9 H), 1.98−2.00 (br m, 2 H), 2.57−2.61 (m, 26 H), 3.55−4.06 (br m, 7 H), 4.13−4.21 (m, 26 H), 4.35−4.63 (br m, 3 H), 4.99 (br s, 1 H), 5.14−5.25 (m, 26 H), 5.85−5.96 (m, 13 H), 6.72 (br d, *J* = 7.0 Hz, 1 H), 7.04 (d, *J* = 3.0 Hz, 1 H), 7.16−7.27 (m, 26 H), 7.58 (br t, *J* = 8.0 Hz, 1 H); ^{13}C NMR ($CDCl_3/CD_3OD$ = 3 : 1, 75 MHz) δ −4.56, 16.59, 25.94, 29.58, 33.05, 66.80, 67.70, 67.90, 68.46, 70.27, 86.85, 87.09, 87.41, 87.25, 94.16, 103.23, 114.28, 114.67, 117.55, 123.47, 133.10, 133.18, 138.47, 142.92, 144.09, 163.37, 165.05; ESI-HRMS *m*/*z* calcd for $C_{165}H_{153}N_{14}O_{20}Si$ ($M + H^+ + 2$): 2680.1215; found: 2680.1210.

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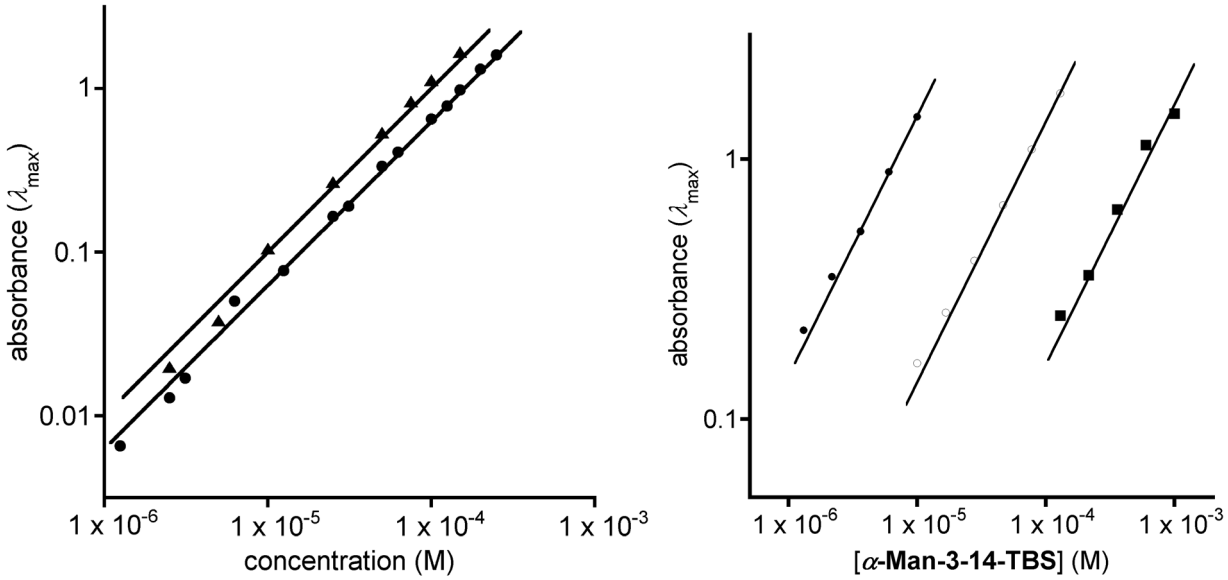


Figure S1. The Beer plots of absorbance at 316 nm against the concentration for (left) ***α*-Man-3-6-TBS** (filled circle) and ***α*-Man-3-10-TBS** (filled triangle), and (right) ***α*-Man-3-14-TBS**. Conditions: CH_2Cl_2, 25 °C, path length = 1 (for ***α*-Man-3-6-TBS** and ***α*-Man-3-10-TBS**), 0.1 (filled square), 1 (open circle), and 10 mm (filled circle) (for ***α*-Man-3-14-TBS**). Lines represent the fitted Beer's equations.

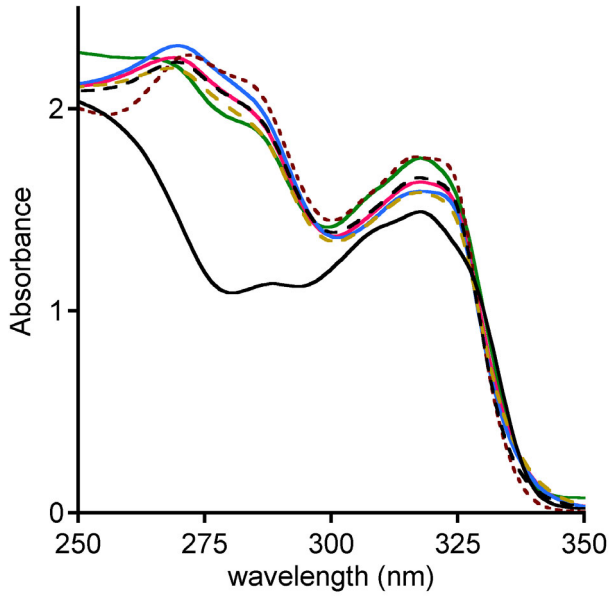


Figure S2. UV spectra of *β*-glucoside-linked oligomers. Pyridine unit concentration was set at 1.5×10^{-3} M. Conditions: CH_2Cl_2, 25 °C, path length = 1 mm. (blue solid) ***β*-Glc-3-14-TBS** (1.1×10^{-4} M), (red solid) ***β*-Glc-3-10-TBS** (1.5×10^{-4} M), (green solid) ***β*-Glc-3-6-TBS** (2.5×10^{-4} M), (black solid) ***β*-Glc-3-3-TBS** (5.0×10^{-4} M), (yellow broken) ***β*-Glc-6-10-TBS** (1.5×10^{-4} M), (black broken) ***β*-Glc-12-10-TBS** (1.5×10^{-4} M), (brown dotted) ***β*-Glc-3-10-H** (1.5×10^{-4} M).

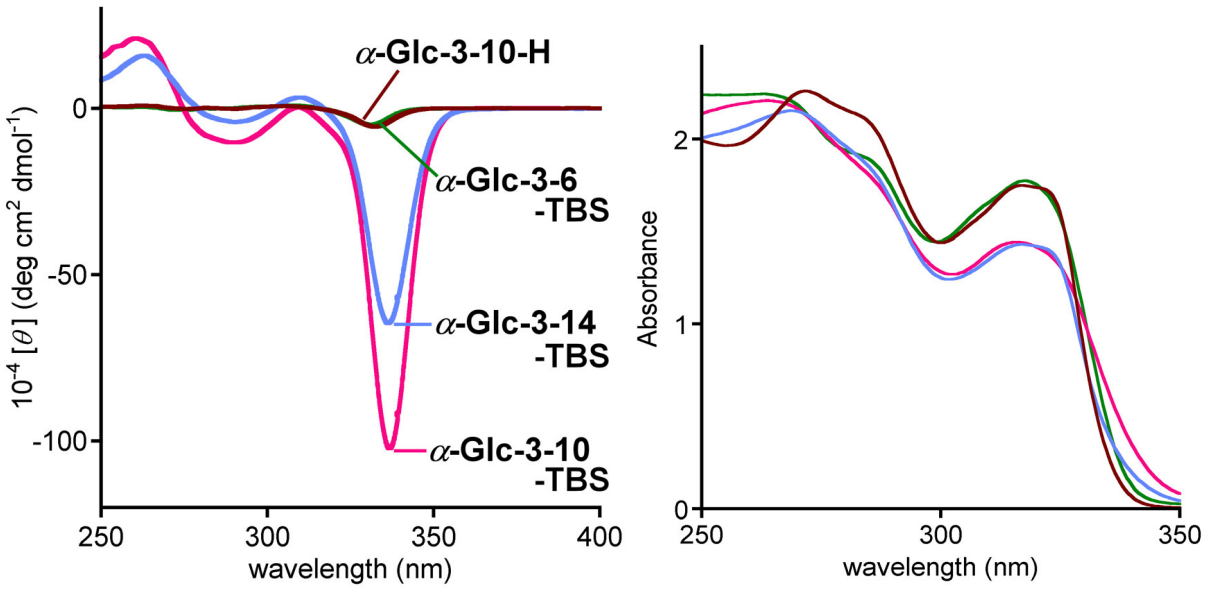


Figure S3. (left) CD and (right) UV spectra of α-glucoside-linked oligomers. Pyridine unit concentration was set at 1.5×10^{-3} M. Conditions: CH_2Cl_2, 25 °C, path length = 1 mm. (blue) **α-Glc-3-14-TBS** (1.1×10^{-4} M), (red) **α-Glc-3-10-TBS** (1.5×10^{-4} M), (green) **α-Glc-3-6-TBS** (2.5×10^{-4} M), (brown) **α-Glc-3-10-H** (1.5×10^{-4} M).

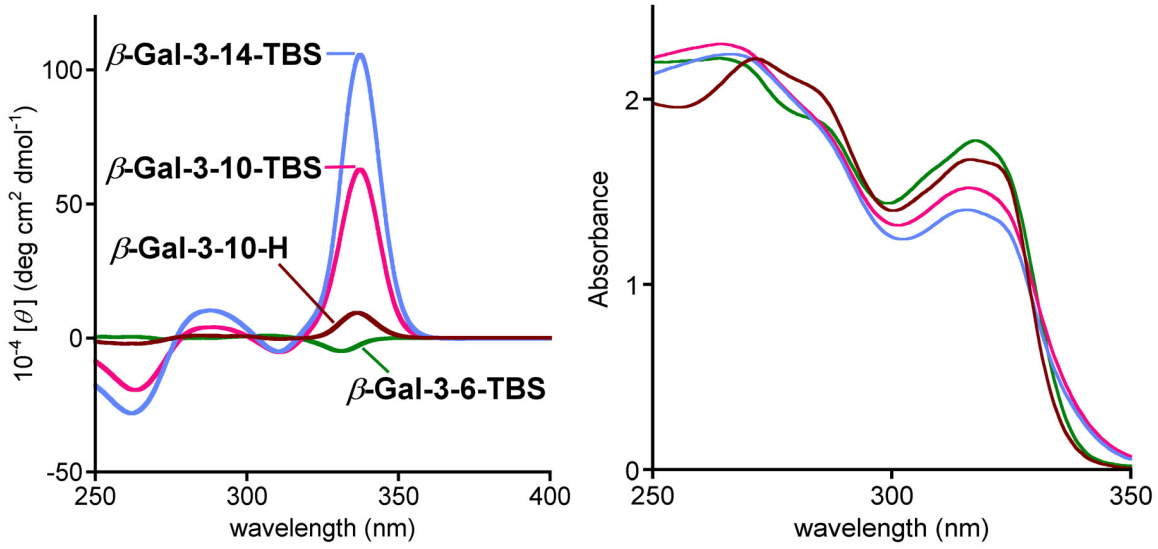


Figure S4. (left) CD and (right) UV spectra of β-galactoside-linked oligomers. Pyridine unit concentration was set at 1.5×10^{-3} M. Conditions: CH_2Cl_2, 25 °C, path length = 1 mm. (blue) **β-Gal-3-14-TBS** (1.1×10^{-4} M), (red) **β-Gal-3-10-TBS** (1.5×10^{-4} M), (green) **β-Gal-3-6-TBS** (2.5×10^{-4} M), (brown) **β-Gal-3-10-H** (1.5×10^{-4} M).

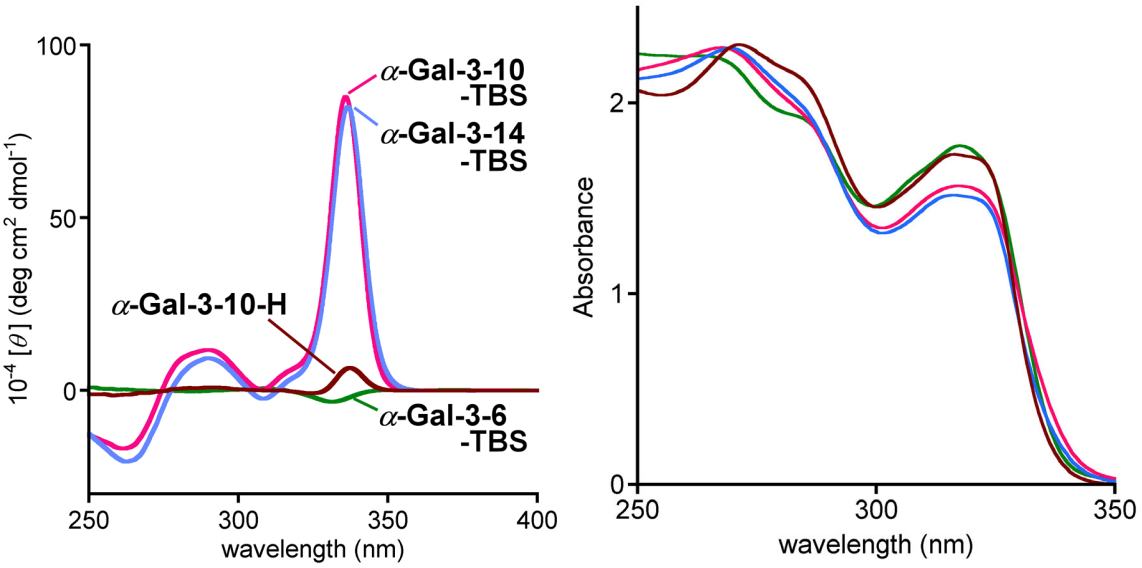


Figure S5. (left) CD and (right) UV spectra of α-galactoside-linked oligomers. Pyridine unit concentration was set at 1.5×10^{-3} M. CH_2Cl_2, 25 °C, path length = 1 mm. (blue) **α-Gal-3-14-TBS** (1.1×10^{-4} M), (red) **α-Gal-3-10-TBS** (1.5×10^{-4} M), (green) **α-Gal-3-6-TBS** (2.5×10^{-4} M), (brown) **α-Gal-3-10-H** (1.5×10^{-4} M).

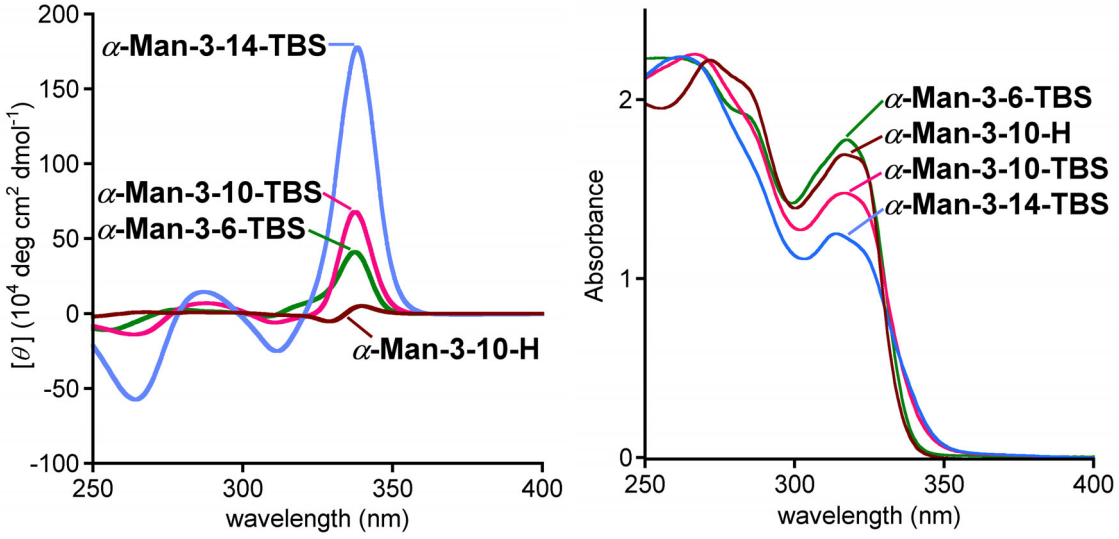


Figure S6. (left) CD and (right) UV spectra of α-mannoside-linked oligomers. Pyridine unit concentration was set at 1.5×10^{-3} M. CH_2Cl_2, 25 °C, path length = 1 mm. (blue) **α-Man-3-14-TBS** (1.1×10^{-4} M), (red) **α-Man-3-10-TBS** (1.5×10^{-4} M), (green) **α-Man-3-6-TBS** (2.5×10^{-4} M), (brown) **α-Man-3-10-H** (1.5×10^{-4} M).

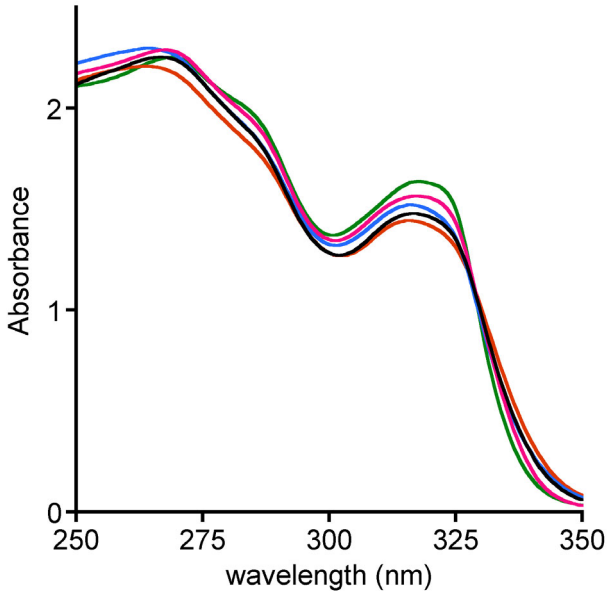


Figure S7. UV spectra of decamers linked with various glycosides. [**Yyy-3-10-TBS**] = 1.5×10^{-4} M in CH_2Cl_2, 25 °C, path length = 1 mm. (green) **β-Glc-3-10-TBS**, (orange) **α-Glc-3-10-TBS**, (blue) **β-Gal-3-10-TBS**, (red) **α-Gal-3-10-TBS**, (black) **α-Man-3-10-TBS**.

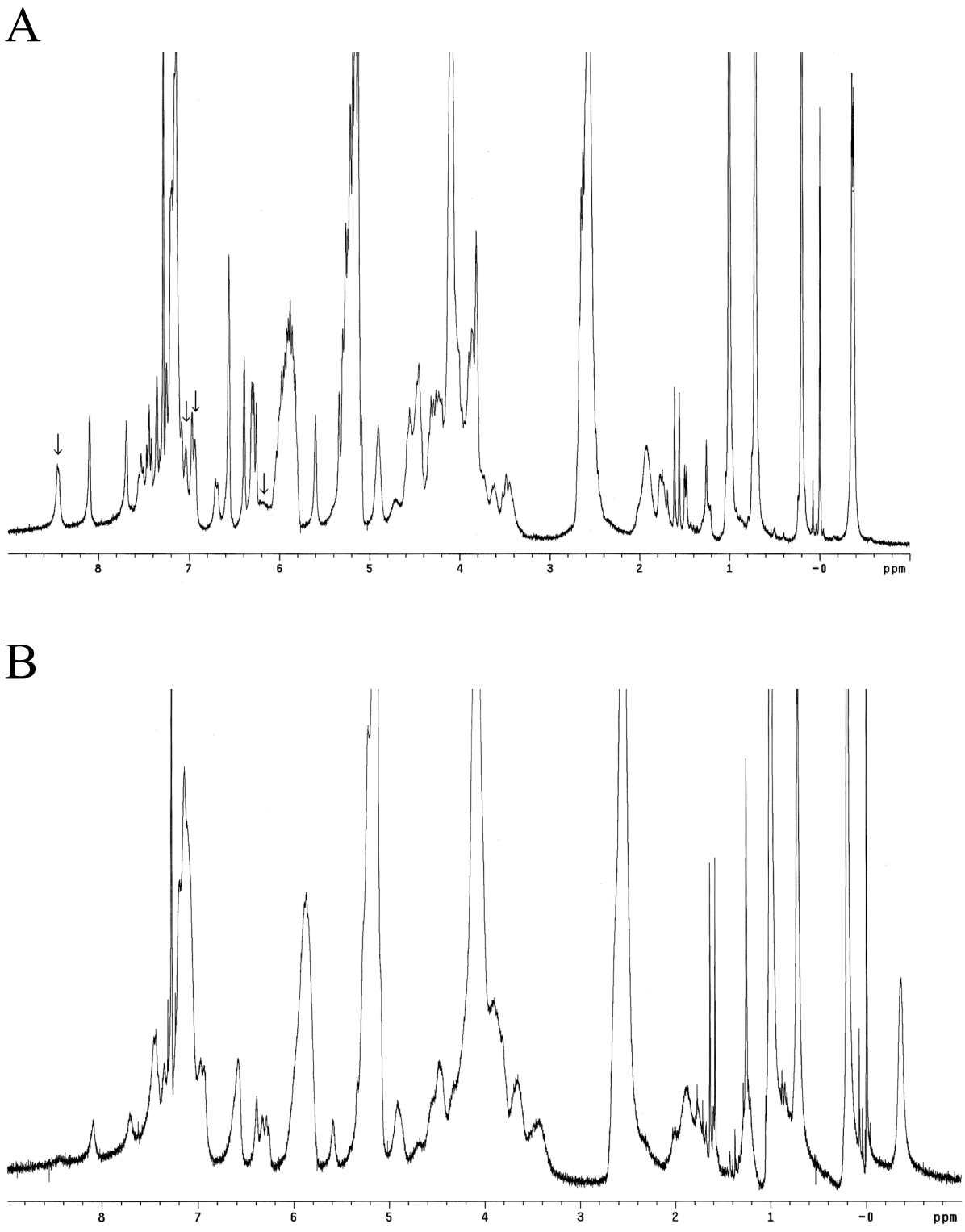


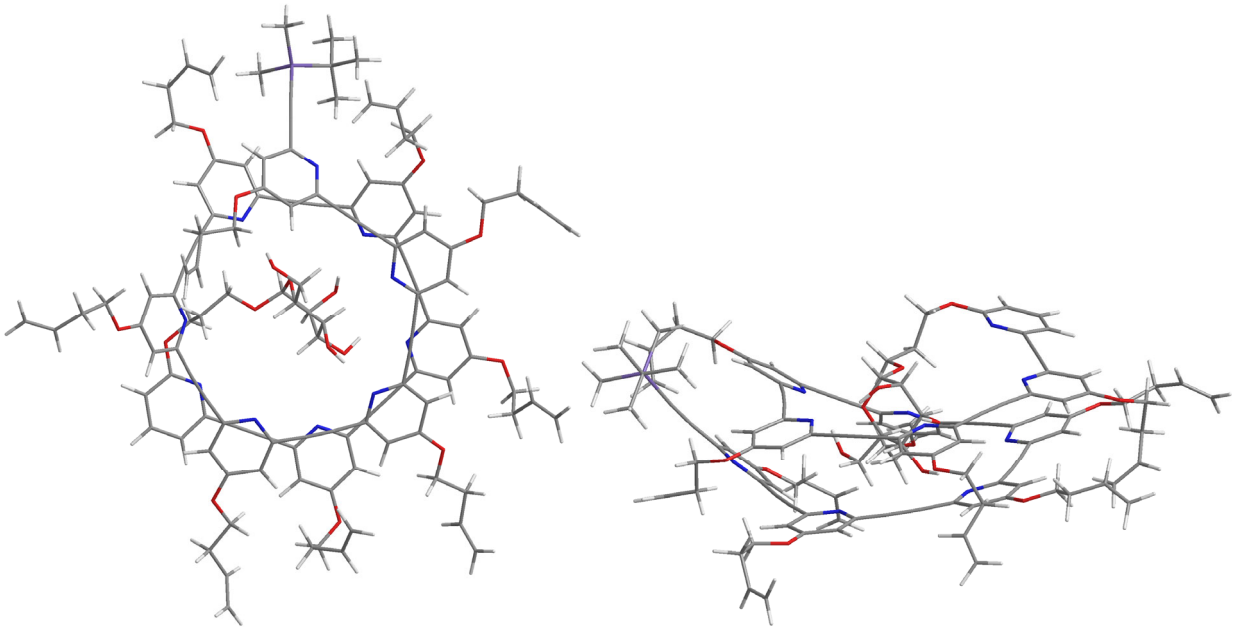
Figure S8. ^{1}H NMR spectra for ***α*-Man-3-6-TBS** (A) in $CDCl_3$, (B) in $CDCl_3$ after D_2O treatment. 23 °C, 300 MHz. Arrows in (A) indicate mannoside moiety's OH protons which disappeared in (B).

Table S1. Calculated ΔE values for optimized minimum structure of decamers.[a]

decamer	ΔE (P-helix) / kJ mol^{-1}	ΔE (M-helix) / kJ mol^{-1}
α-Glc-3-10-TBS	−2530.797	−2544.594
β-Glc-3-10-TBS	−2525.005	−2535.028
α-Gal-3-10-TBS	−2533.422	−2534.645
β-Gal-3-10-TBS	−2521.810	−2516.606
α-Man-3-10-TBS	−2533.685	−2535.868

[a]Optimized in $CHCl_3$ by Monte Carlo molecular mechanics method performed on MacroModel 9.5 using OPLS_2005 force field.

P-helix



M-helix

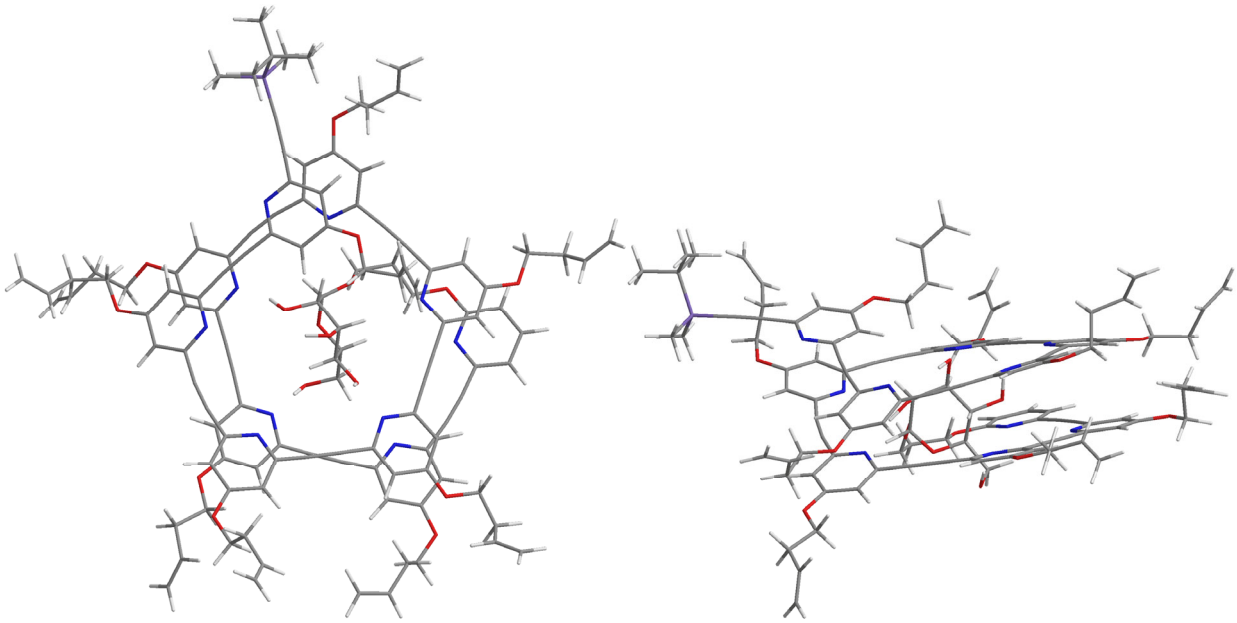
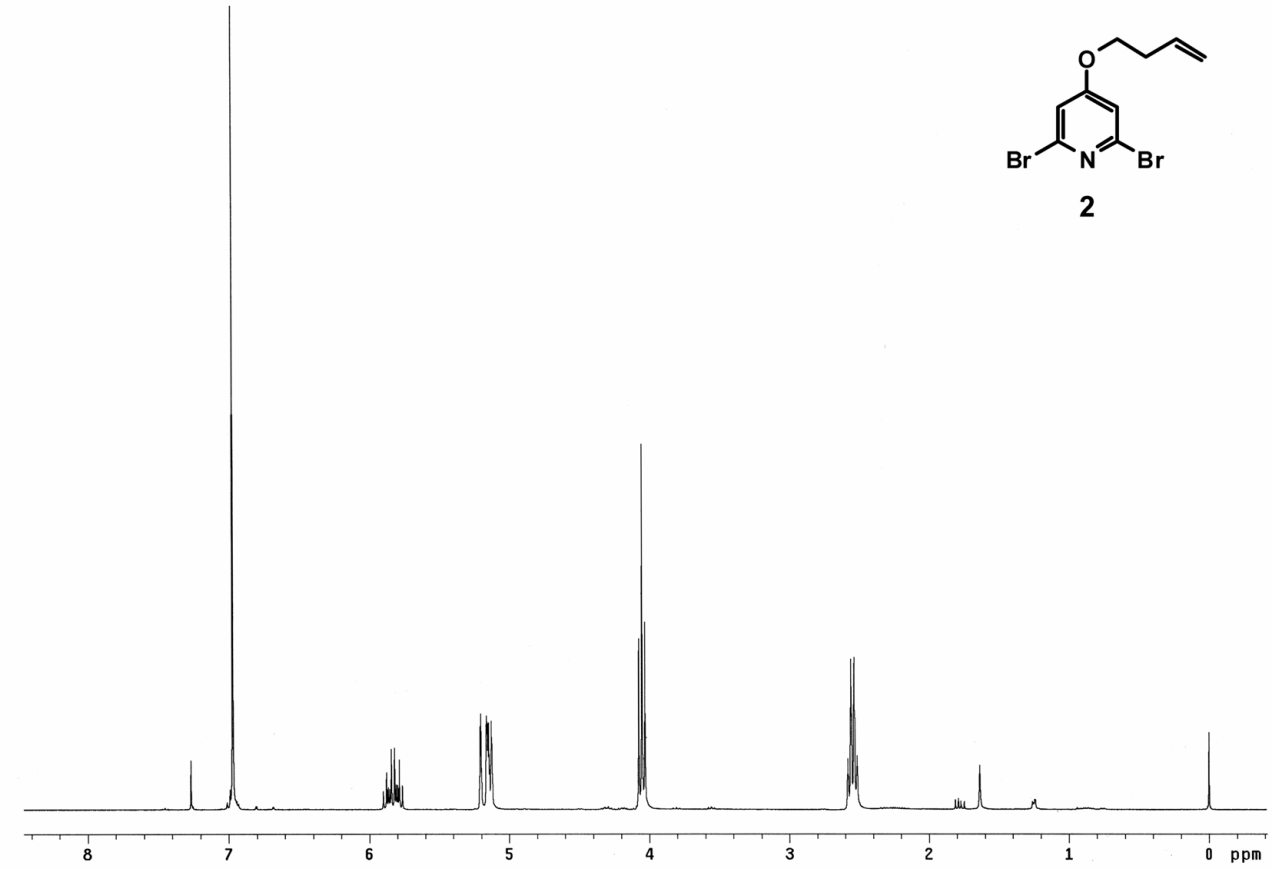
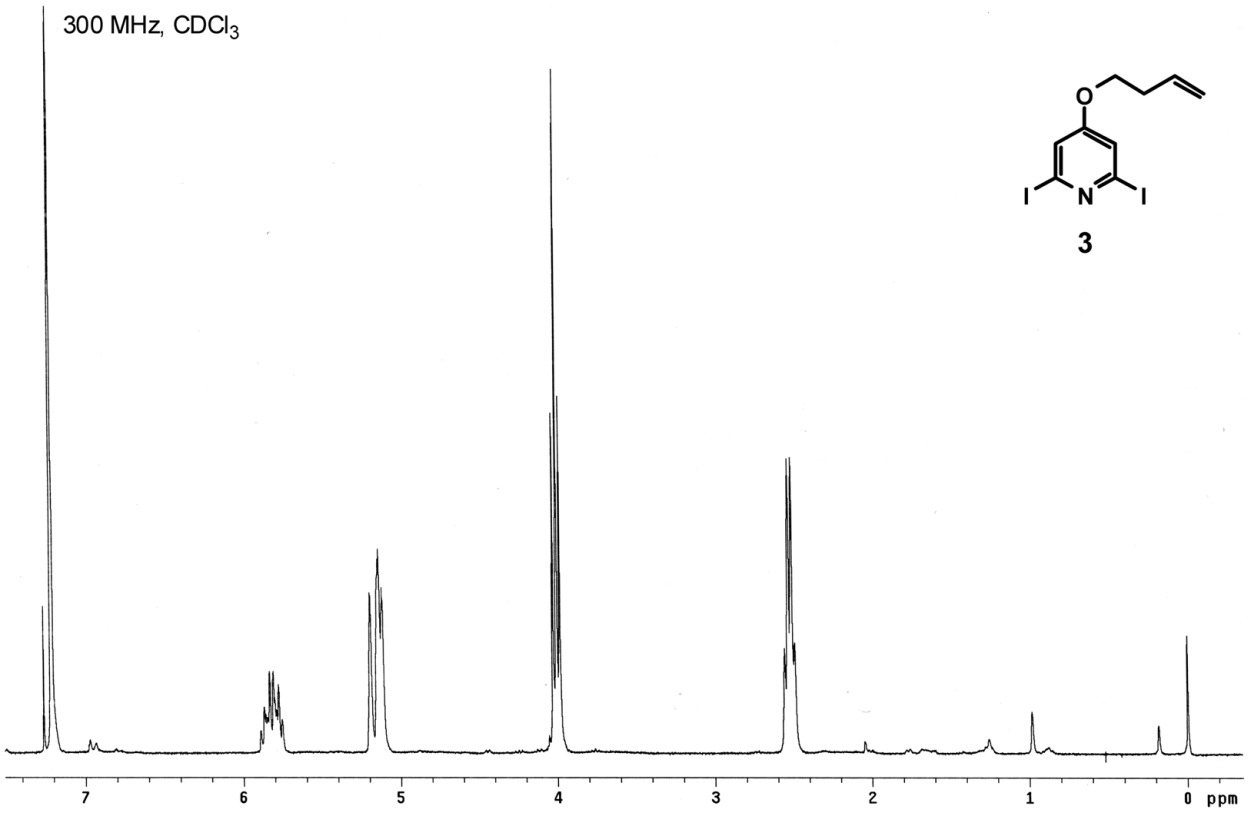


Figure S9. Stick models of optimized structures for (top) P- and (bottom) M-helix of ***α*-Man-3-10-TBS**. Left figures are top views in which TBS group is located at top, and right figures are side views in which TBS group is located at left. In the model of P-helix, TBS group is clipped by two butenyloxy groups, and four butenyloxy groups at left-top are interdigitating. One pitch consisted of six pyridines and five acetylenes (or five pyridines and six acetylenes). In M-helix, a side group and TBS group interact with another group to make pairs. One pitch consisted of five pyridines and five acetylenes.

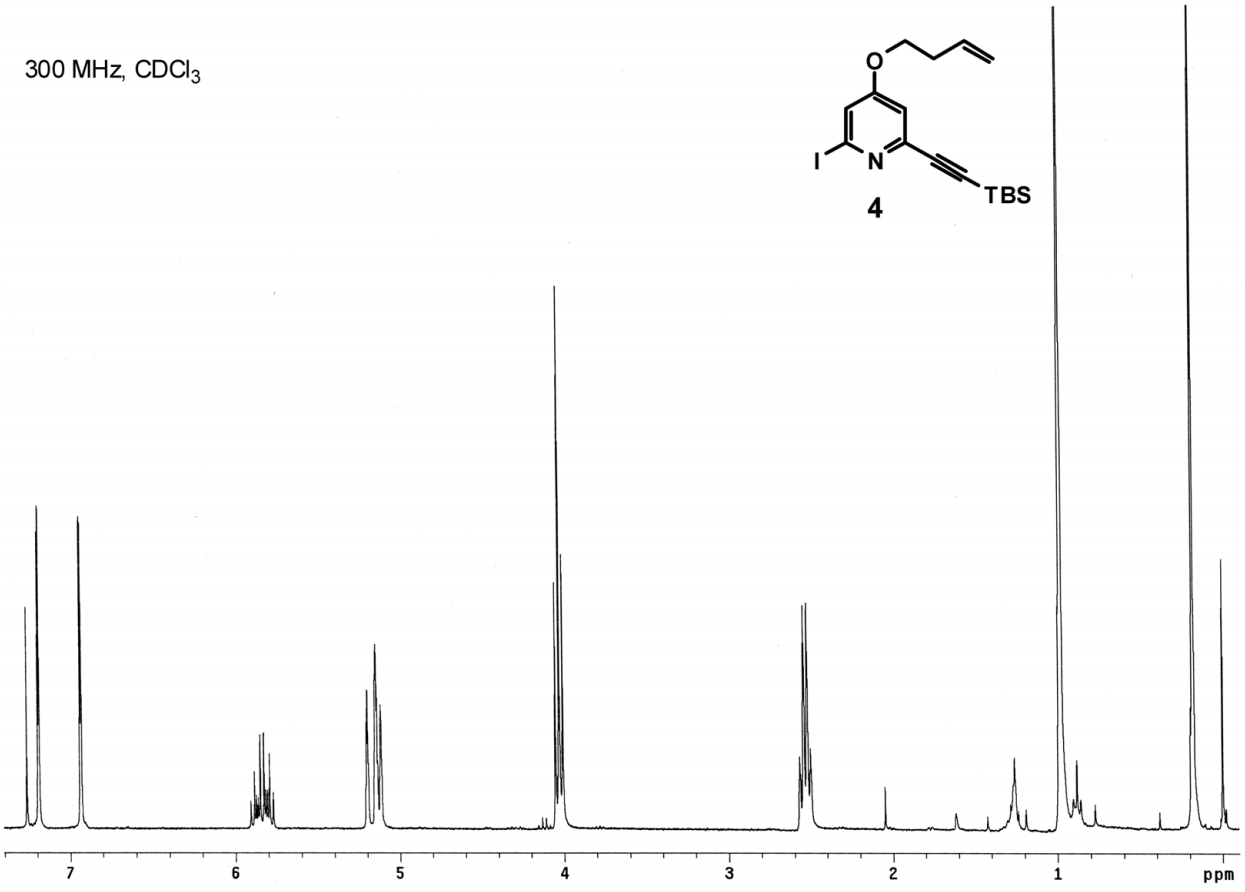
^{1}H NMR spectra, HPLC charts





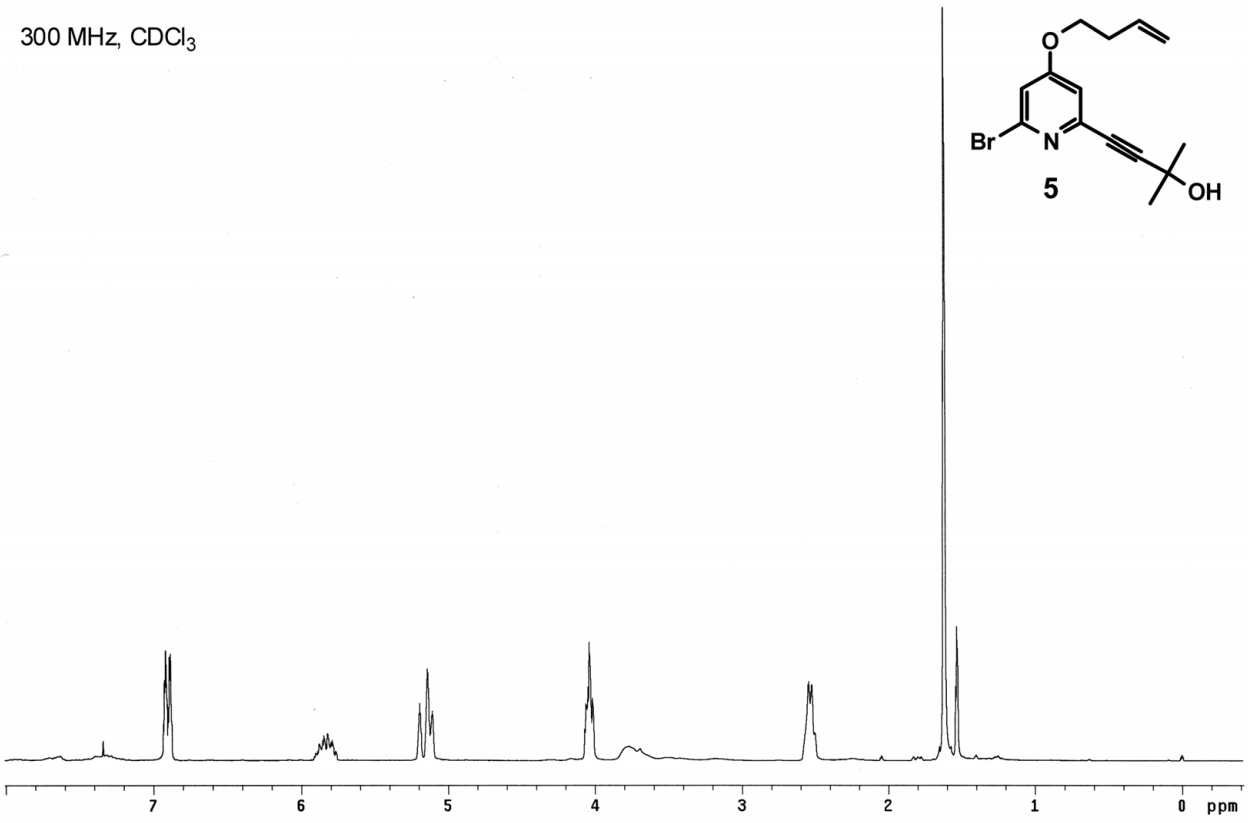
300 MHz, $CDCl_3$

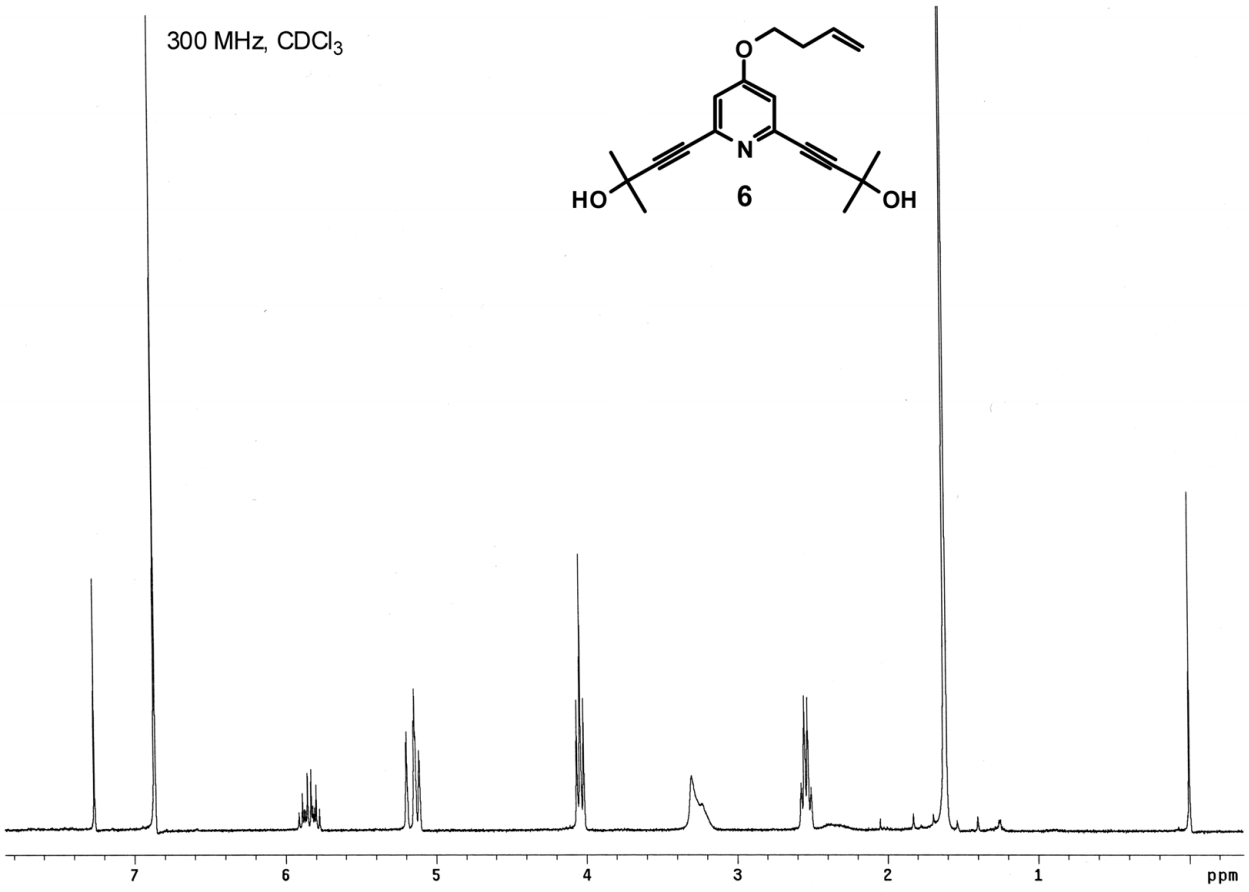
4

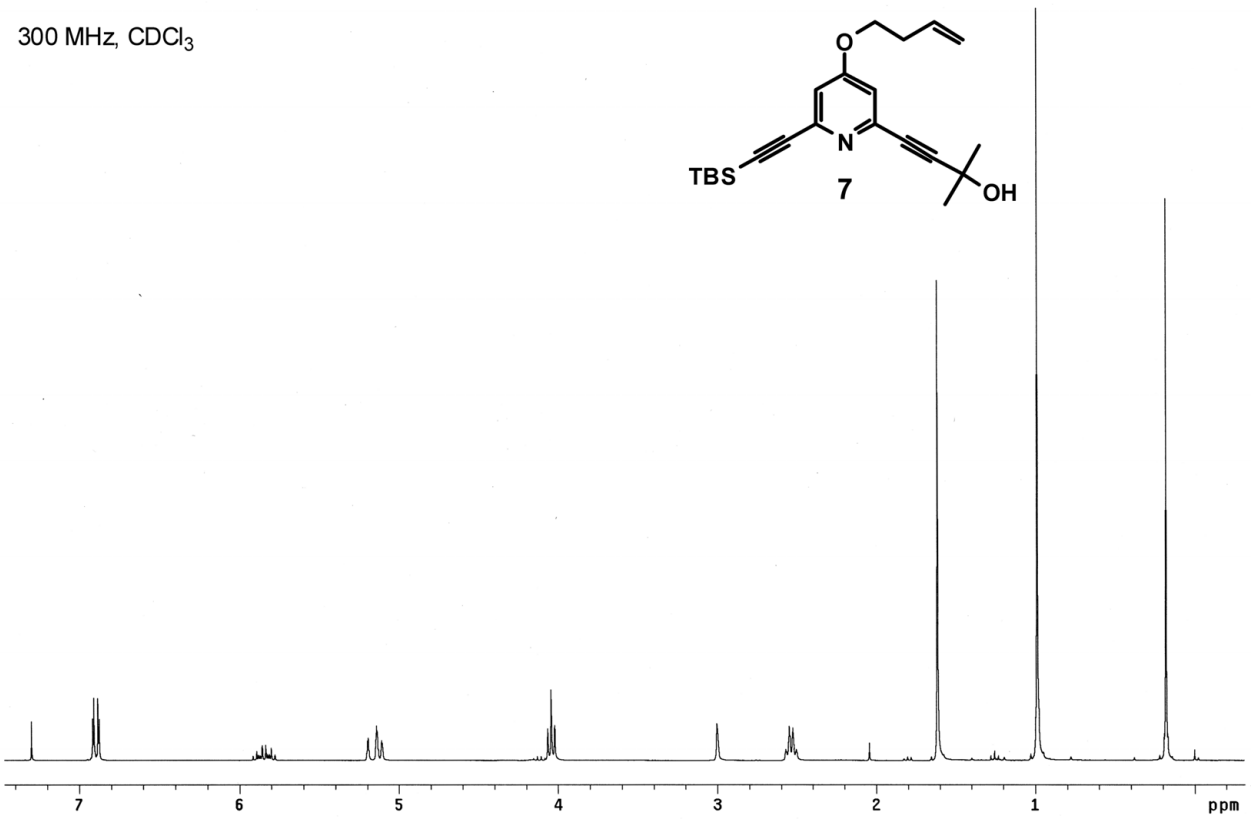


300 MHz, $CDCl_3$

5




300 MHz, CDCl3
O
N
HO
OH
6
7
6
5
4
3
2
1
ppm


300 MHz, CDCl3
O
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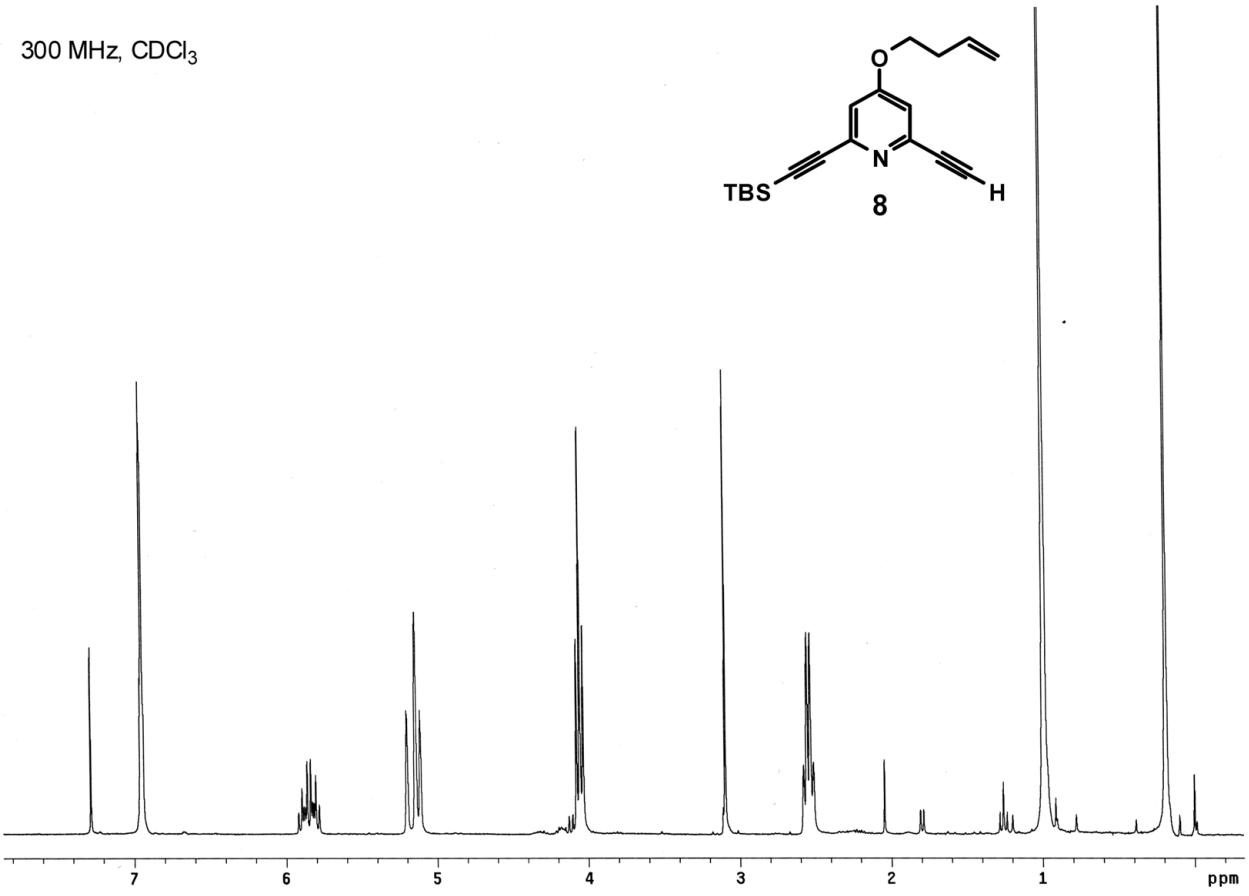
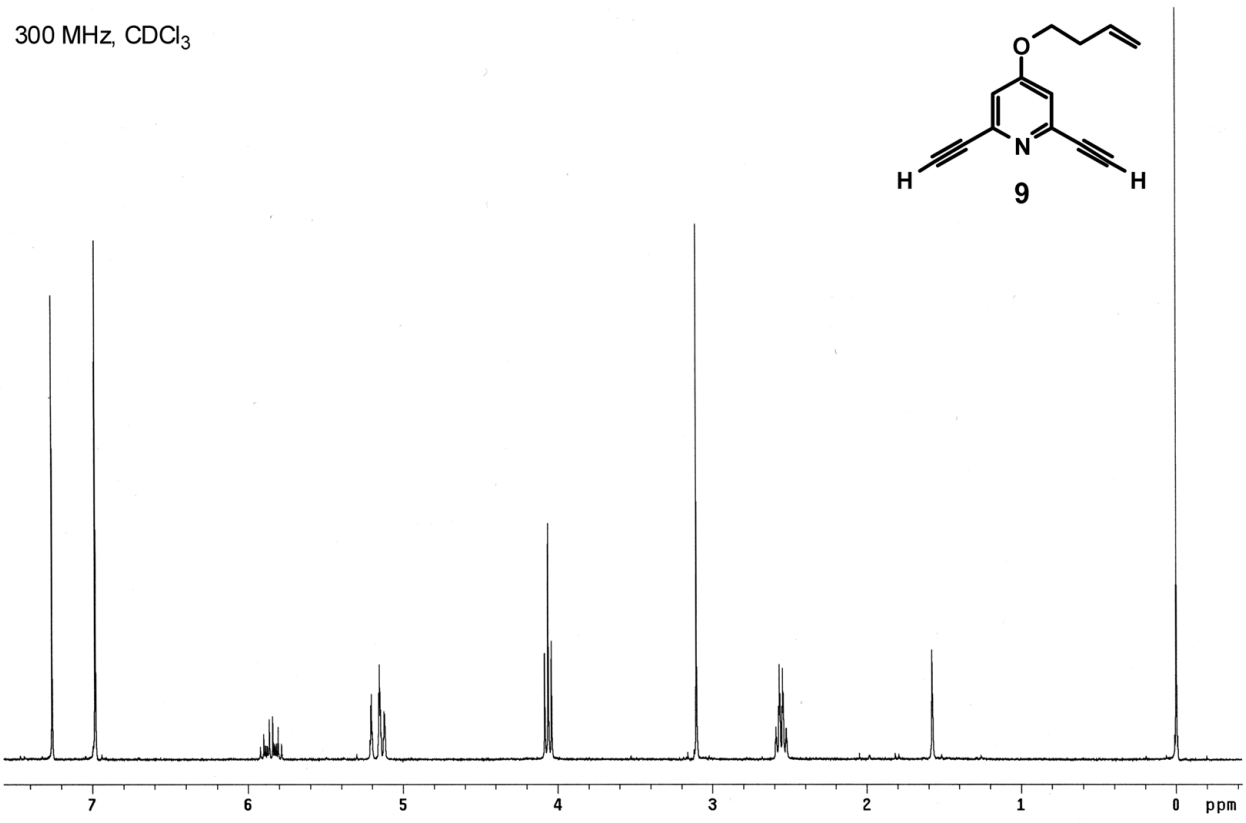
300 MHz, $CDCl_3$

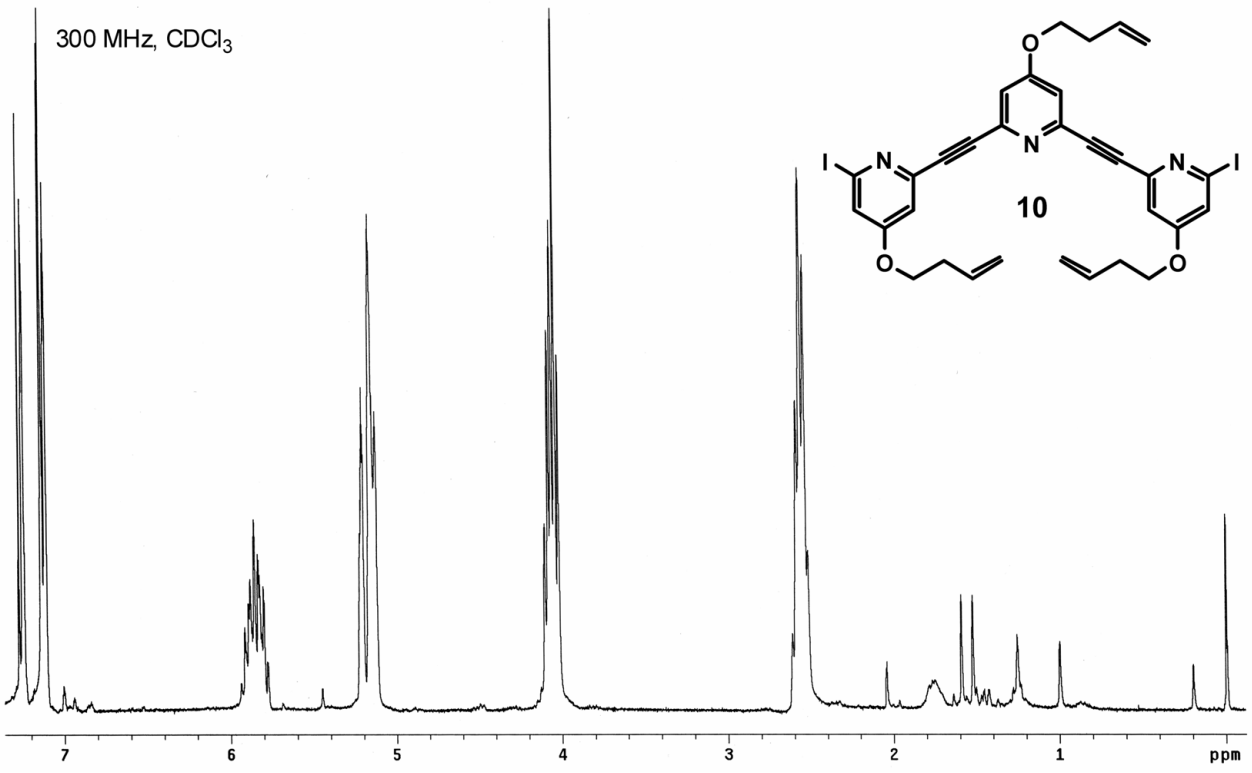
8

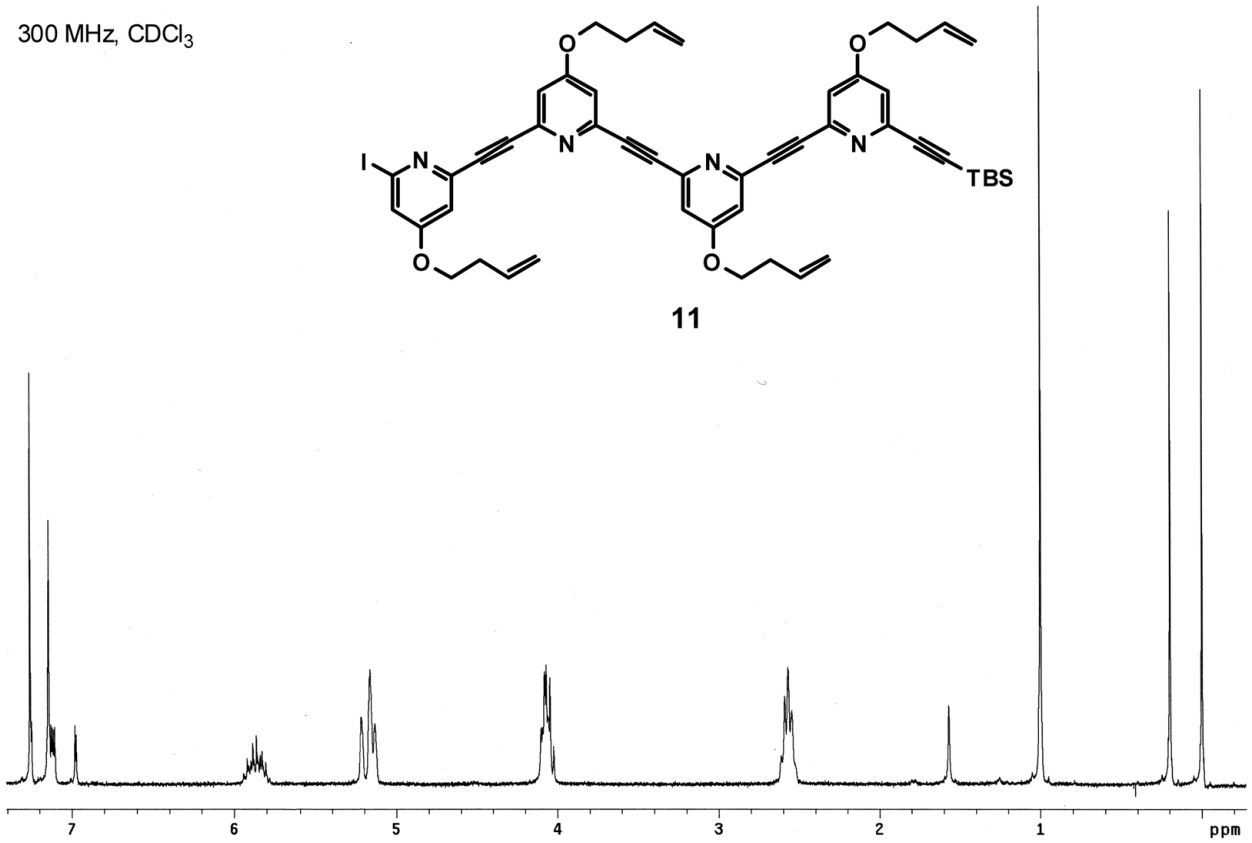


300 MHz, $CDCl_3$

9

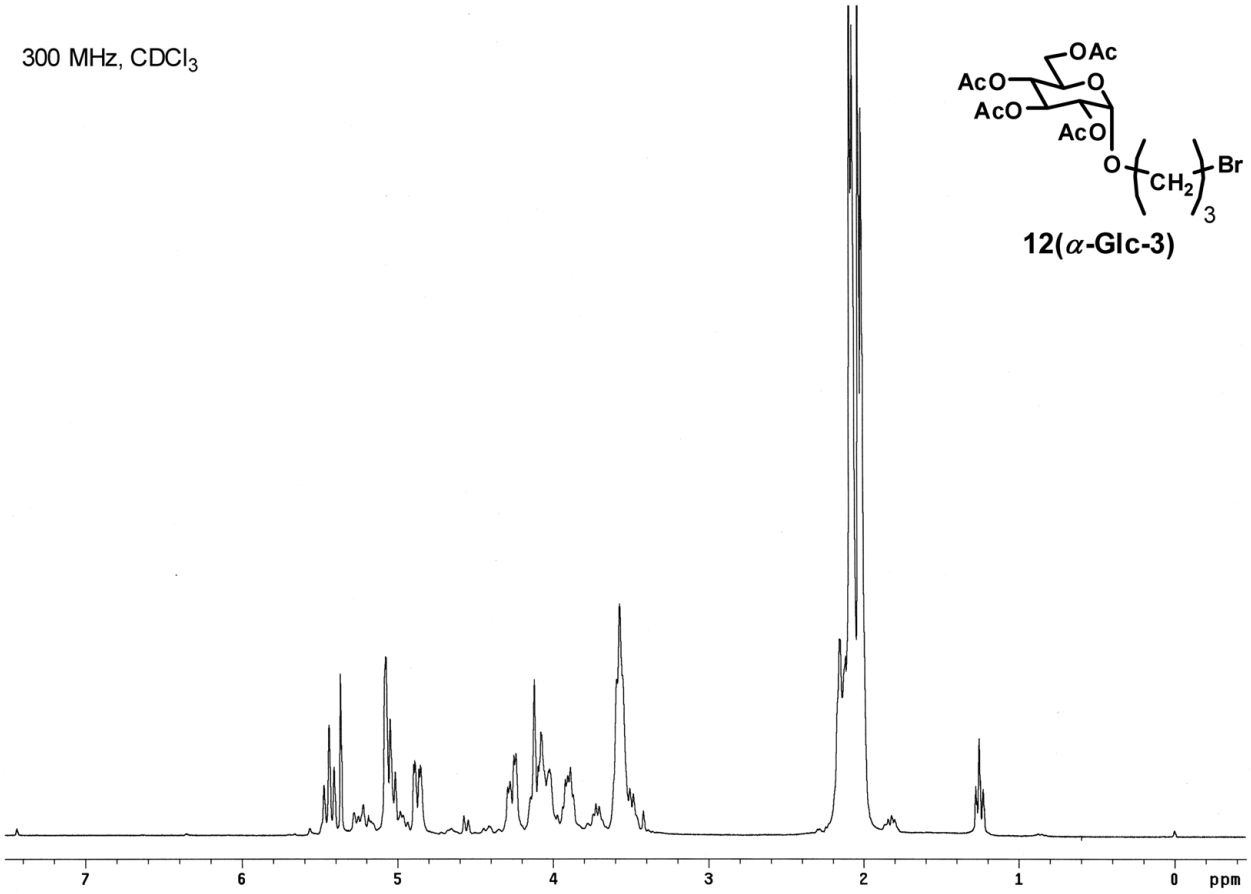



300 MHz, CDCl3
10
7
6
5
4
3
2
1
ppm


300 MHz, CDCl3
TBS
11
7
6
5
4
3
2
1
ppm

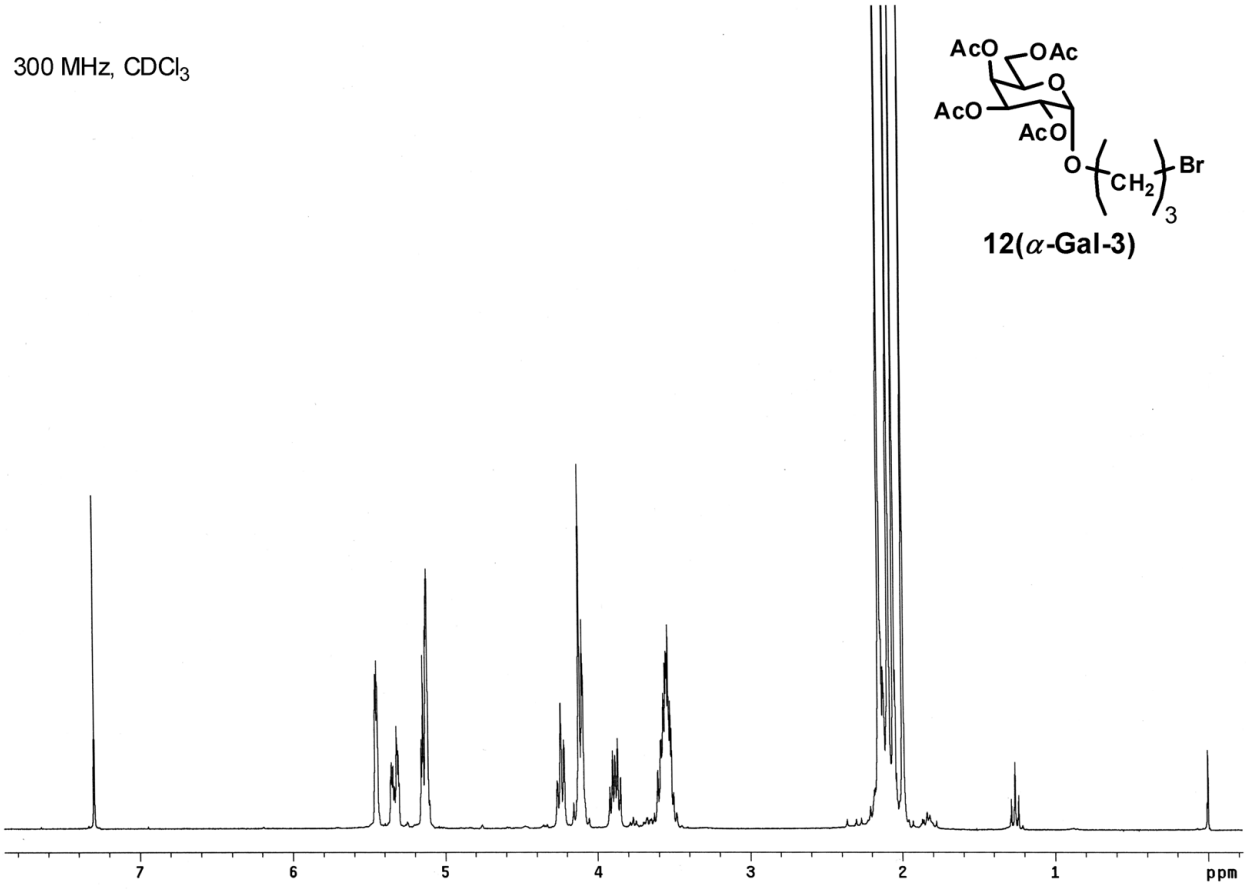
300 MHz, $CDCl_3$

12(α-Glc-3)



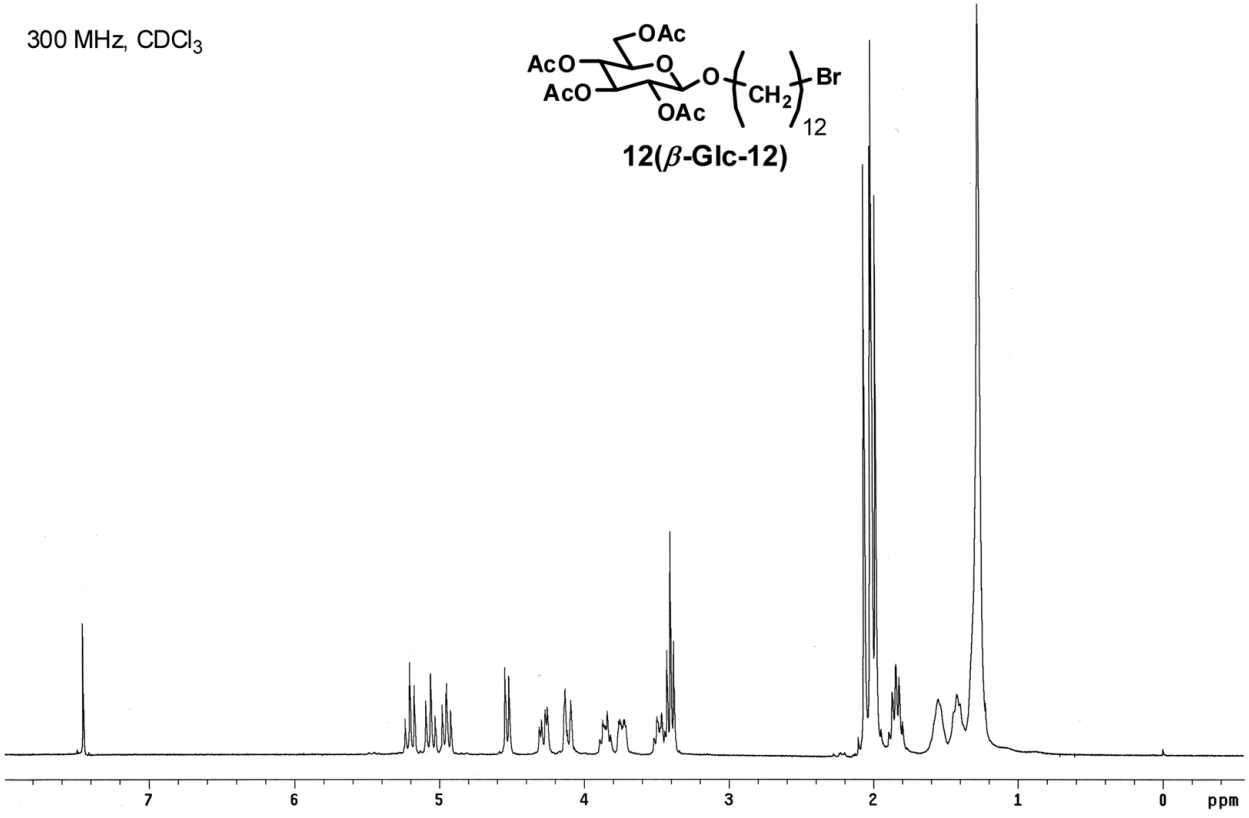
300 MHz, $CDCl_3$

12(α-Gal-3)

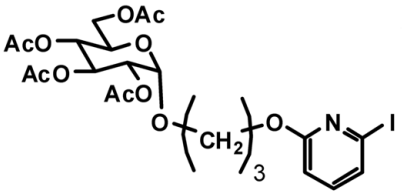


300 MHz, $CDCl_3$

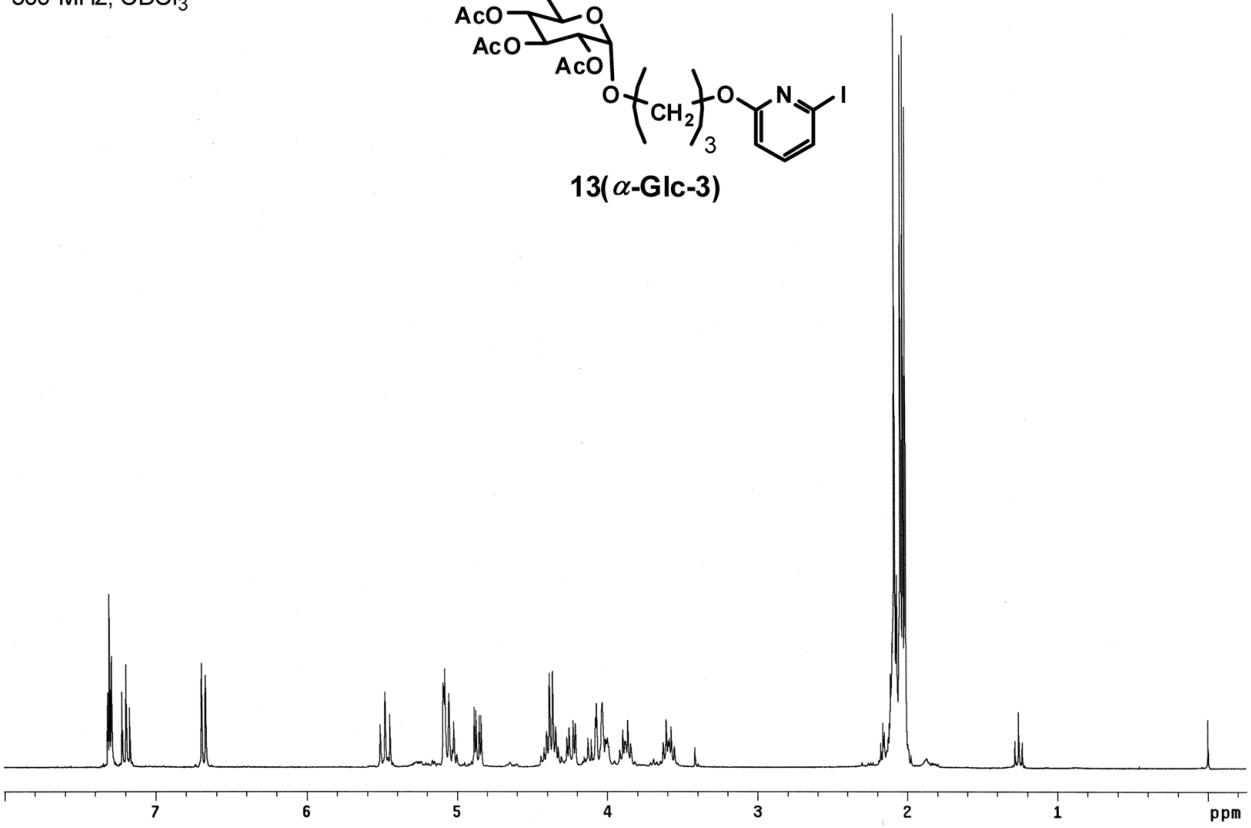
12(β-Glc-12)



300 MHz, $CDCl_3$

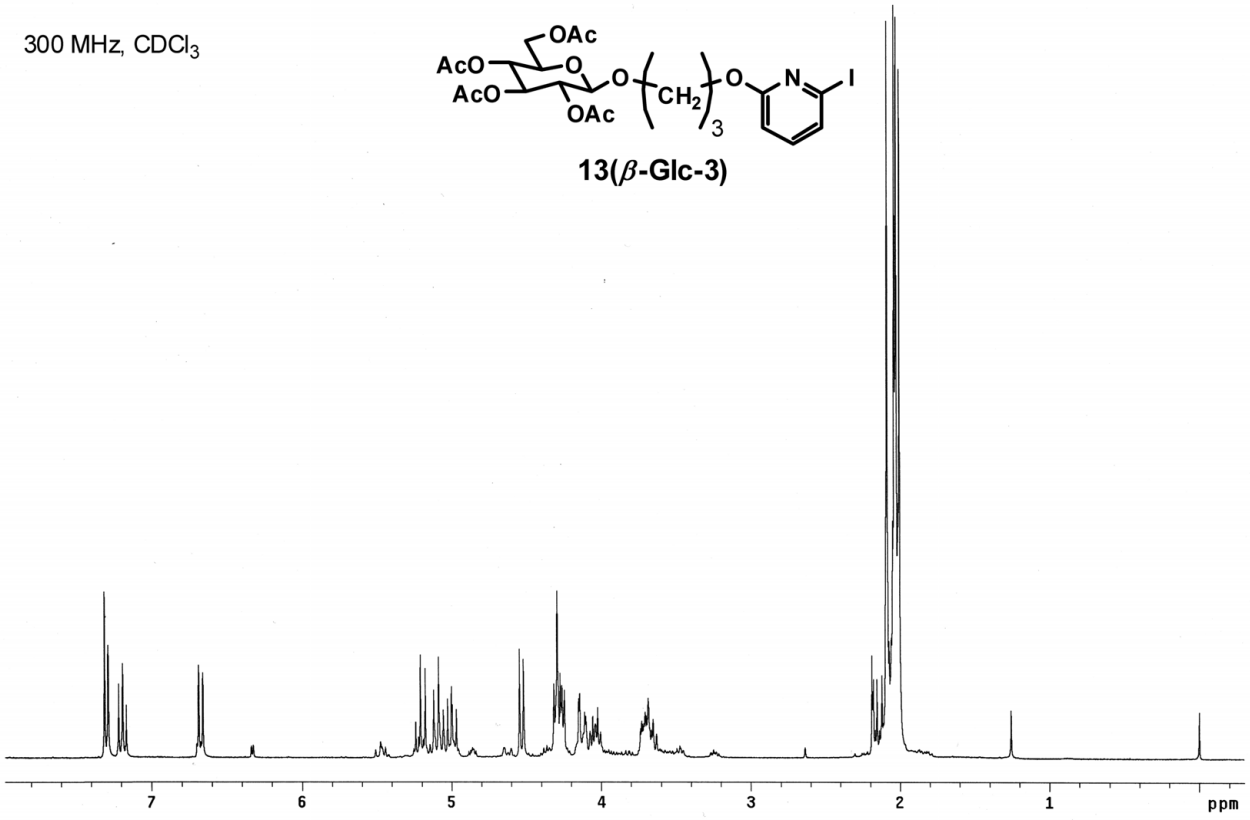


13(α-Glc-3)



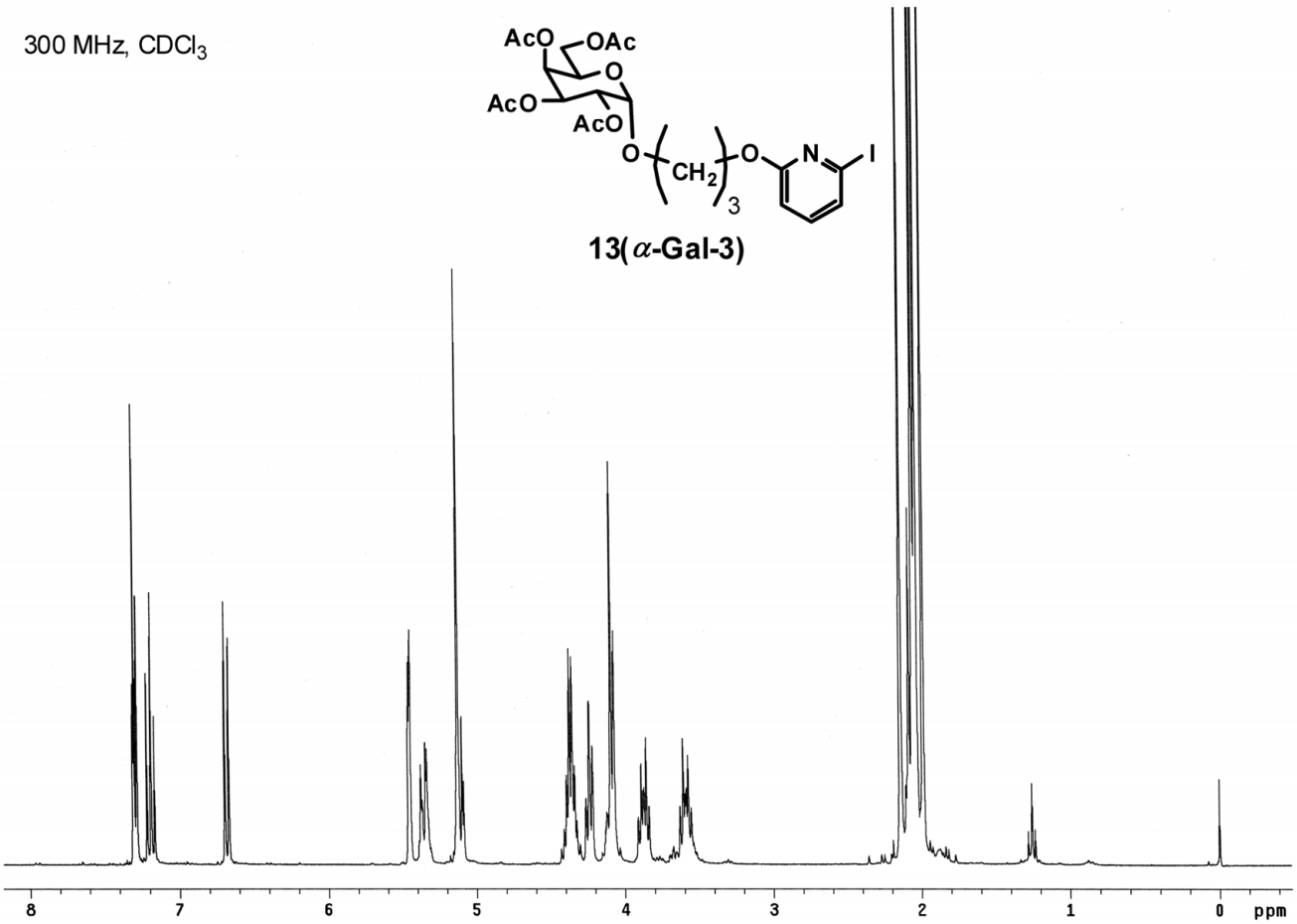
300 MHz, $CDCl_3$

13(β-Glc-3)



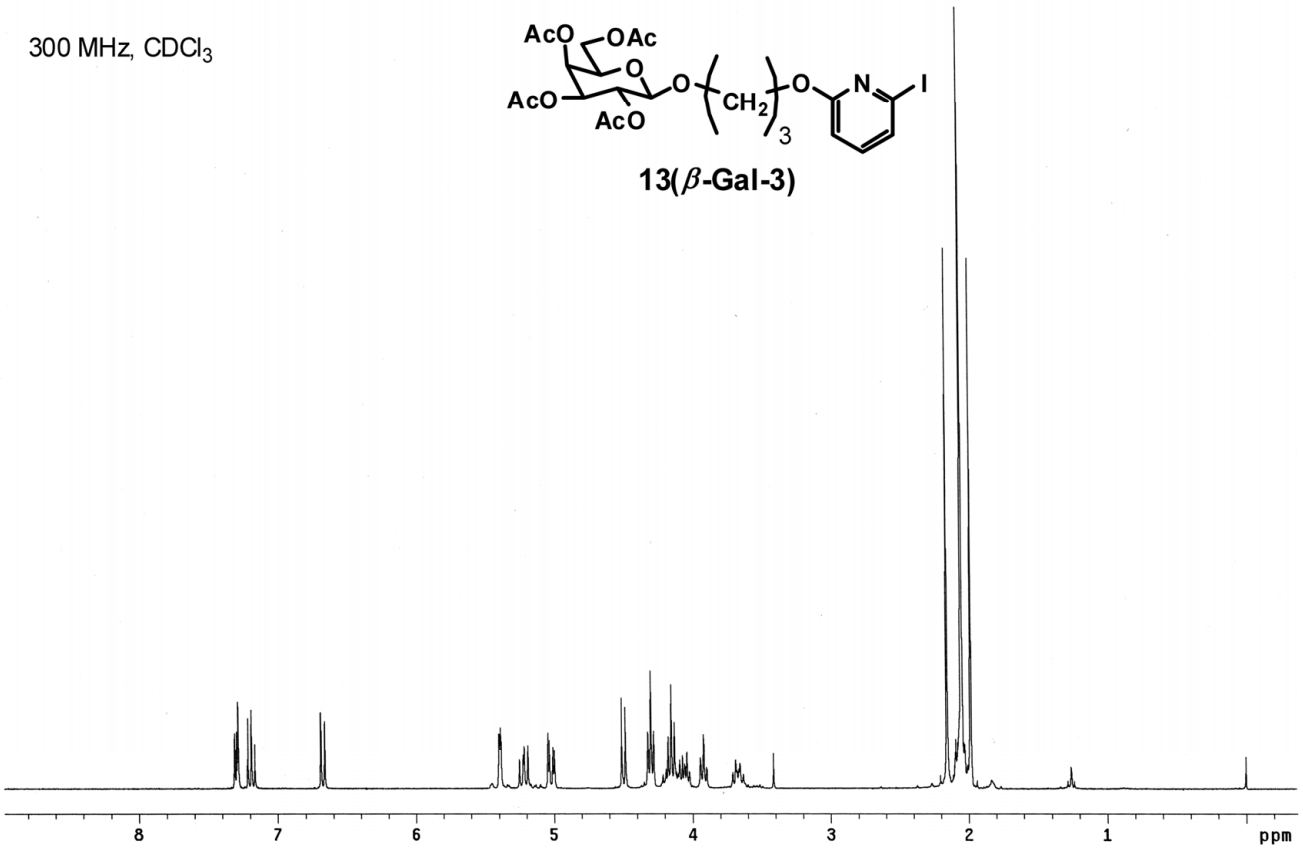
300 MHz, $CDCl_3$

13(α-Gal-3)



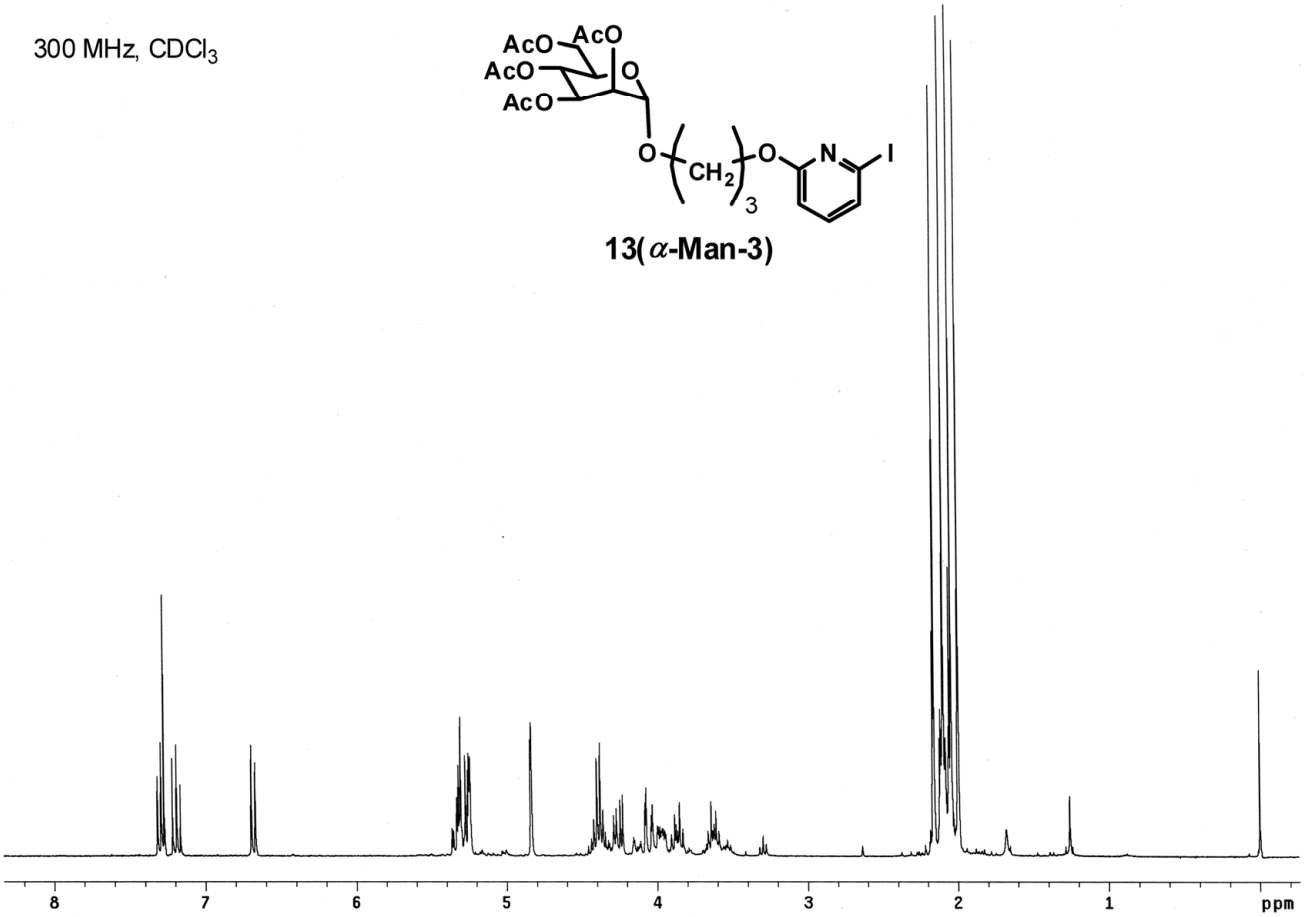
300 MHz, $CDCl_3$

13(β-Gal-3)



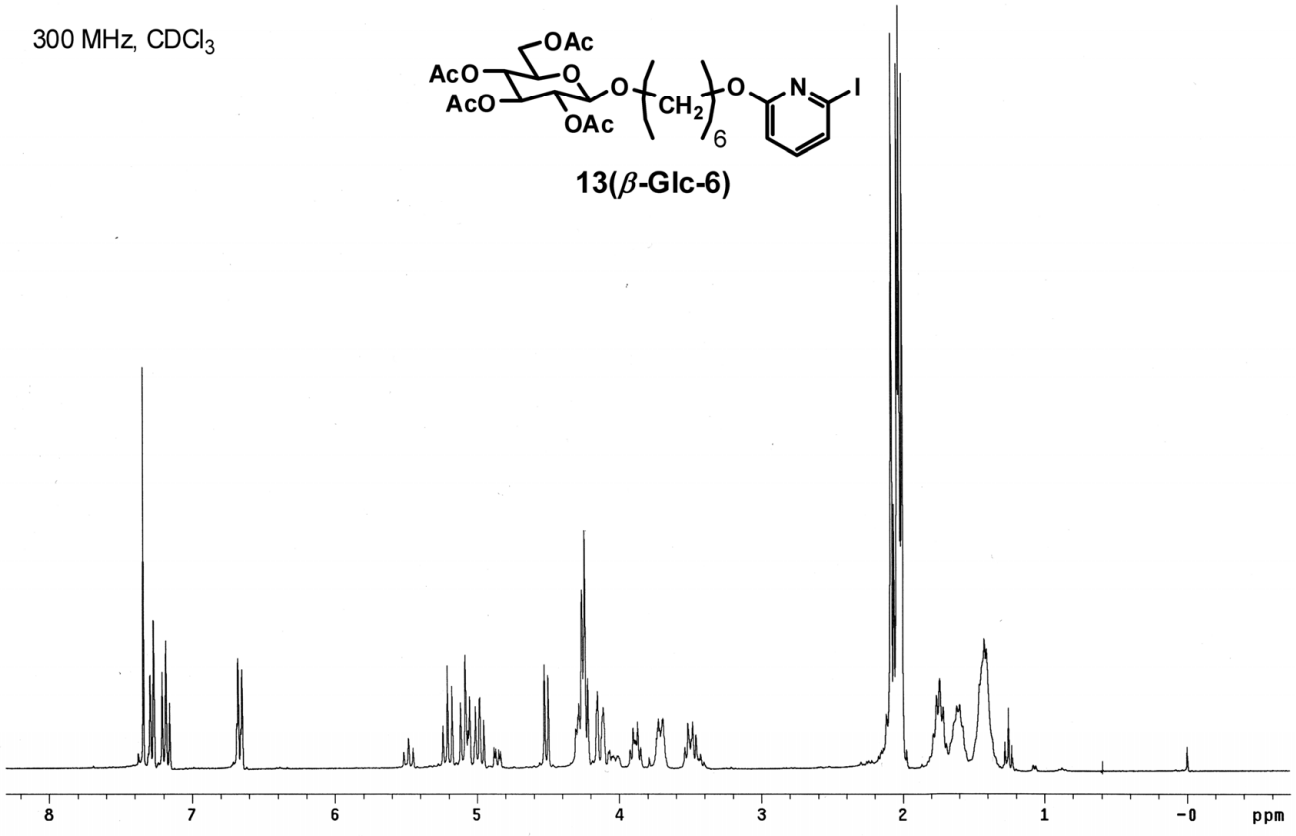
300 MHz, $CDCl_3$

13(α-Man-3)



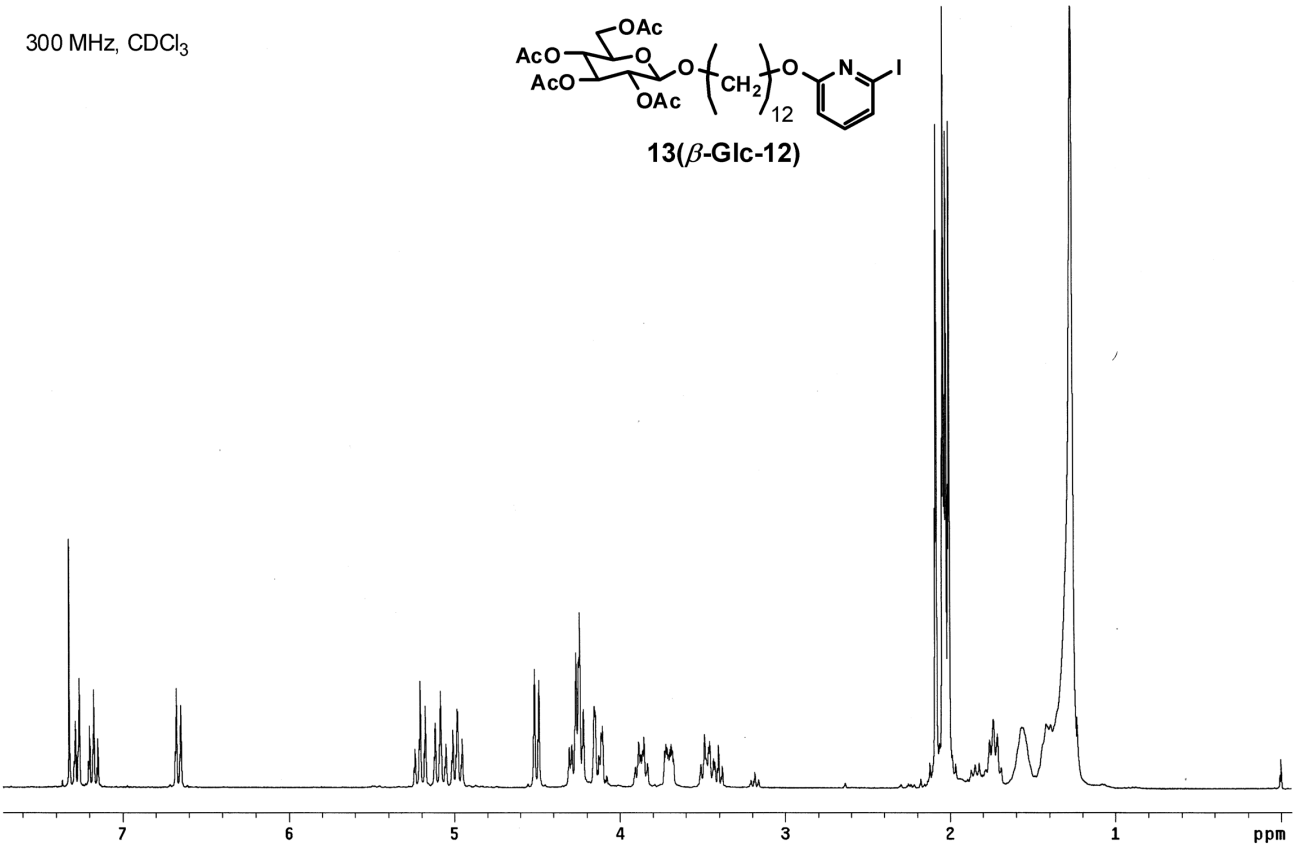
300 MHz, $CDCl_3$

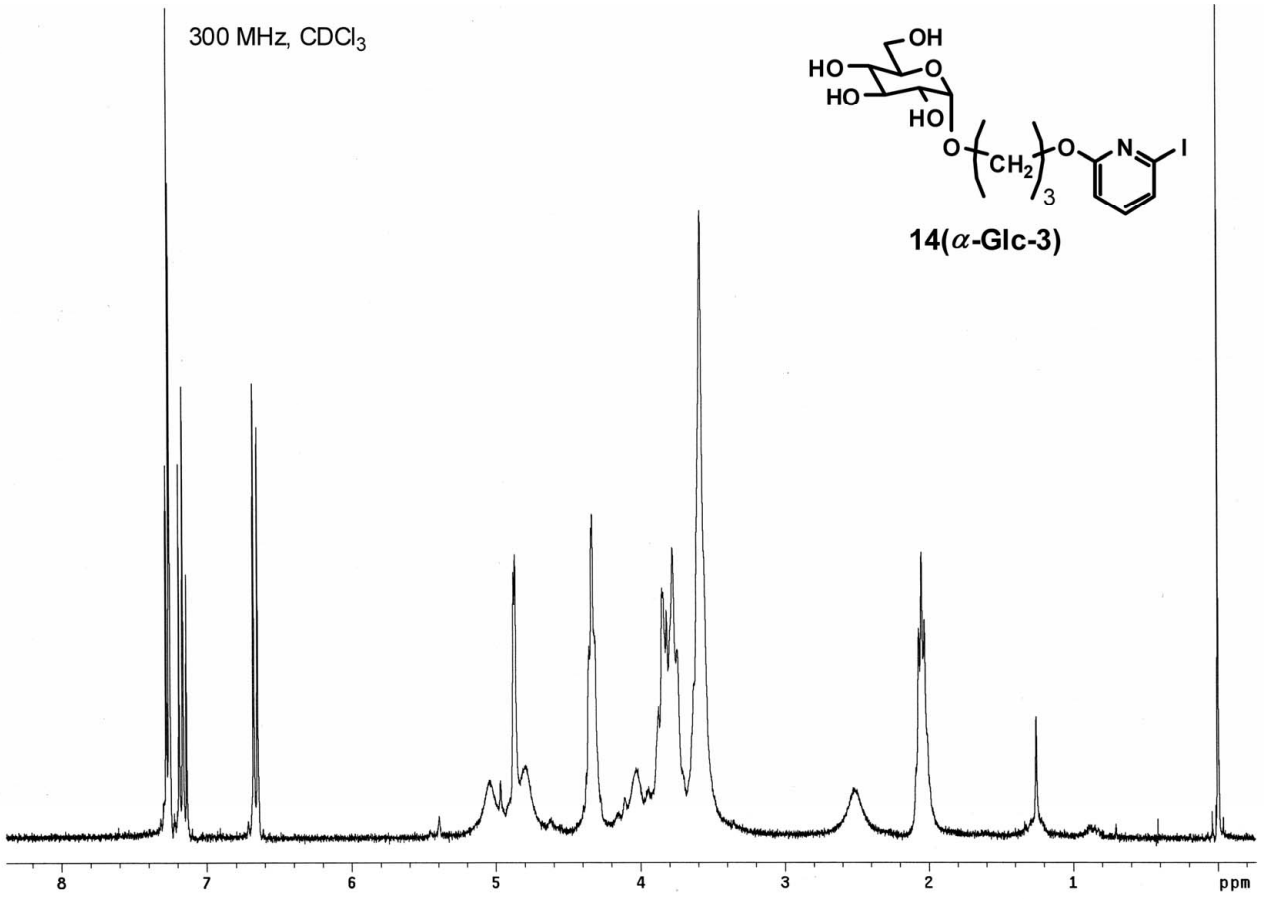
13(β-Glc-6)

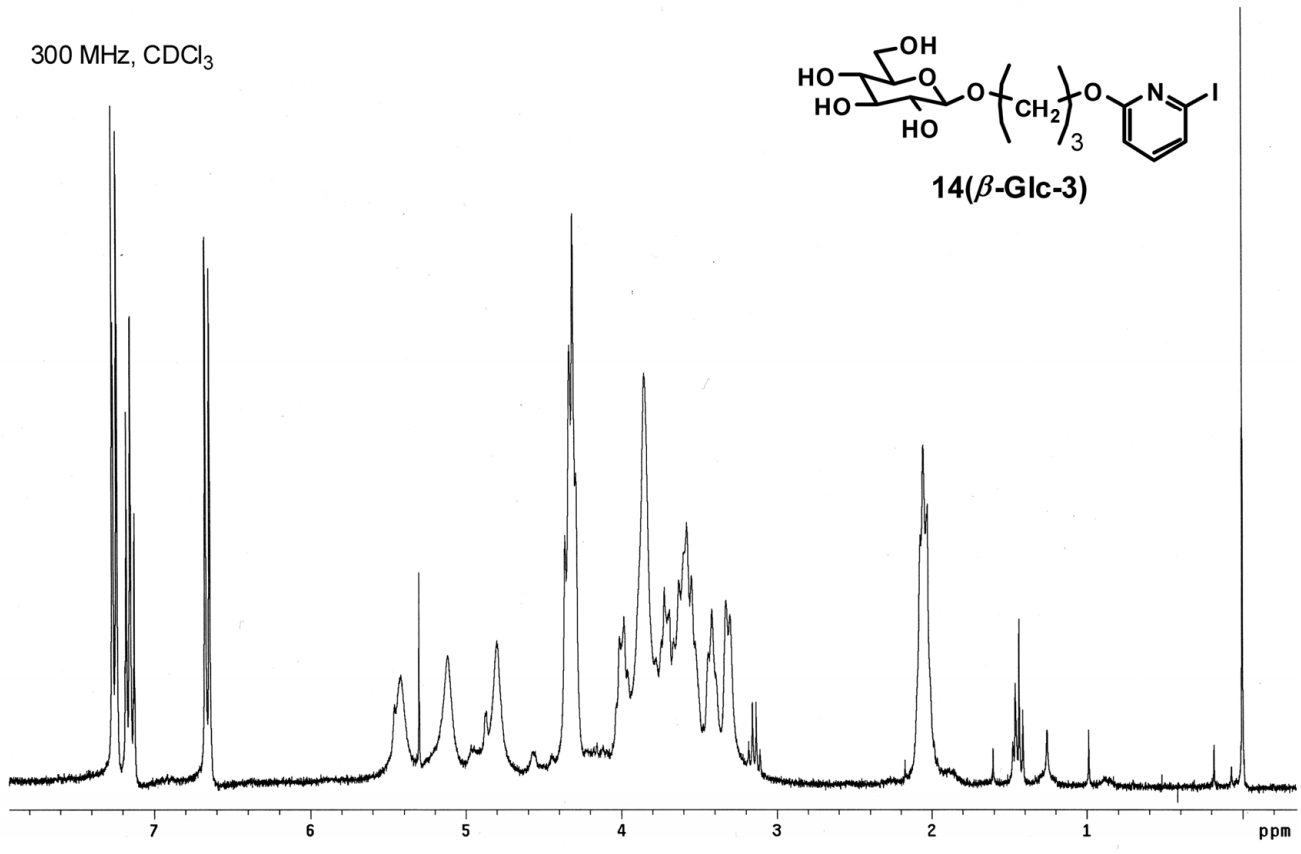


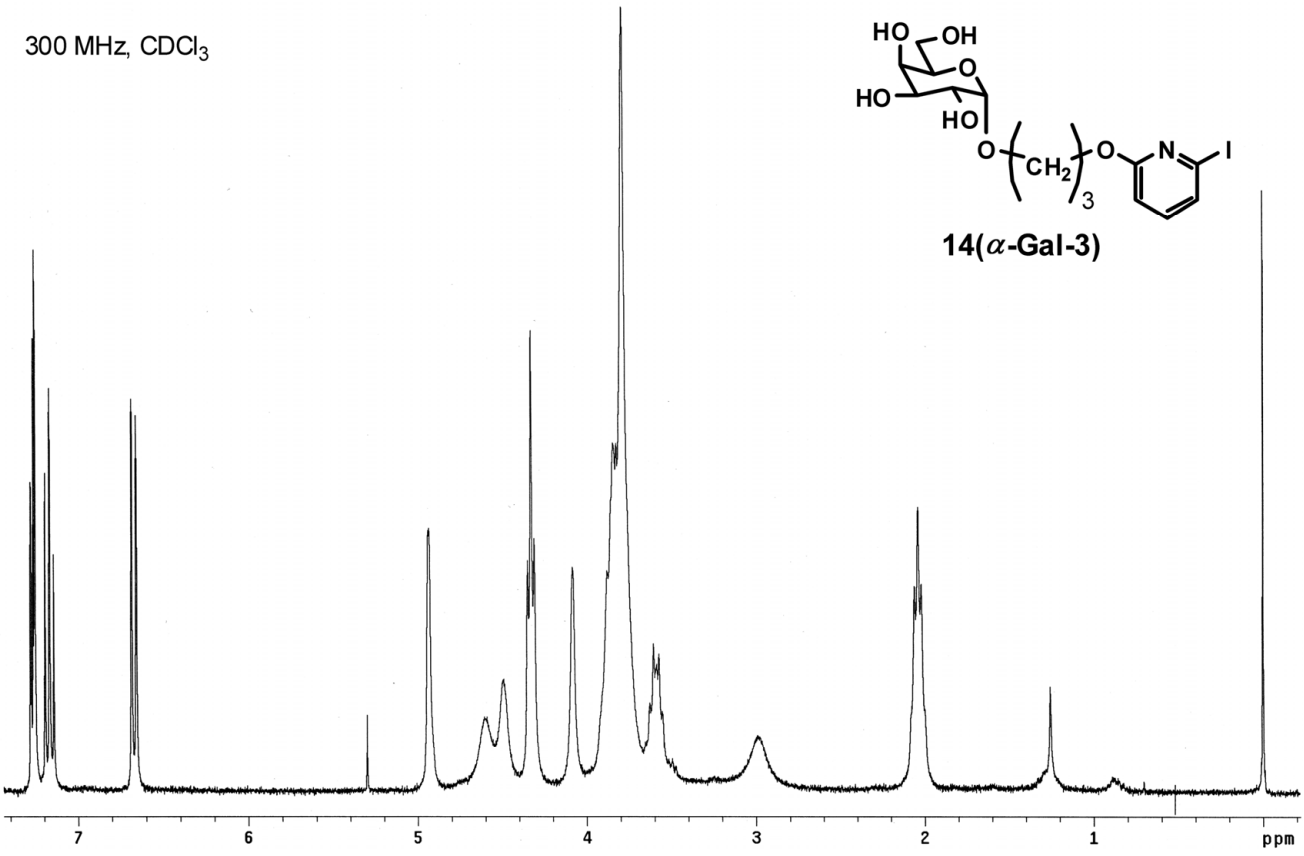
300 MHz, $CDCl_3$

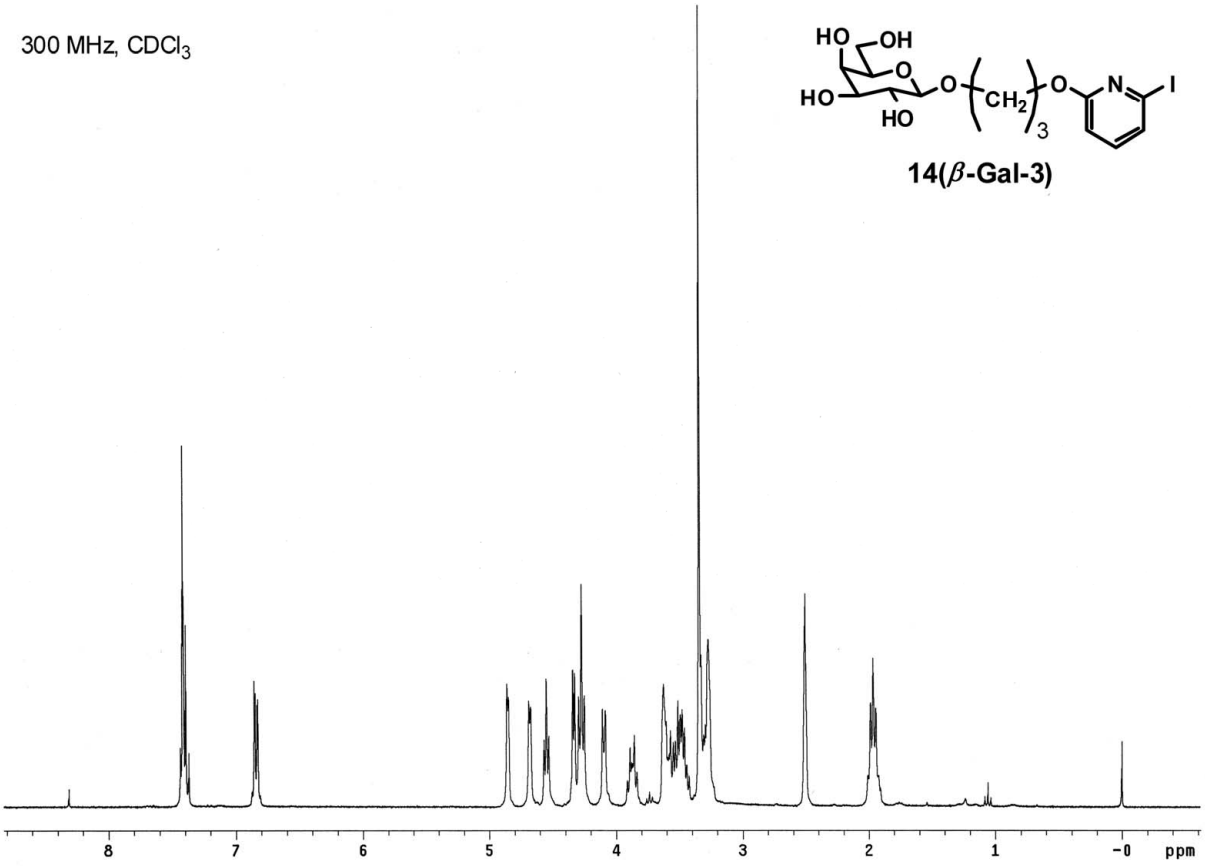
13(β-Glc-12)



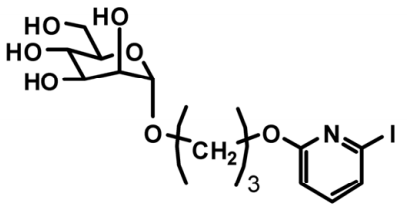

300 MHz, CDCl3
OH
HO
O
HO
HO
O
CH2
3
O
N
I
14(α-Glc-3)
8
7
6
5
4
3
2
1
ppm


300 MHz, CDCl3
OH
HO
O
HO
HO
O
CH2
3
O
N
I
14(β-Glc-3)
7
6
5
4
3
2
1
ppm

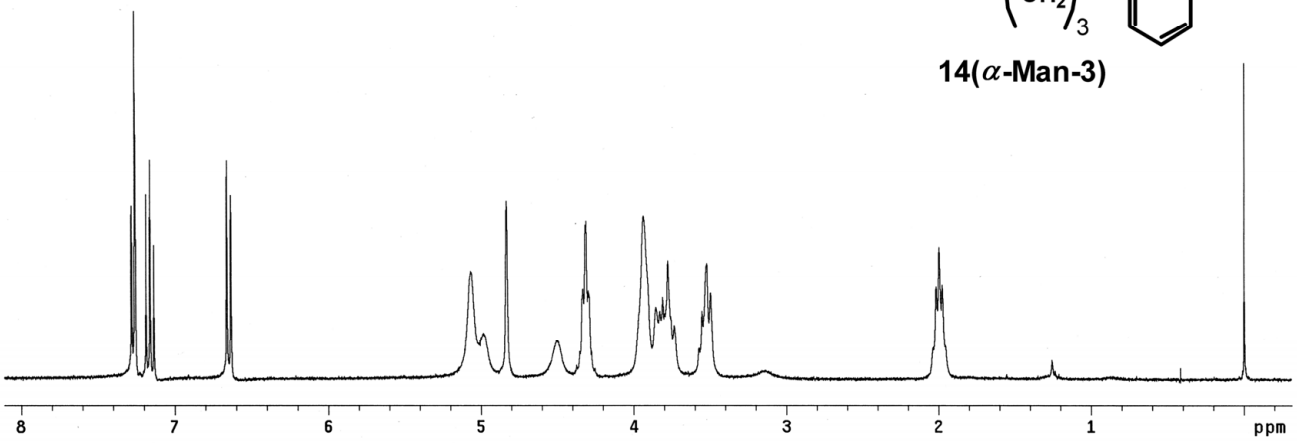

300 MHz, CDCl3
HO
OH
O
HO
HO
O
CH2
3
O
N
I
14(α-Gal-3)
7
6
5
4
3
2
1
ppm


300 MHz, CDCl3
HO
OH
O
HO
HO
O
CH2
3
O
N
I
14(β-Gal-3)
8
7
6
5
4
3
2
1
-0
ppm

300 MHz, $CDCl_3$

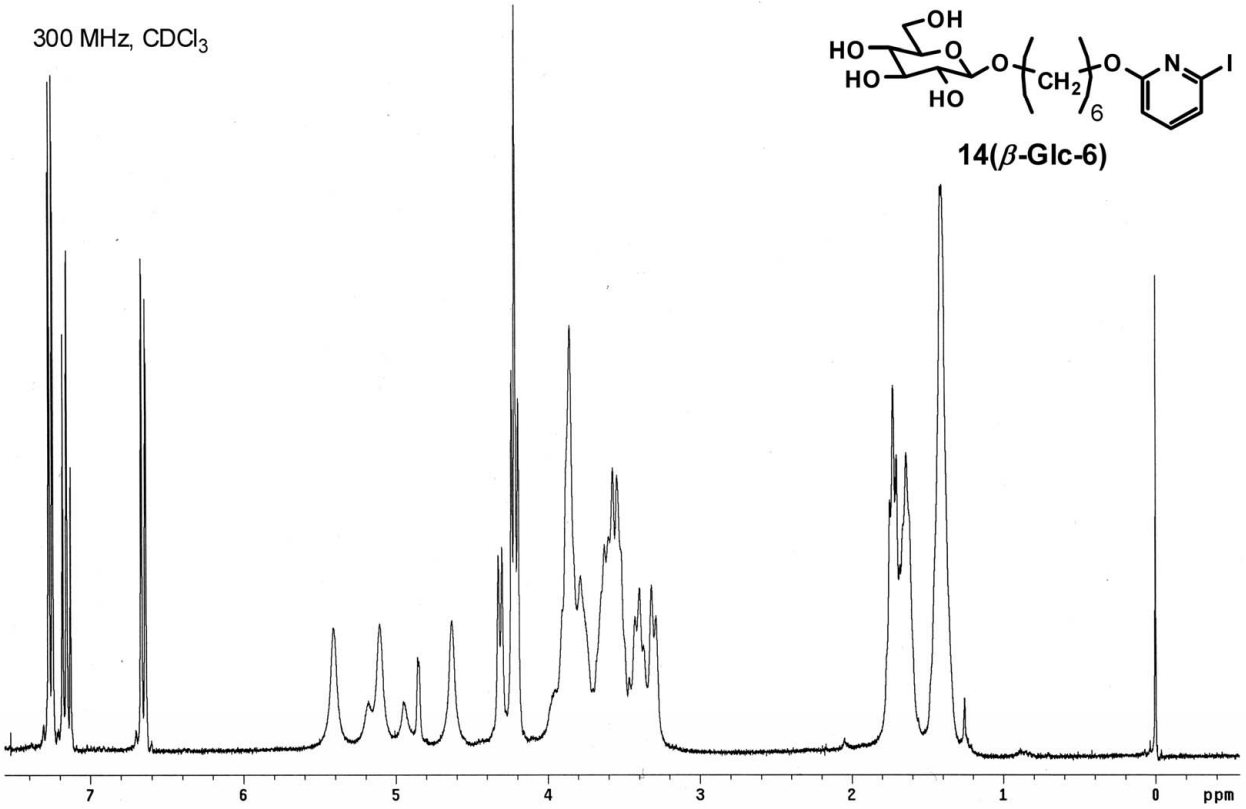


14(α-Man-3)



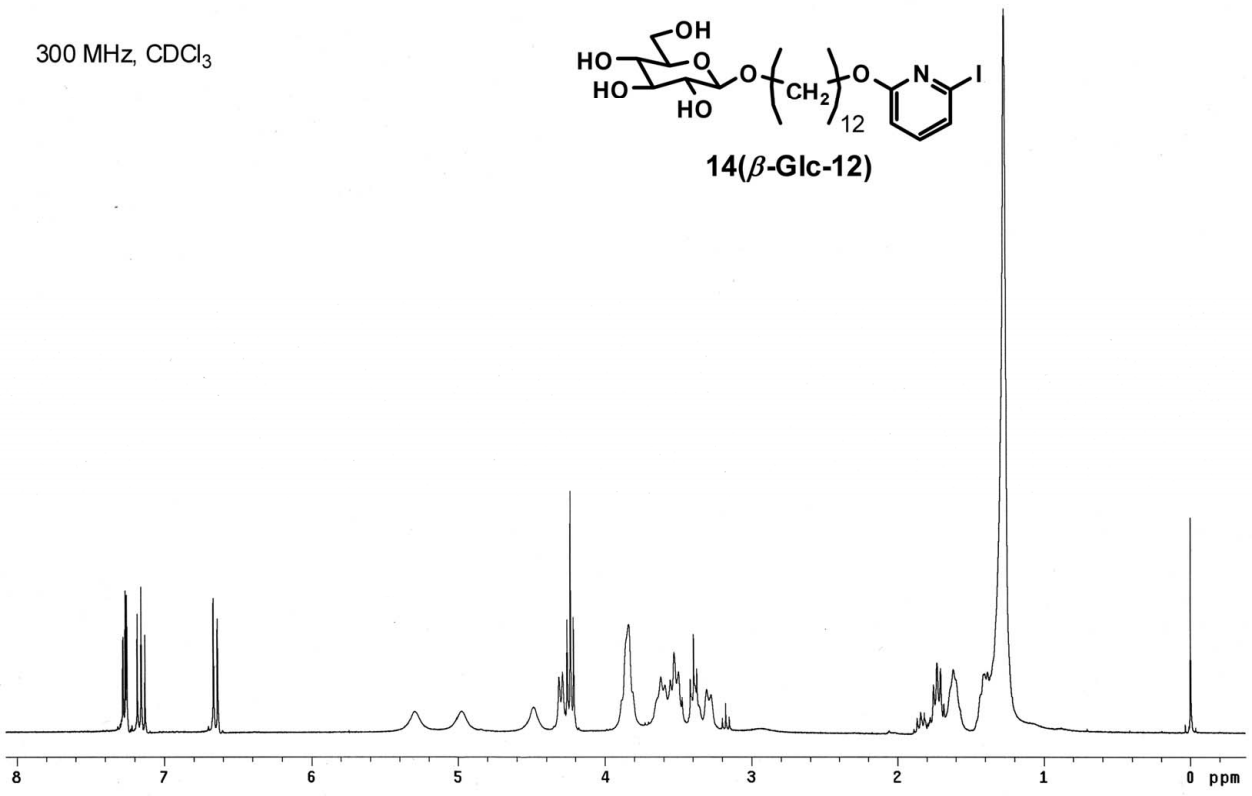
300 MHz, $CDCl_3$

14(β-Glc-6)



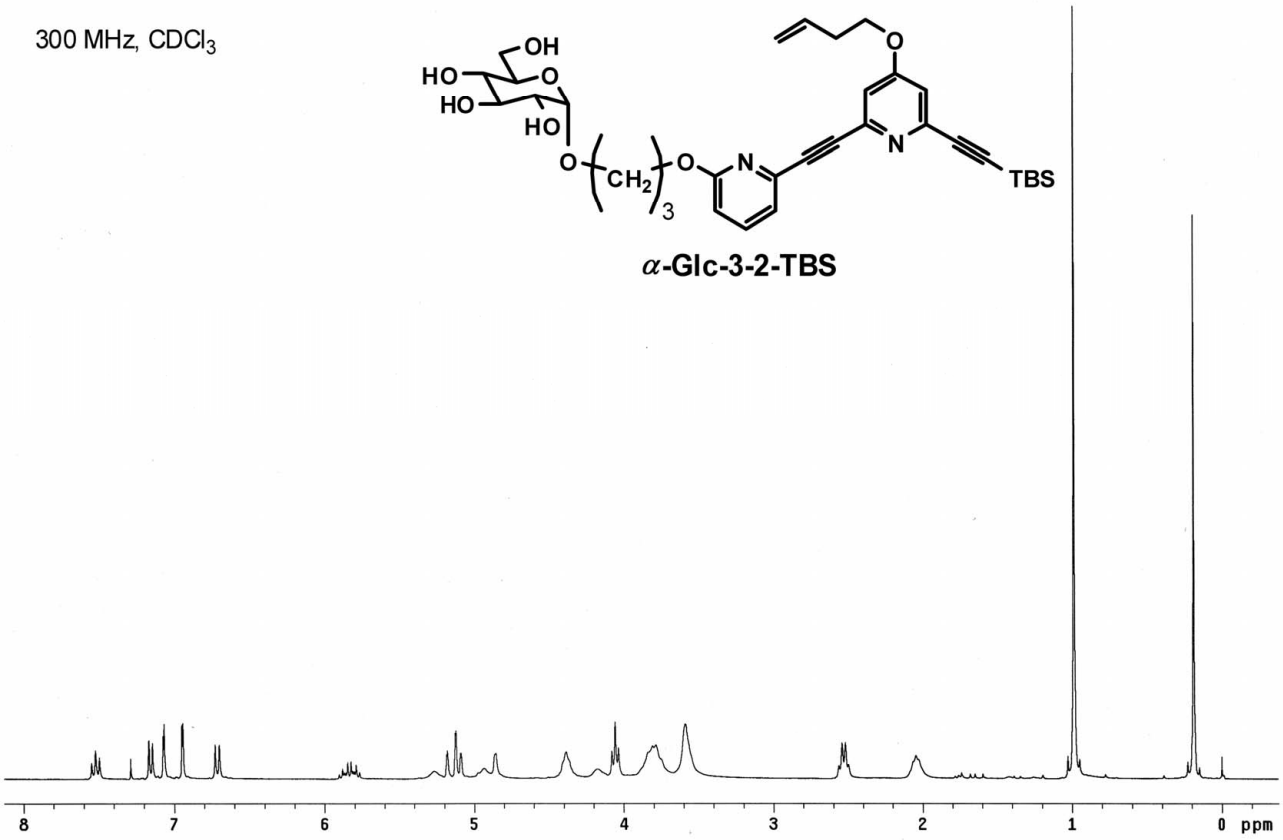
300 MHz, $CDCl_3$

14(β-Glc-12)



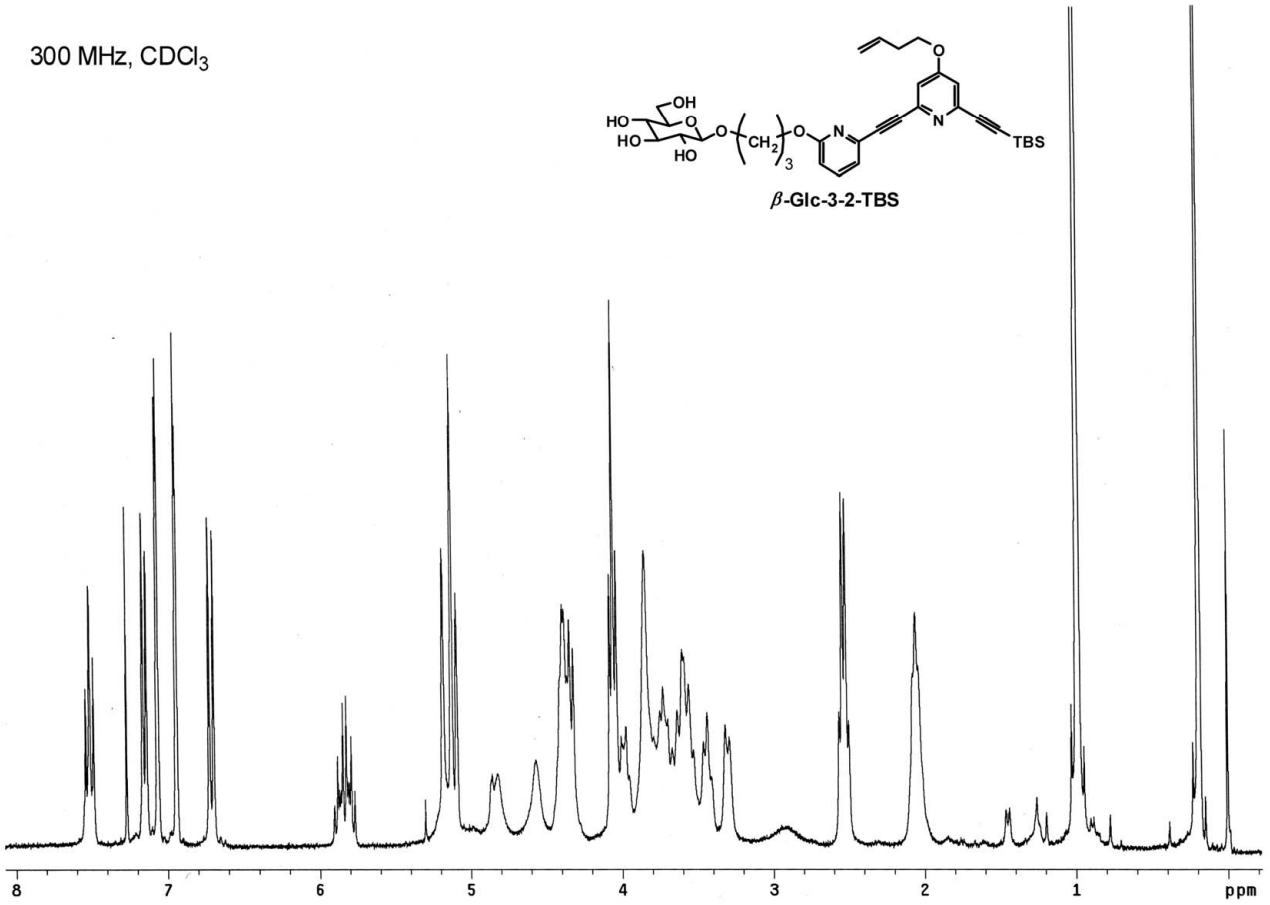
300 MHz, $CDCl_3$

α-Glc-3-2-TBS



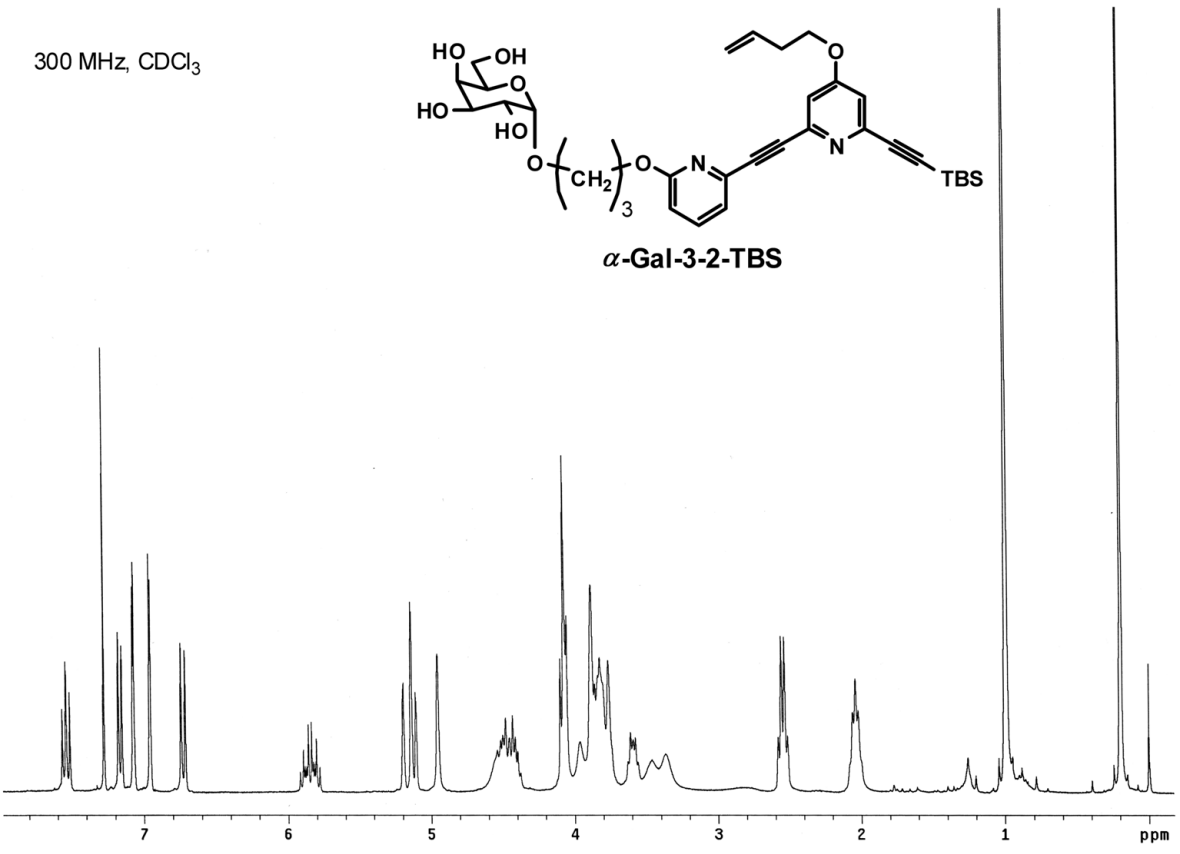
300 MHz, $CDCl_3$

β-Glc-3-2-TBS



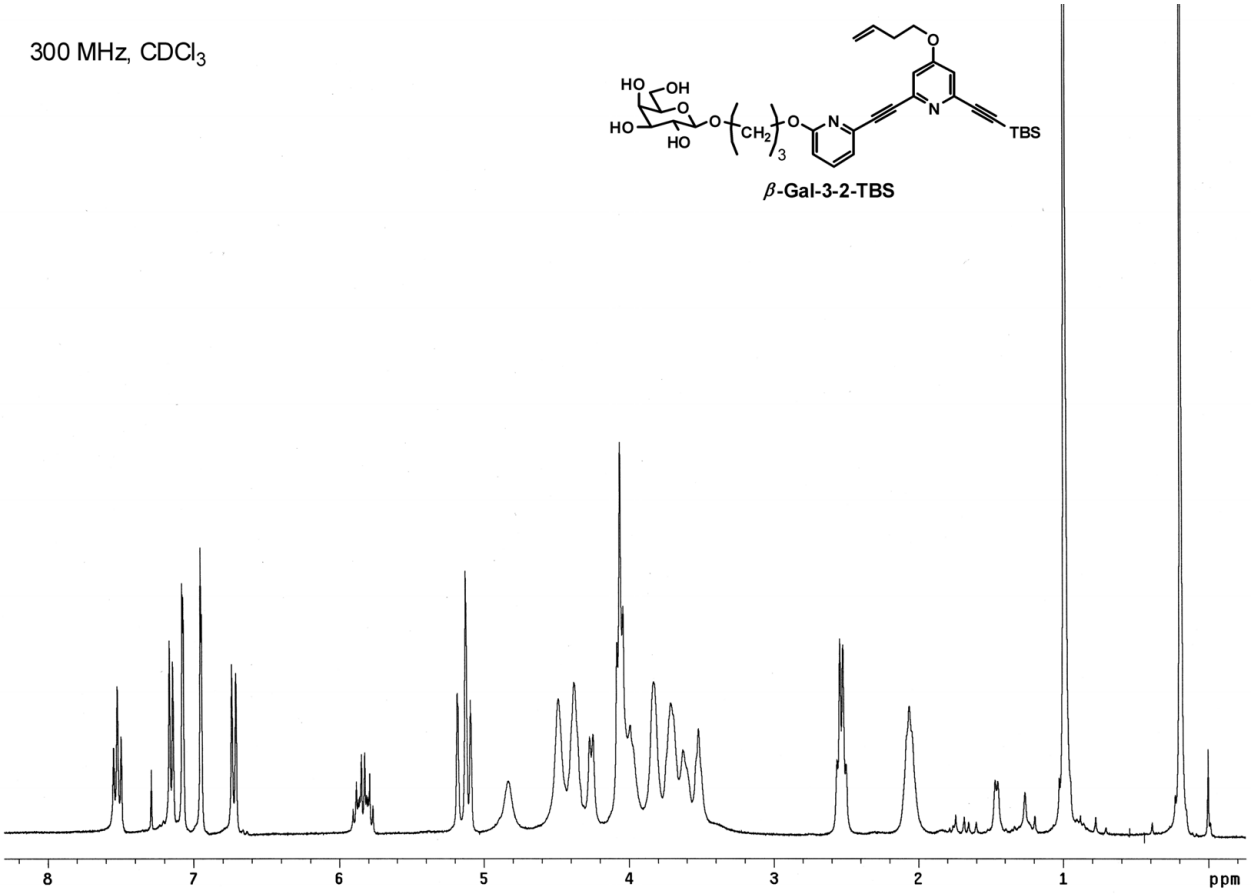
300 MHz, $CDCl_3$

α-Gal-3-2-TBS



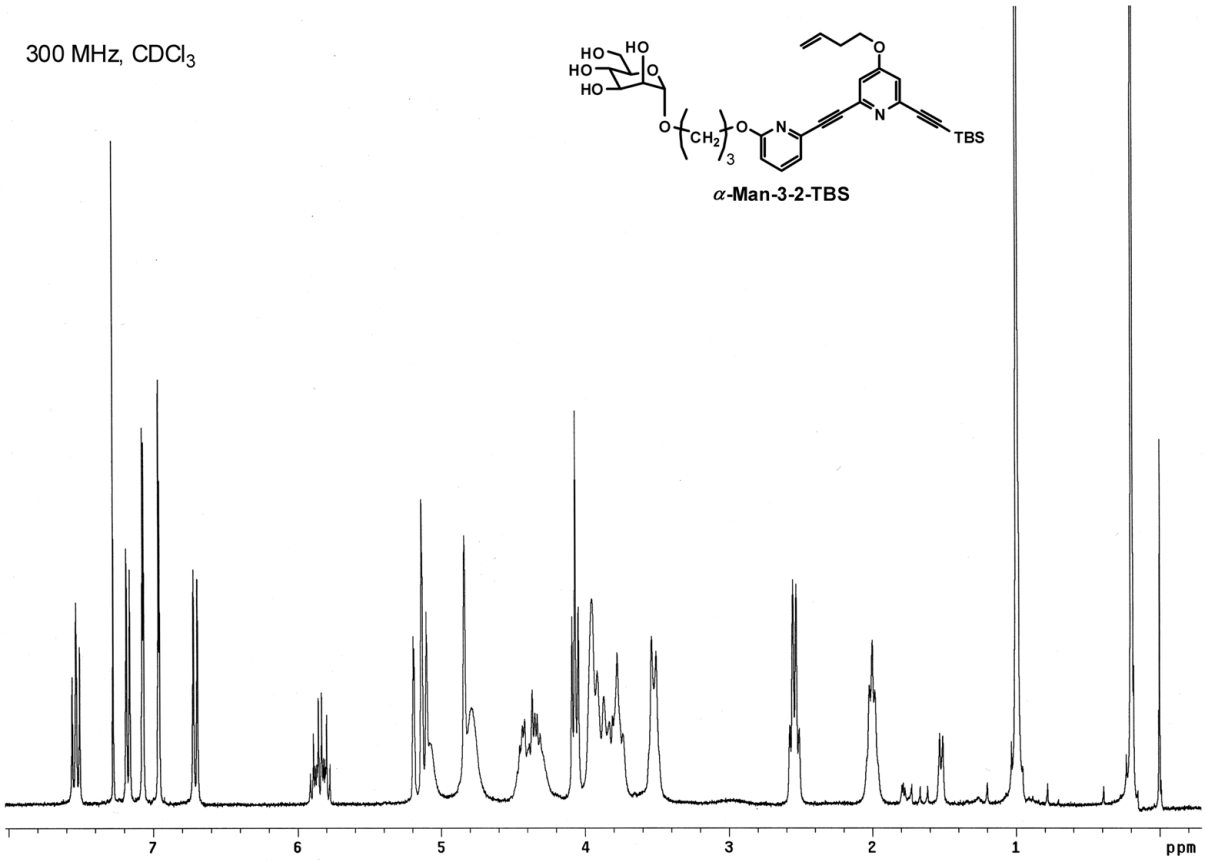
300 MHz, $CDCl_3$

β-Gal-3-2-TBS

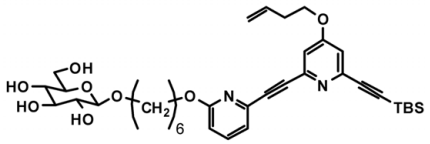


300 MHz, $CDCl_3$

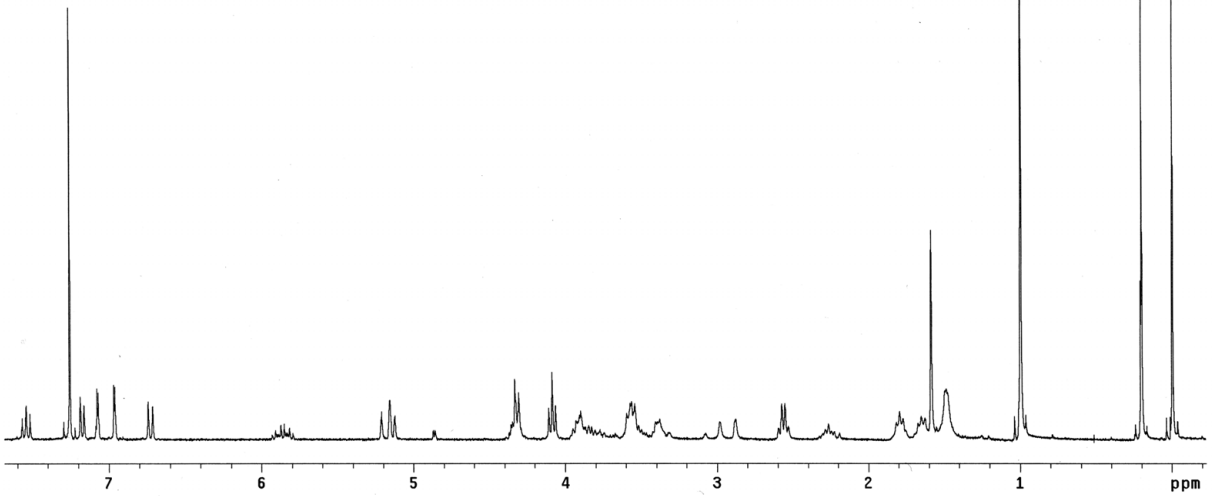
α-Man-3-2-TBS



300 MHz, $CDCl_3$

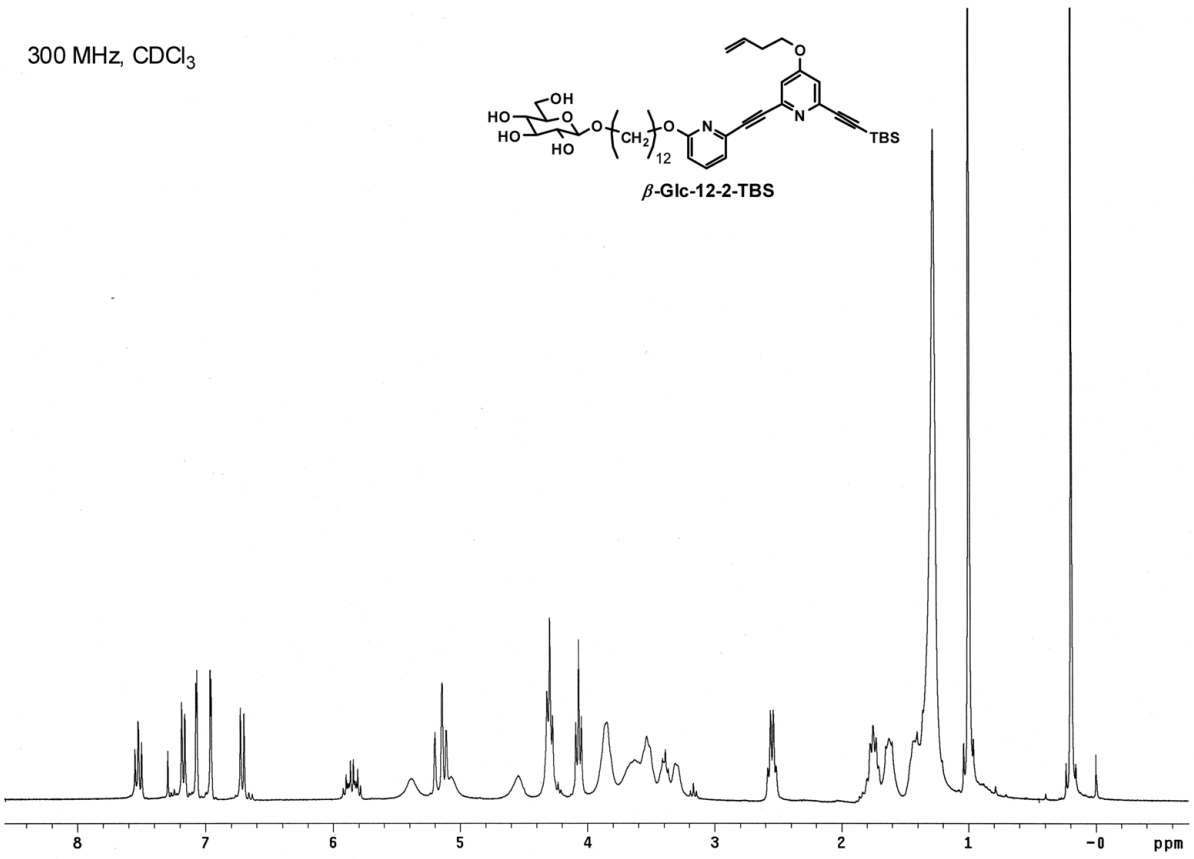


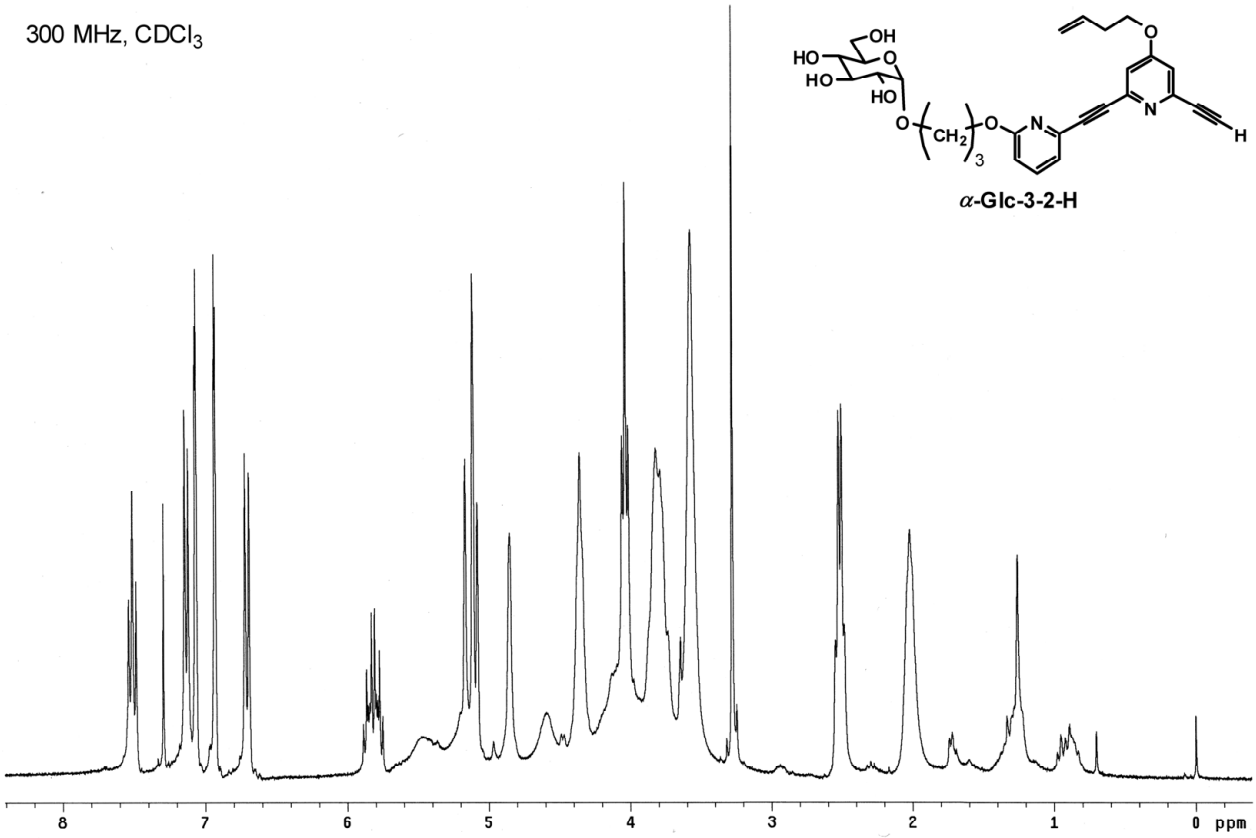
β-Glc-6-2-TBS



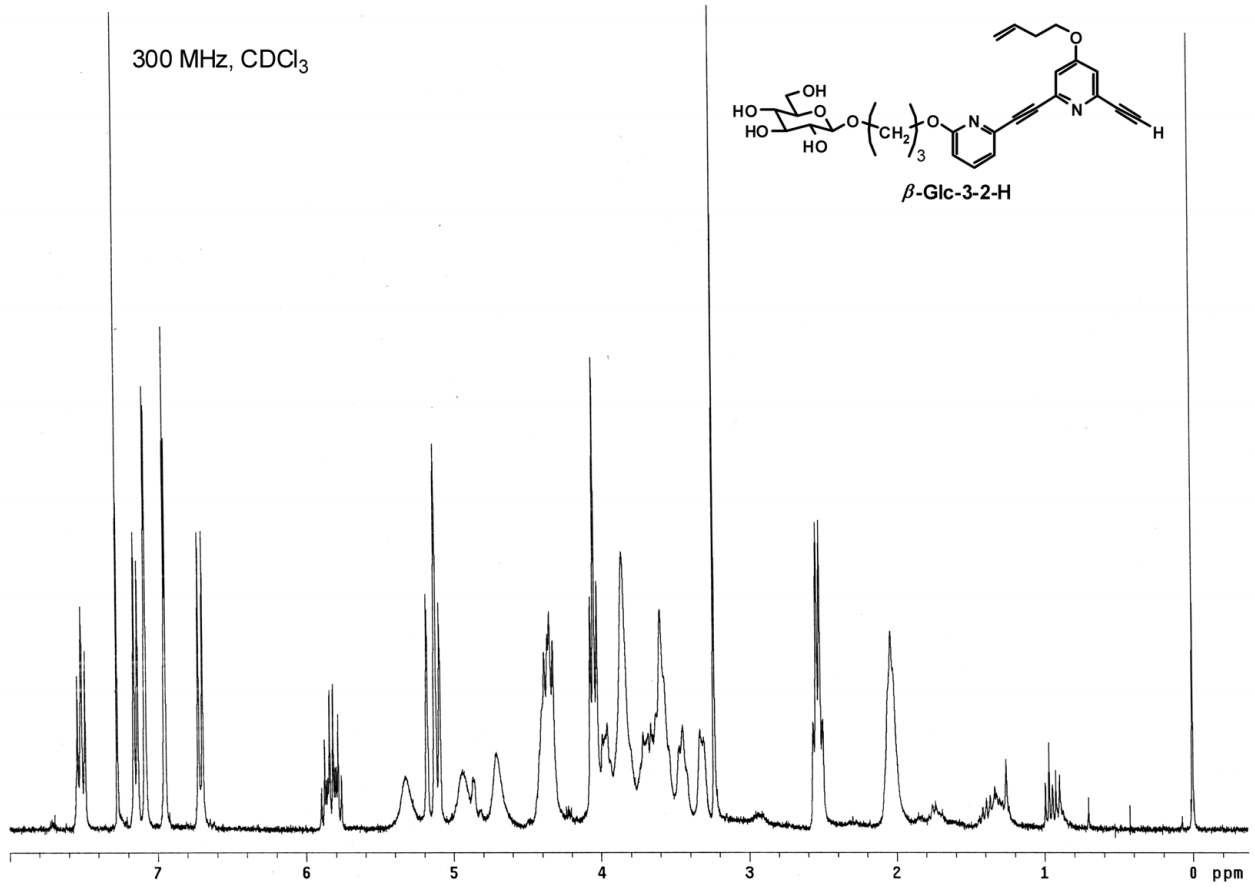
300 MHz, $CDCl_3$

β-Glc-12-2-TBS





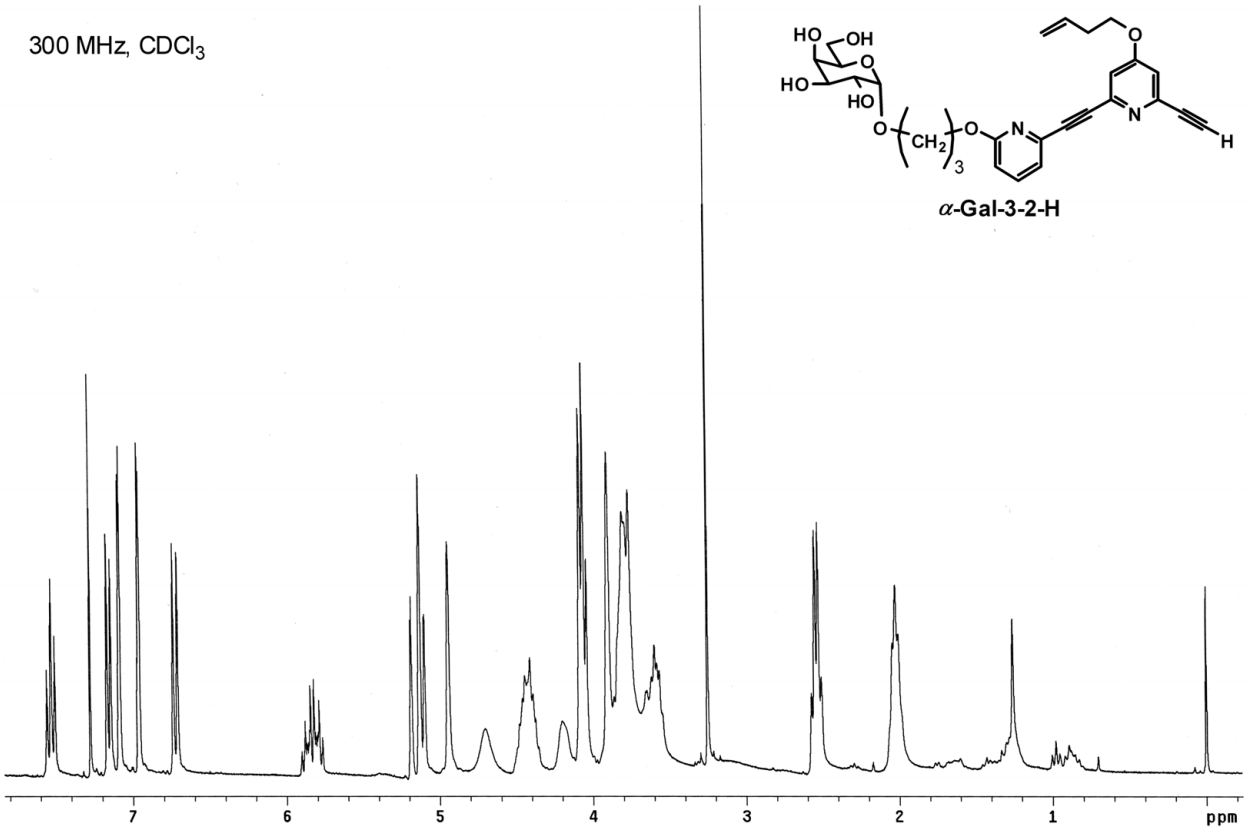
α-Glc-3-2-H



β-Glc-3-2-H

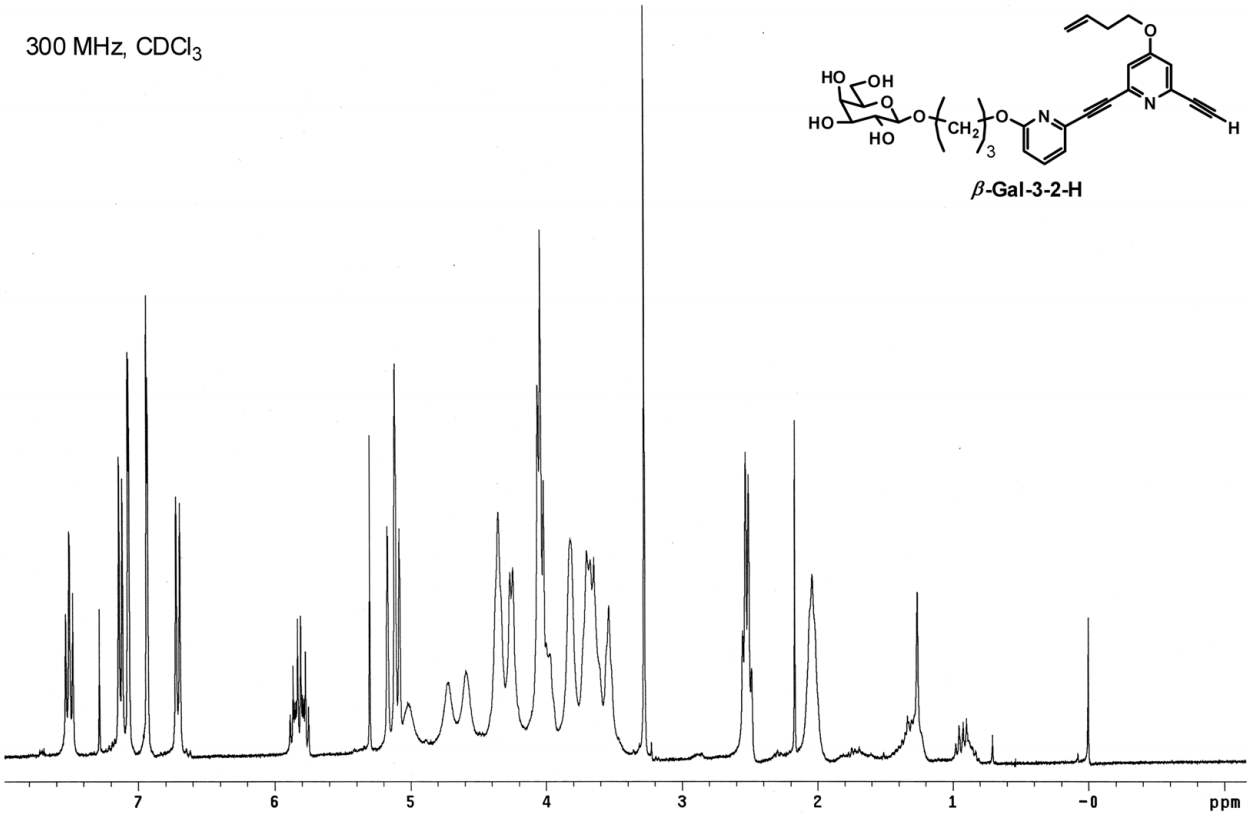
300 MHz, $CDCl_3$

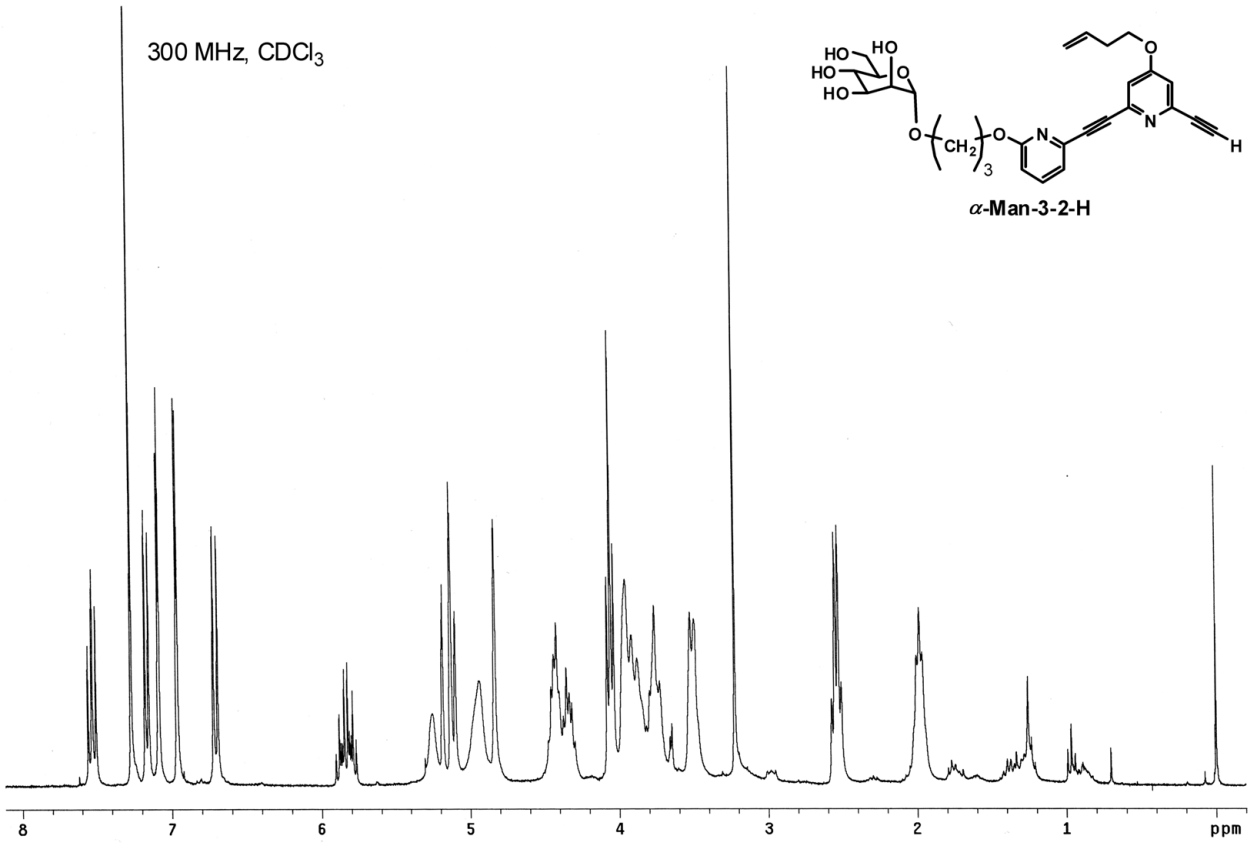
α-Gal-3-2-H

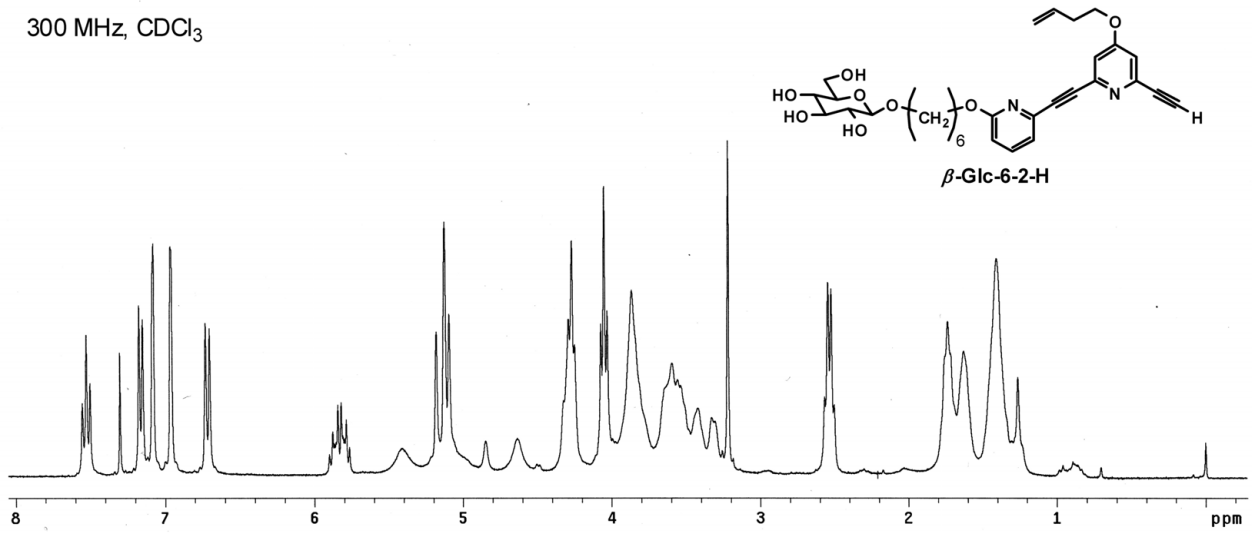


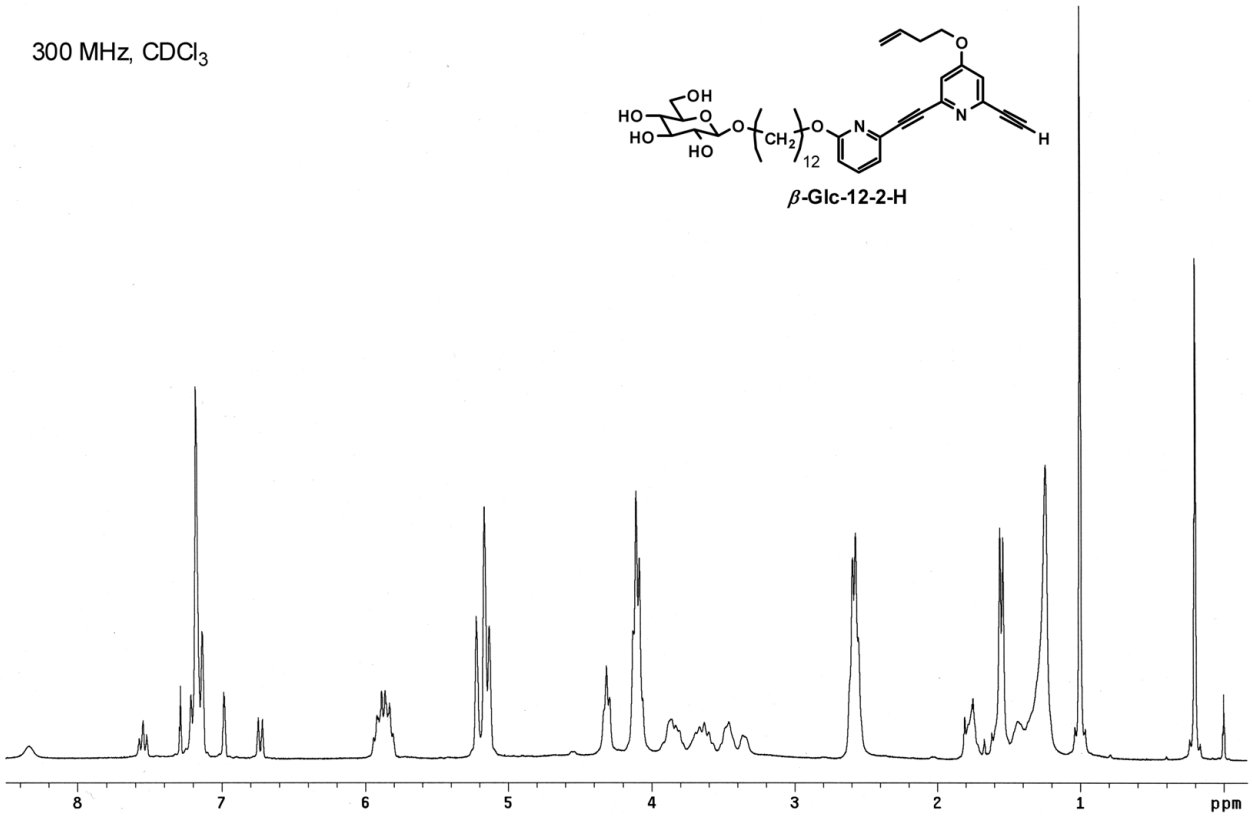
300 MHz, $CDCl_3$

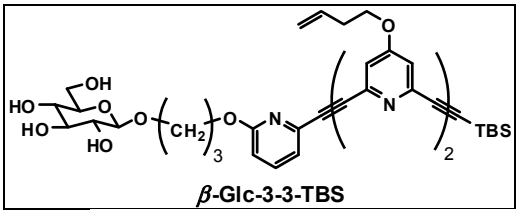
β-Gal-3-2-H



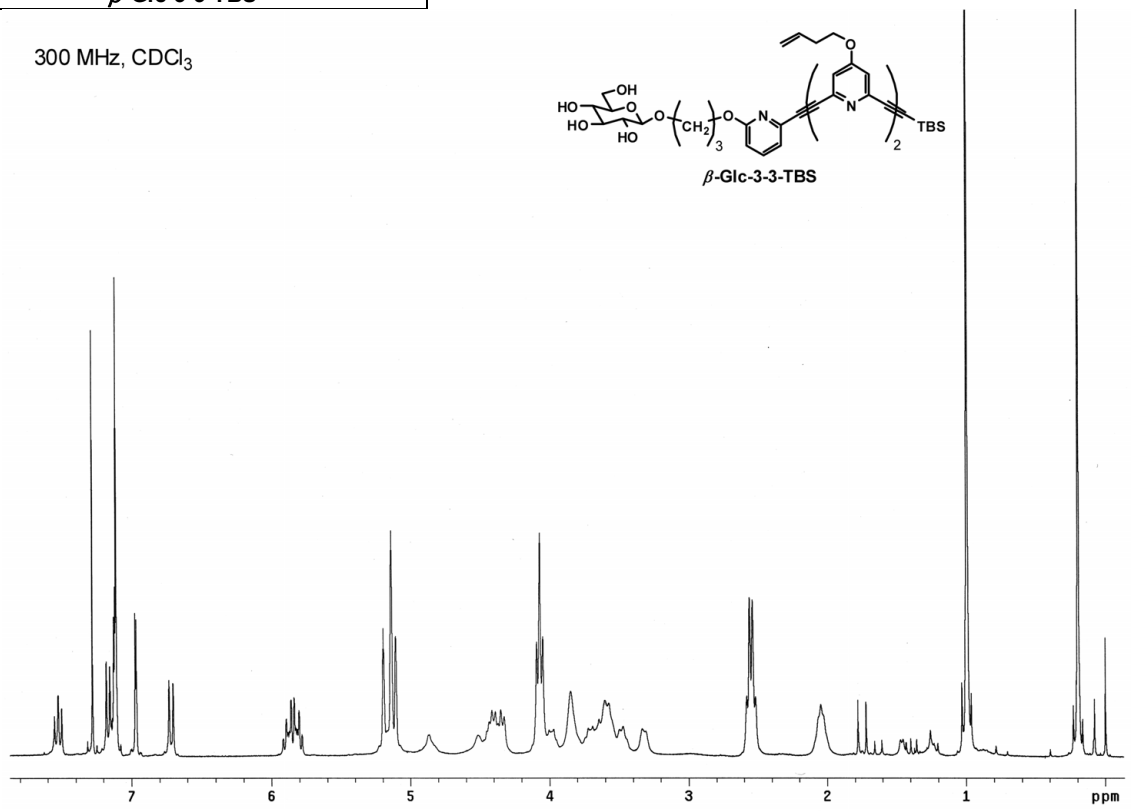

300 MHz, CDCl3
α-Man-3-2-H
8
7
6
5
4
3
2
1
ppm

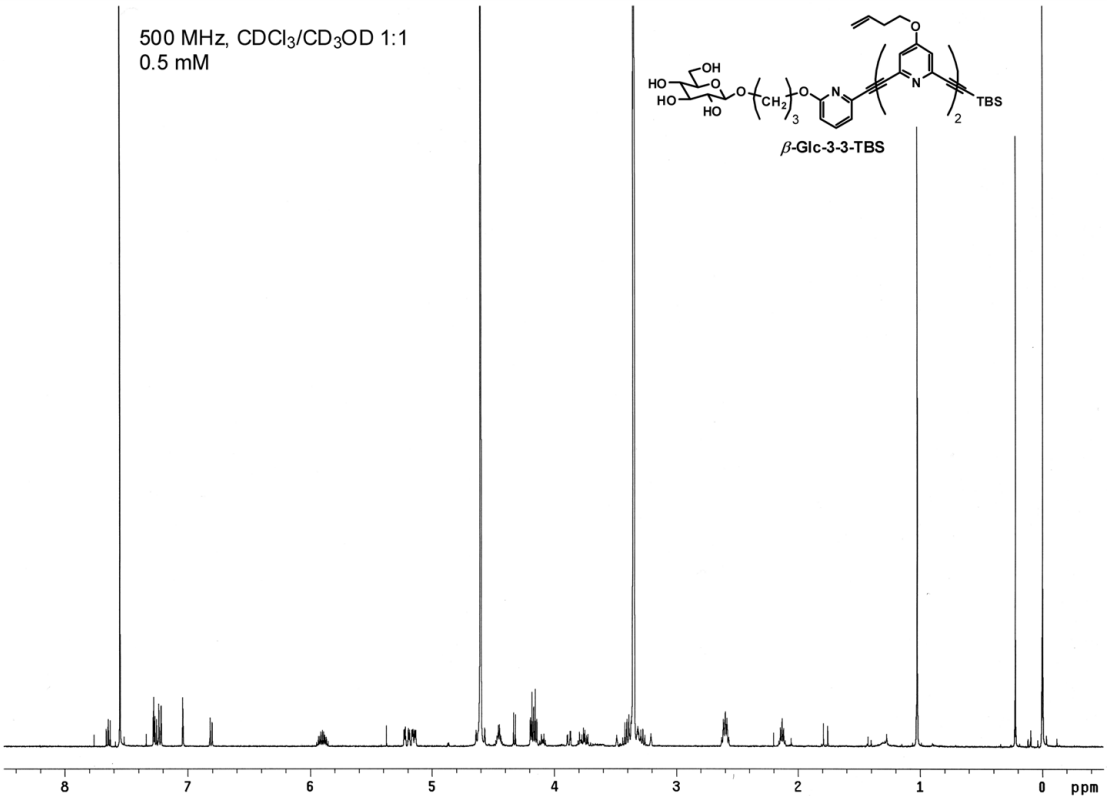

300 MHz, CDCl3
β-Glc-6-2-H
8
7
6
5
4
3
2
1
ppm

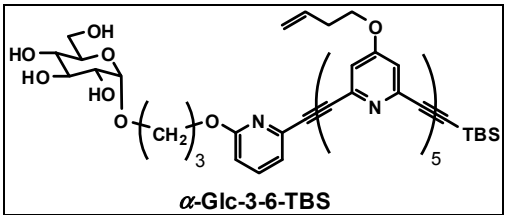

300 MHz, CDCl3
β-Glc-12-2-H
8
7
6
5
4
3
2
1
ppm


OH
HO
O
HO
HO
O
CH2
3
O
N
N
O
TBS
2

β-Glc-3-3-TBS


300 MHz, CDCl3
OH
HO
O
HO
HO
O
CH2
3
O
N
N
O
TBS
2
β-Glc-3-3-TBS
7
6
5
4
3
2
1
ppm

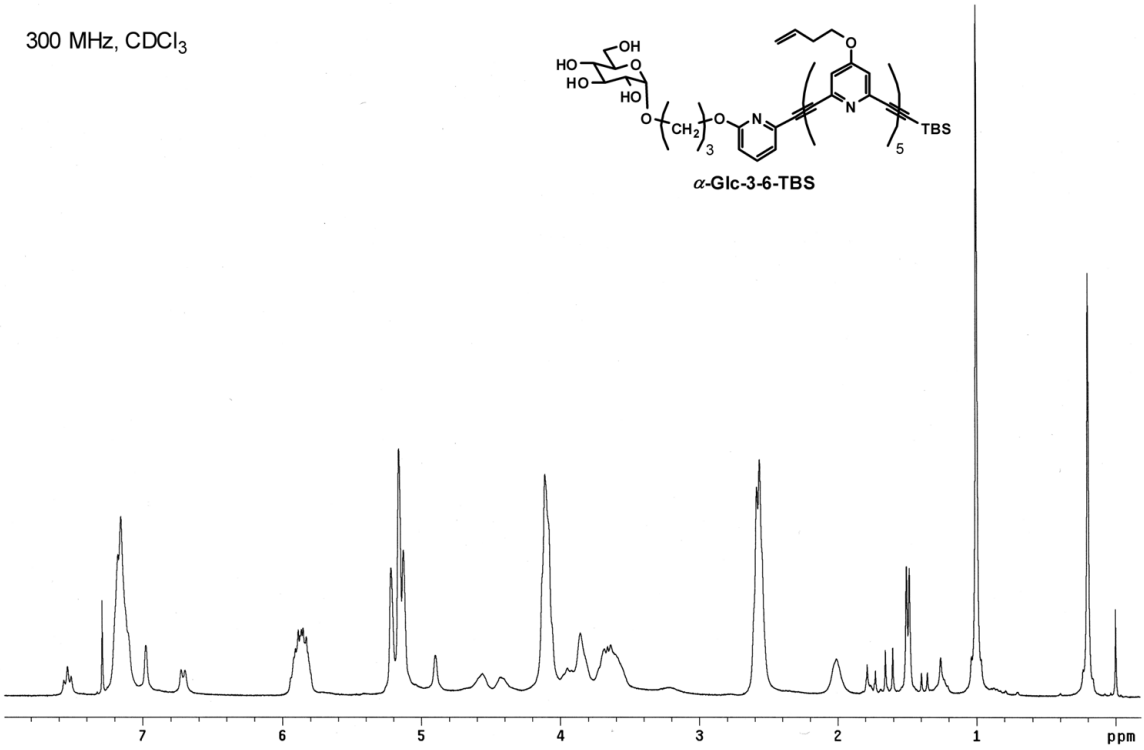

500 MHz, CDCl3/CD3OD 1:1
0.5 mM
OH
HO
O
HO
HO
O
CH2
3
O
N
N
O
TBS
2
β-Glc-3-3-TBS
8
7
6
5
4
3
2
1
0
ppm



α-Glc-3-6-TBS

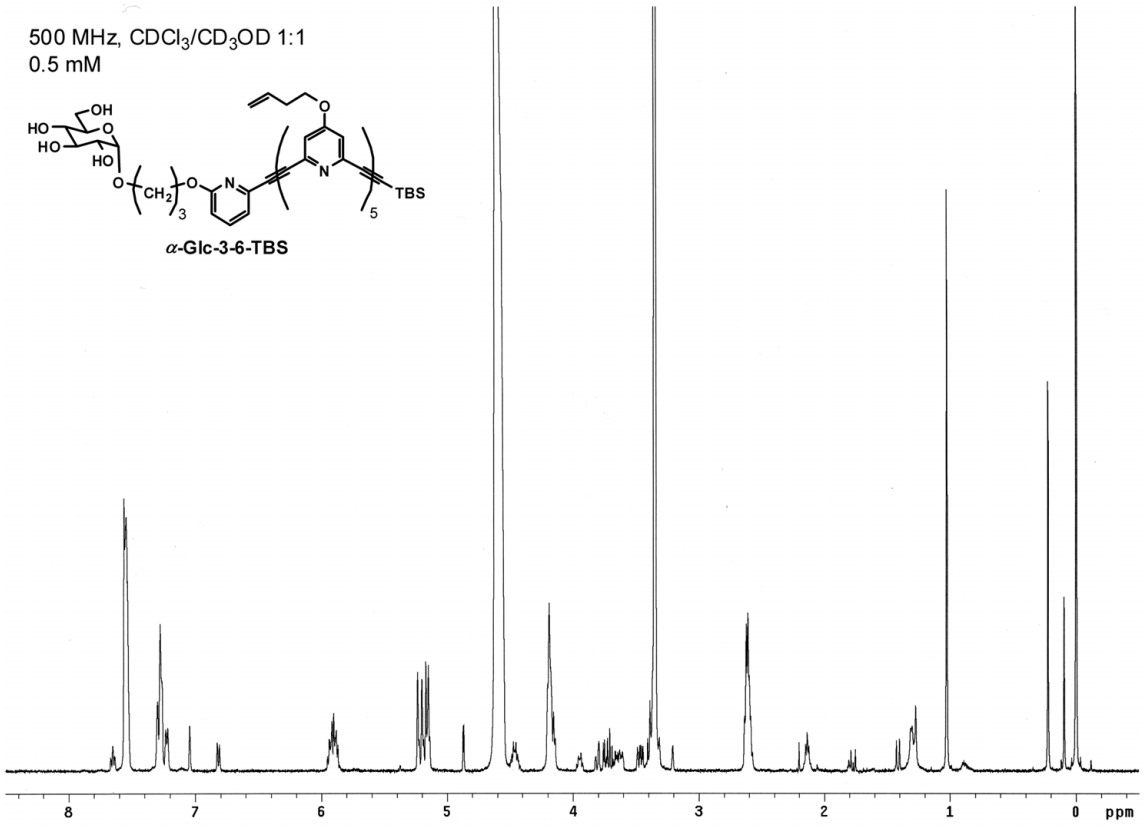
300 MHz, $CDCl_3$

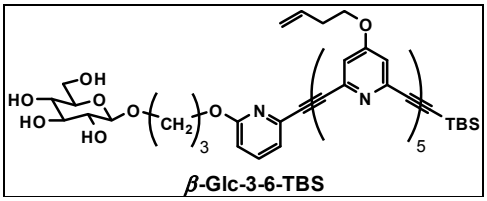
α-Glc-3-6-TBS



500 MHz, $CDCl_3/CD_3OD$ 1:1
0.5 mM

α-Glc-3-6-TBS

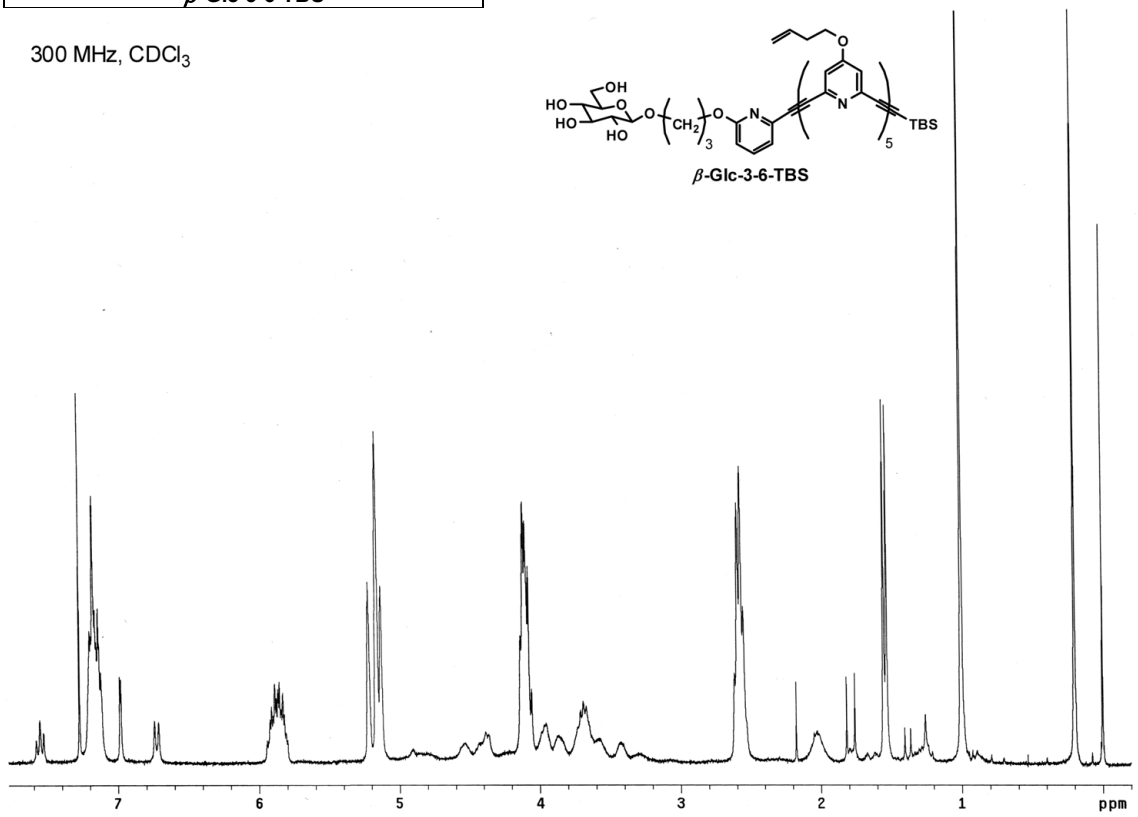




β-Glc-3-6-TBS

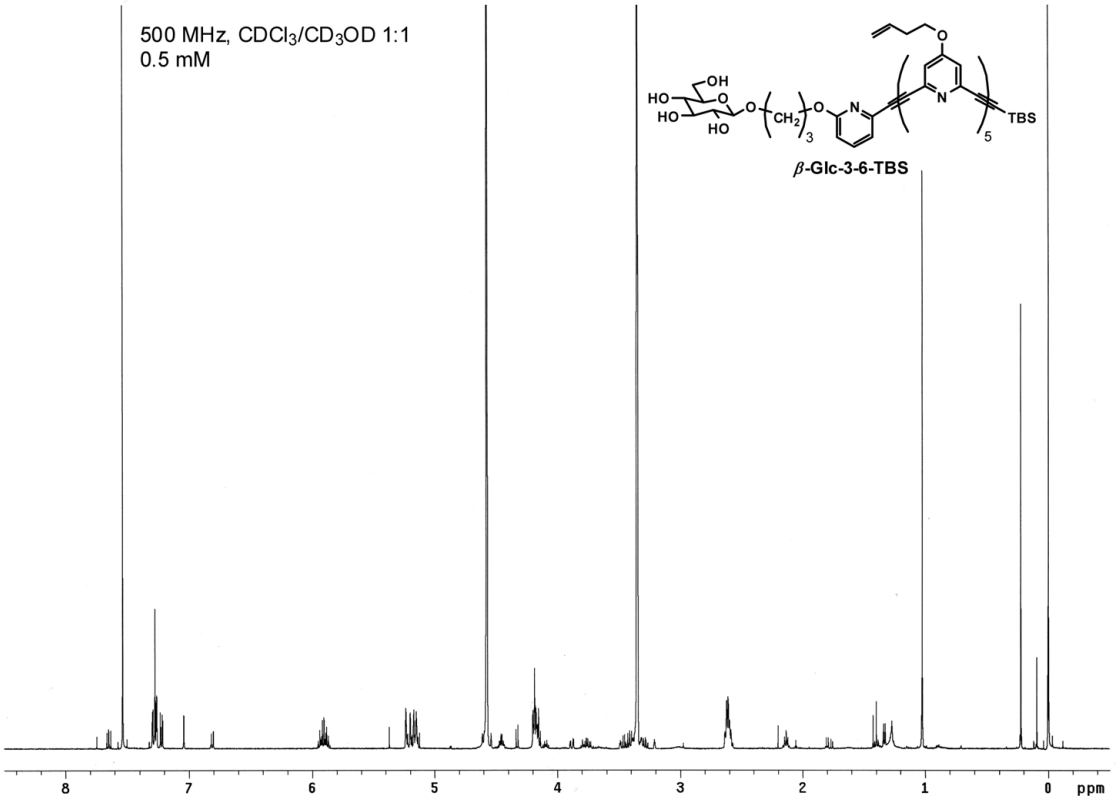
300 MHz, $CDCl_3$

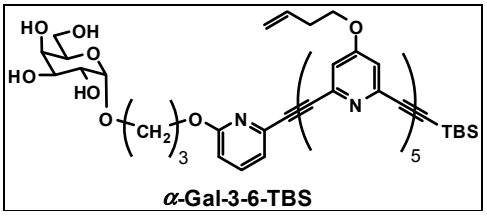
β-Glc-3-6-TBS



500 MHz, $CDCl_3/CD_3OD$ 1:1
0.5 mM

β-Glc-3-6-TBS

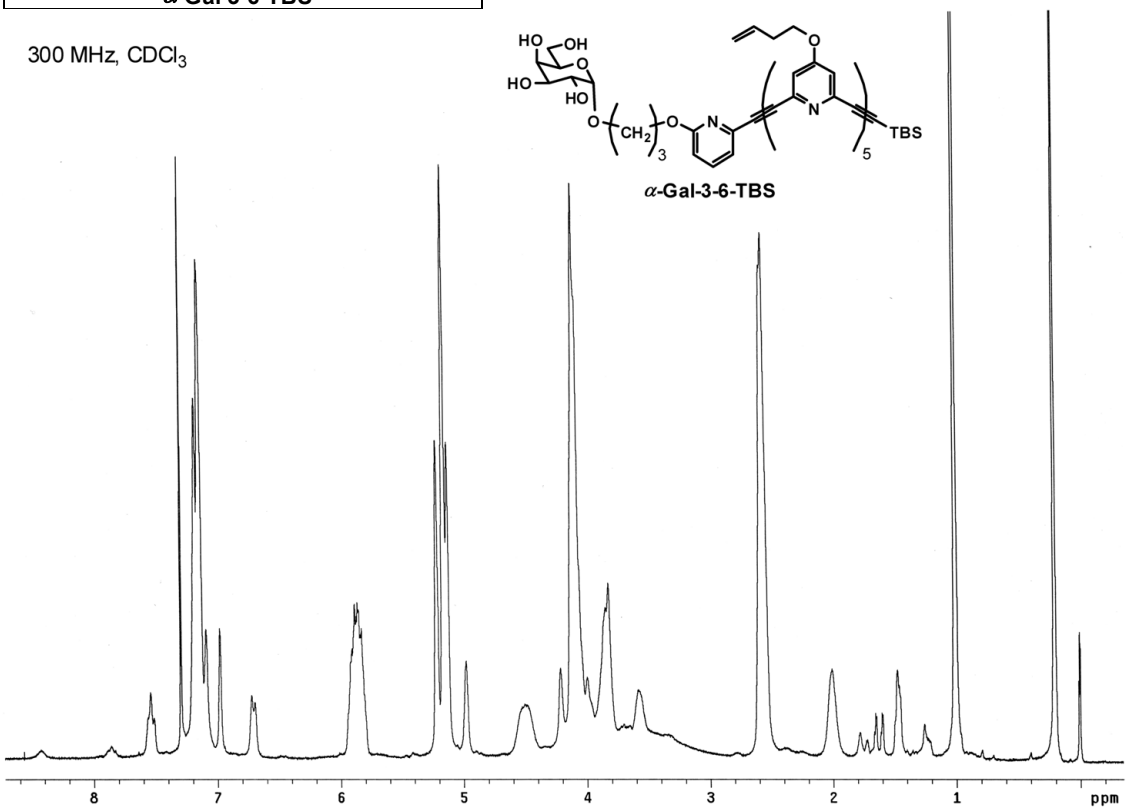




α-Gal-3-6-TBS

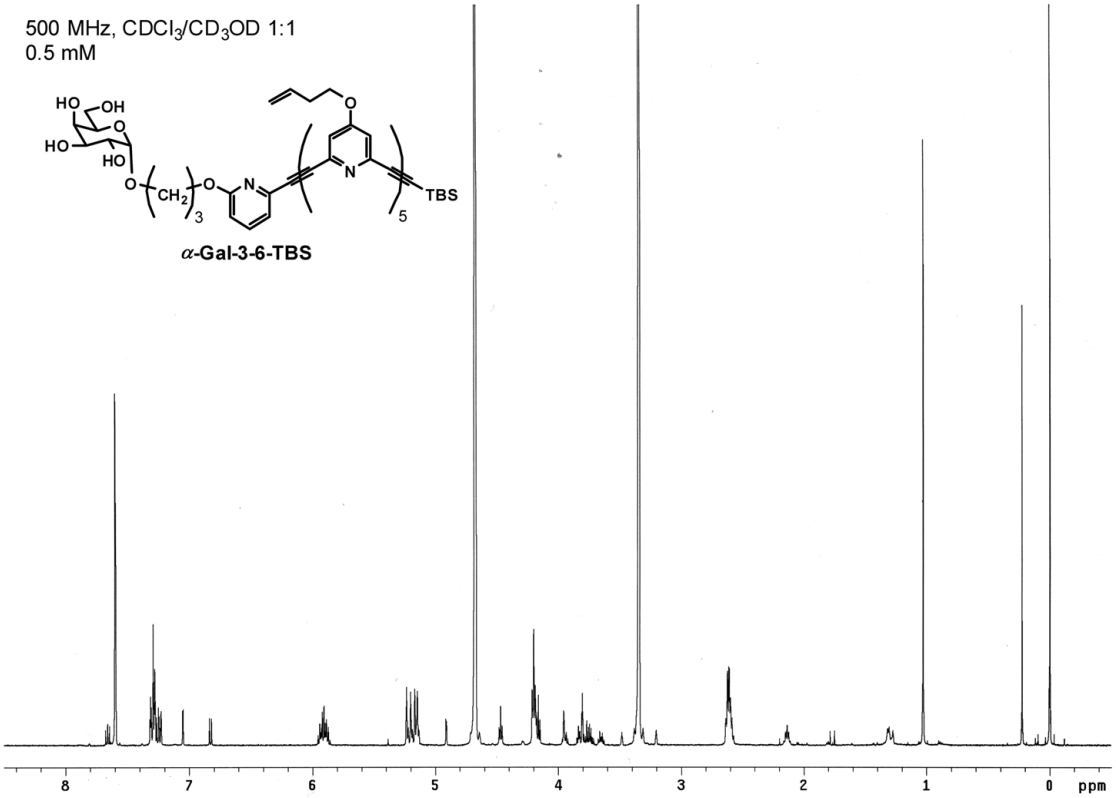
300 MHz, $CDCl_3$

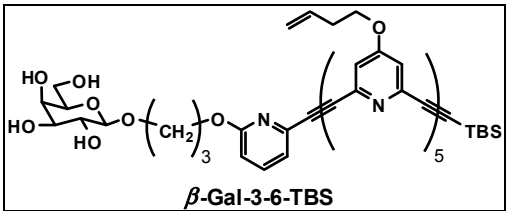
α-Gal-3-6-TBS



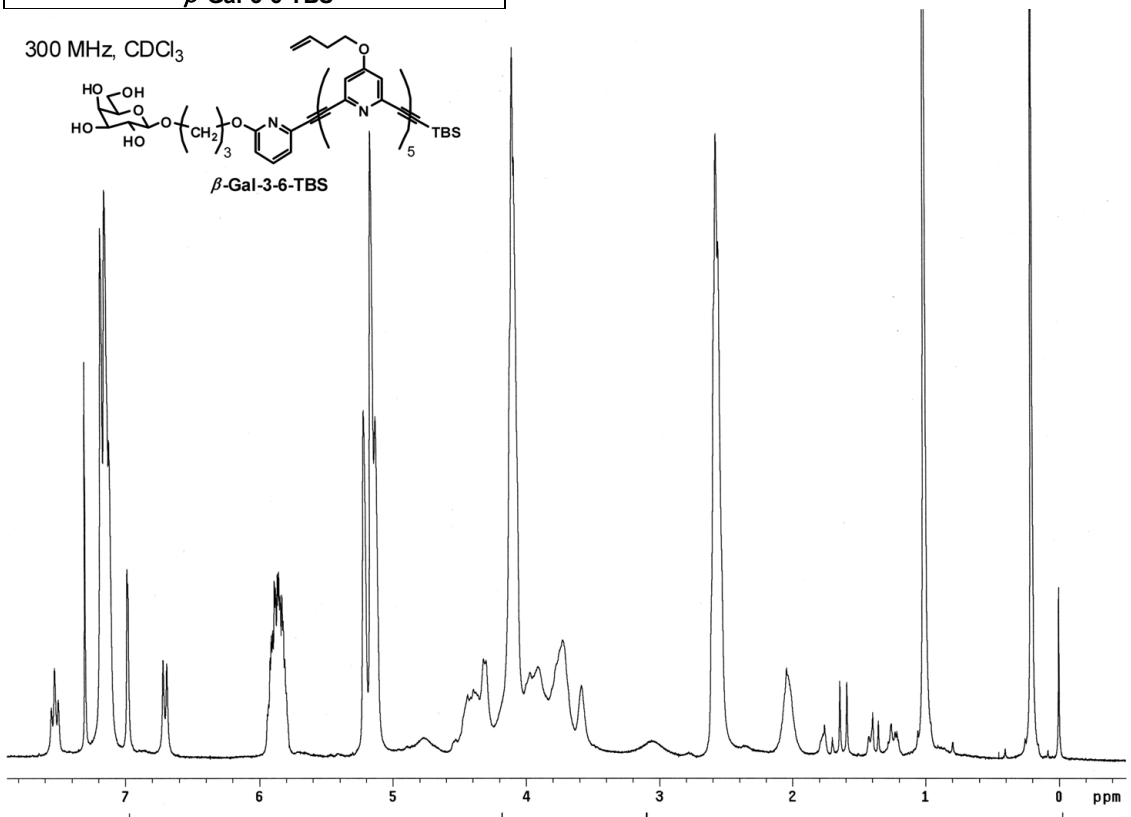
500 MHz, $CDCl_3/CD_3OD$ 1:1
0.5 mM

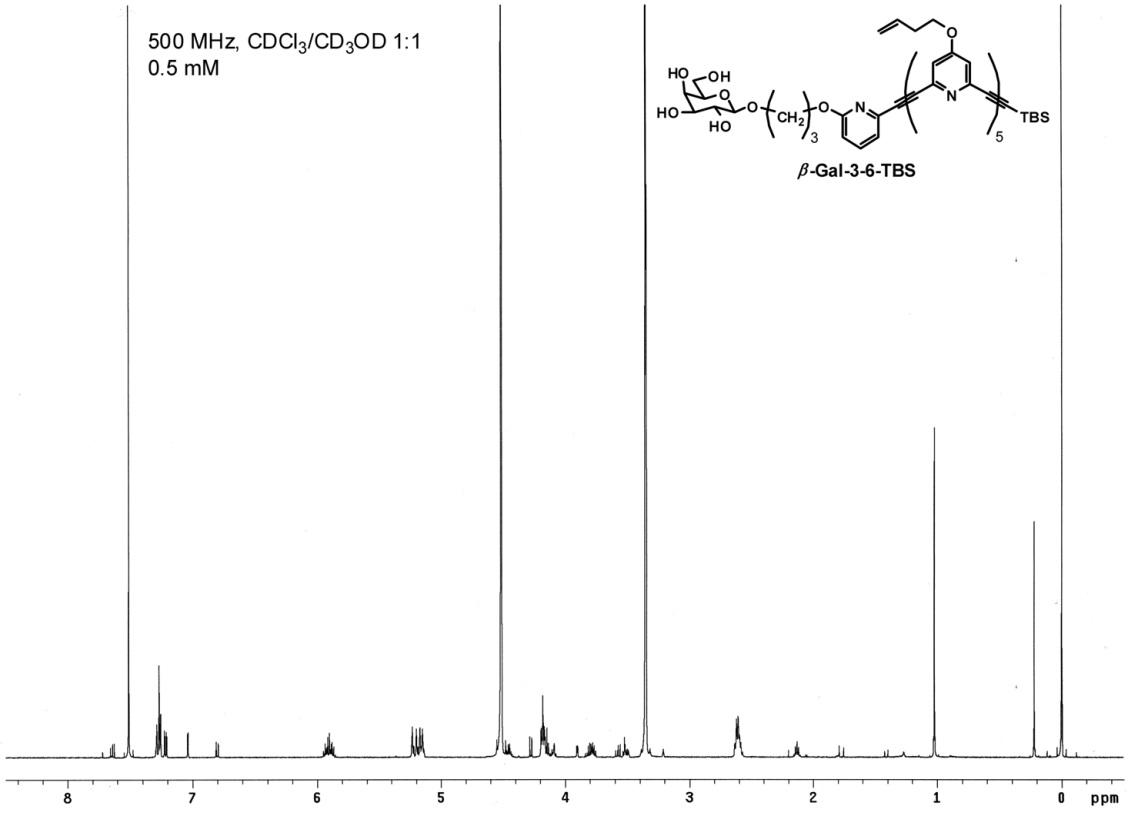
α-Gal-3-6-TBS

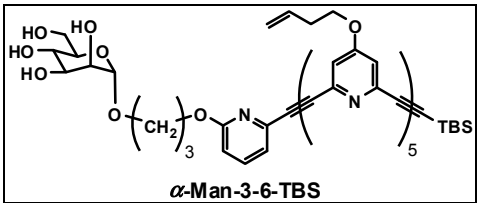



HO
OH
O
HO
HO
O
CH2
3
O
N
N
5
TBS

***β*-Gal-3-6-TBS**

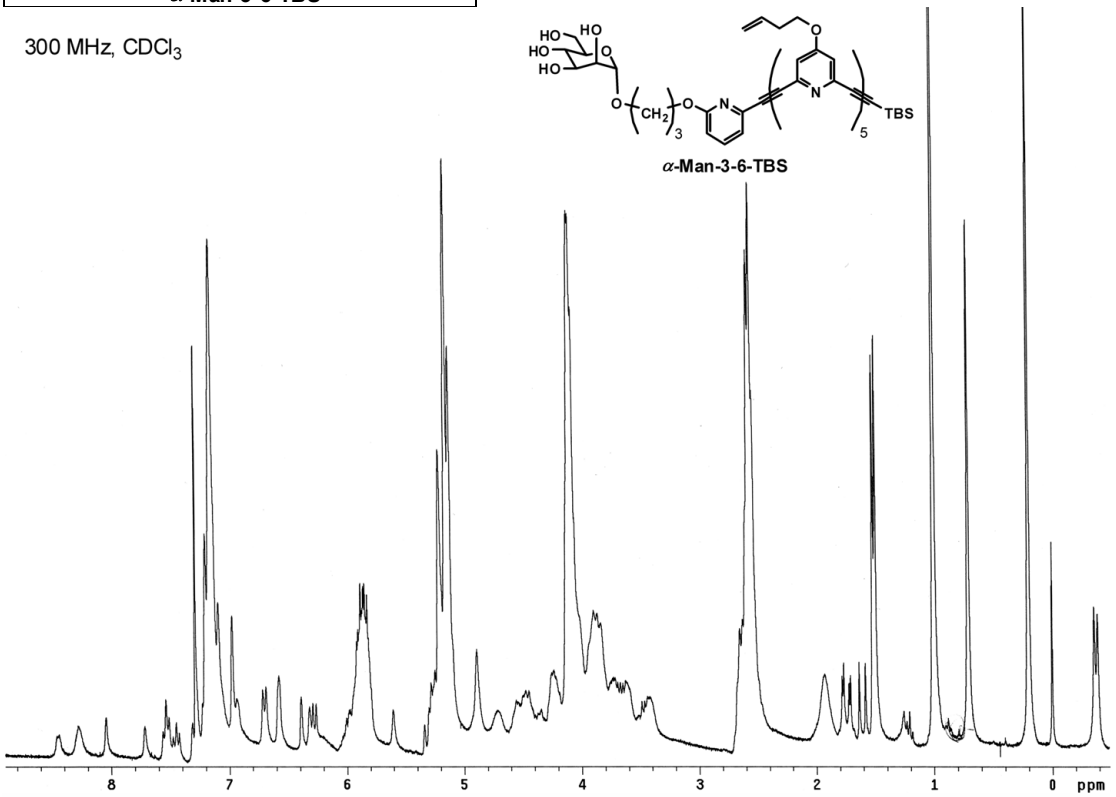

300 MHz, CDCl3
β-Gal-3-6-TBS
7
6
5
4
3
2
1
0
ppm


500 MHz, CDCl3/CD3OD 1:1
0.5 mM
β-Gal-3-6-TBS
8
7
6
5
4
3
2
1
0
ppm

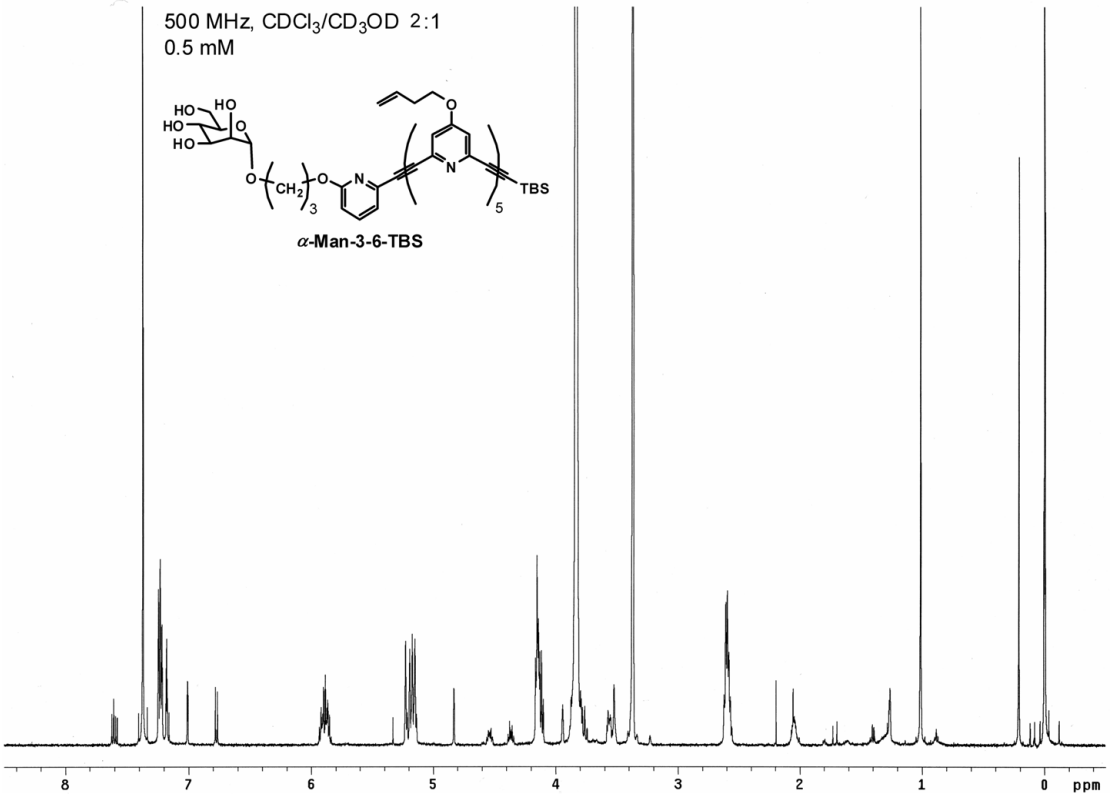


α-Man-3-6-TBS

300 MHz, $CDCl_3$

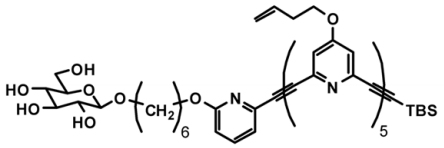


500 MHz, $CDCl_3/CD_3OD$ 2:1
0.5 mM

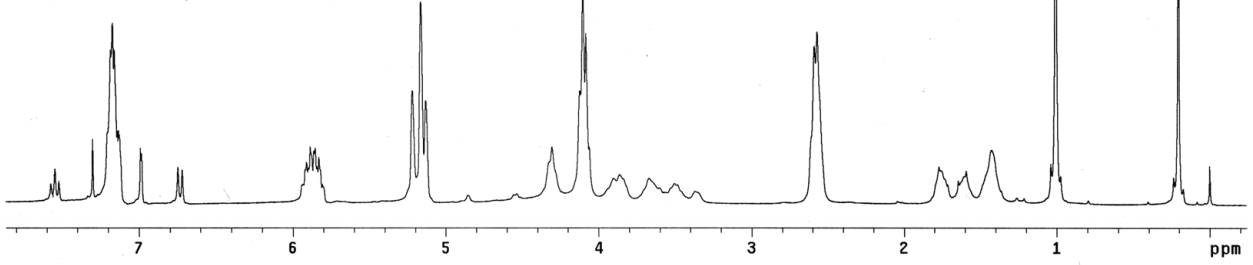


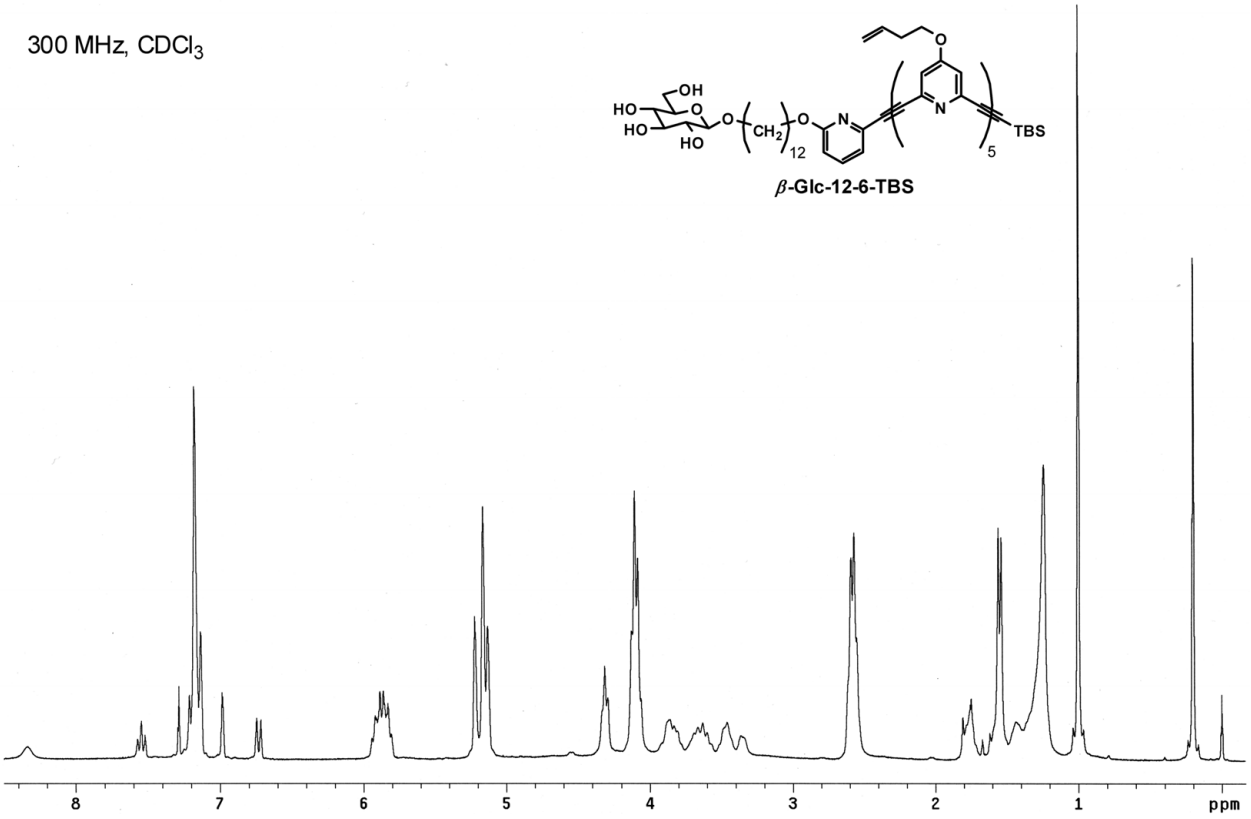
α-Man-3-6-TBS

300 MHz, $CDCl_3$



β-Glc-6-6-TBS



300 MHz, $CDCl_3$

β-Glc-12-6-TBS