Supporting Information

A Room Temperature Negishi Cross-Coupling Approach to C-Glycosides

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Experimental Section

General. All reagents were reagent grade quality and used as received from Aldrich unless otherwise indicated. All reactions were carried out under an atmosphere of argon or nitrogen unless otherwise indicated. Anhydrous THF and diethyl ether were distilled from sodium/ benzophenone ketyl prior to use. All other solvents were technical unless noted. Anhydrous *N,N*-dimethylacetamide (DMA), anhydrous *N,N*-dimethylimidazolone (DMI; Fluka), NiCl₂·glyme, NiBr₂·diglyme, *S*-*i*Pr-PyBox, *R*-*i*Pr-PyBox, *S*-*t*Bu-PyBox, *R*-Ph-PyBox (Strem), terpyridine, 2,6-bis[1-(2-methylphenylimino)ethyl]pyridine (Ph-bisimine; Strem) and terthiophene were used as received. The unsubstituted Py-Box was prepared according to a literature procedure.¹ Acetobromo- α -D-glucose (1% CaCO₃) and acetobromo- α -D-galactose (1% CaCO₃) were purified by passing through a silica column prior to use. Acetobromo- α -D-mannose,² benzylbromo- α -D-glucose, benzylchloro- α -D-glucose, benzylchloro- α -D-mannose were prepared according to reported procedures.³ 2,3,4,6-tetra-O-benzyl-D-mannopyranose was purchased from TRC Biomedical Research Chemicals. Alkylzinc reagents in polar solvents such as DMI and DMA were prepared based on a literature procedure.⁴ Column chromatography was performed using Merck silica gel 60 as the solid support. All NMR spectra were recorded on Varian Inova 600 MHz, Bruker Avance 400 MHz or 300 MHz spectrometer at STP unless otherwise indicated. Deuterated solvents were used as received from Cambridge Isotope Laboratories, Inc. ¹H NMR and ¹³C NMR chemical shifts are reported in δ units, parts per million (ppm) relative to the chemical shift of residual solvent. Reference peaks for chloroform in ¹H NMR and ¹³C NMR spectra were set at 7.24 ppm and 77.0 ppm, respectively. High-resolution mass spectra (HRMS) were obtained using a Bruker Biotof-II instrument.

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(3) (a) Blom, P.; Ruttens, B.; Van Hoof, S.; Hubrecht, I.; Van der Eycken, J.; Sas, B.; Van hemel, J.; Vandenkerckhove, J. *J. Org. Chem.* **2005**, *70*, 10109-10112. (b) Takeo, K.; Nakagen, M.; Teramoto, Y.; Nitta, Y. *Carbohydr. Res.* **1990**, *201*, 261-275.

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General Procedure for Negishi Coupling. To a flame-dried Schlenk tube equipped with a stir bar was loaded $\text{NiCl}_2\cdot\text{glyme}$ (0.0054 g, 0.0243 mmol, 10 mol%), PyBox (0.0079 g, 0.0365 mmol, 15 mol%), and Acetobromo- α -D-glucose (100.0 mg, 0.2432 mmol, 100 mol%). The mixture was evacuated and recharged with Argon three times, after which DMI (0.5 mL) was added *via* syringe. The resulting mixture was stirred for 20 min at rt, followed by addition of an alkylzinc reagent (1.0 M in DMI, 0.5 mL, 210 mol% or 0.73 mL, 300 mol%). The color changes from green to red upon addition of the zinc reagent solution. The reaction solution was allowed to stir for 12 h, and then it was directly loaded onto a silica column without work-up. The flash column chromatography provided the product as a colorless oil.

Proton labeling: For the purpose of spectral assignment, the proton labeling outlined in the following box was used throughout the text (including mannosides).

(2*R*, 3*R*, 4*R*, 5*R*, 6*R*)-Acetic acid 3, 4, 5-triacetoxy-6-(3-phenylpropyl)-tetrahydropyran-2-ylmethyl ester. This compound was prepared according to the General Procedure using acetobromo- α -D-mannose (100 mg, 0.24 mmol, 100 mol%) and phenylpropylzinc bromide (0.73 mL, $\sim$ 1.0 M, 0.73 mmol, 300 mol%). Flash column chromatography (SiO₂: 15% ethyl acetate in hexanes) gave an inseparable mixture of diastereomers (8:1 α to β anomers based on NMR) as a colorless oil (82 mg, 0.18 mmol, 75% yield). ¹H NMR (600 MHz, CDCl₃): δ 7.27 (t, J = 7.6 Hz, 2H), 7.15-7.19 (m, 3H), 5.21 (dd, J = 9.0 and 3.6 Hz, 1H; *H*3), 5.18 (t, J = 9.0 Hz, 1H; *H*4), 5.14 (t, J = 3.0 Hz, 1H; *H*2). 4.29 (dd, J = 12.0 and 6.0 Hz, 1H; *H*6), 4.07 (dd, J = 12.0 and 2.4 Hz 1H; *H*7), 3.97 (dt, J = 9.6 and 3.6 Hz, 1H; *H*1), 3.78 (ddd, J = 9.0, 6.0 and 3.0 Hz, 1H; *H*5), 2.59-2.69 (m, 2H), 2.11 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.74-1.83 (m, 2H), 1.62-1.72 (m, 1H), 154-1.62 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 170.6, 170.2, 170.0, 169.6, 141.6, 128.4, 128.3, 125.9, 74.9, 70.7, 70.1, 69.0, 66.9, 62.5, 35.1, 27.8, 27.0, 20.9, 20.68, 20.65. HRMS (ESI): m/z [M+Na]⁺ found 473.181, calcd 473.179 for C₂₃H₂₀O₉Na (mixture of isomers).

(2*S*, 3*R*, 4*R*, 5*R*, 6*R*)-Acetic acid 3, 4, 5-triacetoxy-6-(3-phenylpropyl)-tetrahydropyran-2-ylmethyl ester. This compound was obtained as a minor inseparable anomer from the above mixture, and the assignment is from a deconvolution of the mixture. ¹H NMR (600 MHz, CDCl₃): δ 7.10-7.28 (m, 5H), 5.30 (d, J = 3.6, 1H), 5.21 (d, J = 3.6 Hz, 2H), 5.01 (dd, J = 10.2 and 3.0 Hz, 1H). 4.23 (dd, J = 6.6 and 3.0 Hz, 1H), 3.54-3.58 (m, 2H), 2.54-2.58 (m, 2H), 2.09 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.96 (s, 3H), 1.74-1.83 (m, 2H), 1.62-1.72 (m, 1H), 154-1.62 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 170.7, 170.5, 170.2, 169.6, 141.7, 128.4, 128.3, 125.8, 76.2, 75.2, 74.6, 72.5, 69.4, 66.2, 62.9, 35.4, 29.8, 29.6, 20.9, 20.8, 20.6, 20.4.

(2*R*, 3*R*, 4*R*, 5*R*, 6*R*)-Acetic acid 4, 5-diacetoxy-6-acetoxymethyl-2-(2-[1,3]dioxolan-2-ylethyl)-tetrahydropyran-3-yl ester. This compound was prepared according to the General Procedure using acetobromo- α -D-mannose (100 mg, 0.24 mmol, 100 mol%) and acetal ethylzinc bromide (0.73 mL, ~1M, 0.73 mmol, 300 mol%). Flash column chromatography (SiO₂: 25% EtOAc in hexanes) gave an inseparable mixture of diastereomers (~8:1 α to β anomers based on NMR) as a colorless oil (73 mg, 0.17 mmol, 69% yield). ¹H NMR (400 MHz, CDCl₃): δ 5.13-5.23 (complex, 3H), 4.85-4.90 (bs, 1H), 4.29 (dd, J = 6.0 Hz, J = 12 Hz, 1H), 4.03-4.07 (complex, 1H), 3.90-4.00 (complex, 3H), 3.78-3.88 (complex, 3H), 2.74 (m, 2H), 2.12 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.60-1.90 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 170.7, 170.2, 170.0, 169.6, 103.4, 74.8, 70.8, 70.0, 68.9, 65.0, 64.9, 62.4, 45.0, 29.4, 22.4, 20.9, 20.7, 20.67. HRMS (ESI): m/z [M+Na]⁺ found 455.157, calcd 455.153 for C₁₉H₂₈O₁₁Na (mixture of isomers).

(2*R*, 3*R*, 4*R*, 5*R*, 6*R*)- 4-(3, 4, 5-Triacetoxy-6-acetoxymethyltetrahydropyran-2-yl)-butyric acid ethyl ester. This compound was prepared according to the General Procedure using acetobromo- α -D-mannose (100 mg, 0.24 mmol, 100 mol%) and carboethoxy propylzinc bromide (0.73 mL, ~1.0 M, 0.73 mmol, 300 mol%). Flash column chromatography (SiO₂: 20% EtOAc in hexanes) gave a mixture of diastereomers (~8:1 α to β anomers based on NMR) as a colorless oil (75 mg, 0.17 mmol, 70% yield). ¹H NMR (400 MHz, CDCl₃): δ 5.21 (dd, J = 8.8 and 3.0 Hz, 1H; *H*3), 5.17 (t, J = 8.8 Hz, 1H; *H*4), 5.12 (t, J = 3.0 Hz, 1H; *H*2), 4.31 (dd, J = 12.0 and 6.0 Hz, 1H; *H*6), 4.11 (q, J = 7.2 Hz, 2H), 4.07 (dd, J = 9.6 and 2.4 Hz, 1H; *H*7), 3.93 (dt, J = 10 Hz and 3.2 Hz, 1H; *H*1), 3.85 (ddd, J = 8.8, 6.0 and 2.4 Hz, 1H; *H*5), 2.40-

2.25 (m, 2H), 2.10 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H), 1.72-1.88 (m, 2H), 1.52-1.67 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 172.8, 170.5, 170.1, 169.8, 169.5, 74.5, 70.5, 70.1, 68.8, 66.7, 62.2, 60.2, 33.2, 27.6, 20.8, 20.6, 20.5, 14.0. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ found 469.177, calcd 469.169 for $\text{C}_{20}\text{H}_{30}\text{O}_{11}\text{Na}$.

(2R, 3S, 4R, 5R, 6R)-Acetic acid 3,4,5-triacetoxy-6-(3-phenylpropyl)-tetrahydropyran-2-ylmethyl ester. This compound was prepared according to the General Procedure using acetobromo- α -D-glucose (100 mg, 0.24 mmol, 100 mol%) and phenylpropylzinc bromide (0.73 mL, $\sim$ 1.0 M, 0.73 mmol, 300 mol%). Flash column chromatography (SiO_2 : 15% EtOAc in hexanes) gave the title compound as a colorless oil (10 mg; partially isolated from a mixture of diastereomers). ^1H NMR (400 MHz, CDCl_3): δ 7.27 (t, $J = 7.2$ Hz, 2H), 7.14-7.19 (m, 3H), 5.27 (t, $J = 9.2$ Hz, 1H; *H3*), 5.04 (dd, $J = 9.6$ and 5.6, Hz, 1H; *H2*), 4.94 (t, $J = 9.2$ Hz, 1H; *H4*), 4.19 (dd, $J = 12.0$ and 5.2 Hz, 1H; *H7*), 4.17-4.21 (m, 1H; *H1*), 4.04 (dd, $J = 12.0$ and 2.0 Hz, 1H; *H6*), 3.73 (ddd, $J = 9.2$, 5.2, and 2.0 Hz, 1H; *H5*), 2.55-2.69 (m, 2H), 2.06 (s, 3H), 2.034 (s, 3H), 2.027 (s, 3H), 2.02 (s, 3H), 1.70-1.90 (m, 2H), 1.40-1.70 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.7, 170.2, 169.7, 169.6, 141.7, 128.4, 128.3, 126.0, 72.3, 70.4, 68.9, 68.6, 62.4, 35.2, 26.5, 24.5, 20.71, 20.66. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ found 473.178, calcd 473.179 for $\text{C}_{23}\text{H}_{20}\text{O}_9\text{Na}$.

(2S, 3S, 4R, 5S, 6R)-Acetic acid 3,4,5-triacetoxy-6-(3-phenylpropyl)-tetrahydropyran-2-ylmethyl ester. This compound was prepared according to the General Procedure using acetobromo- α -D-galactose (100 mg, 0.24 mmol, 100 mol%) and phenylpropylzinc bromide (0.73 mL, $\sim$ 1.0 M, 0.73 mmol, 300 mol%). Flash column chromatography (SiO_2 : 15% EtOAc in hexanes) gave an inseparable mixture of

diastereomers (~1:2 α to β anomers based on NMR) as a colorless oil (46 mg, 0.10 mmol, 43% yield). ^1H NMR (600 MHz, CDCl_3): 7.27 (t, $J = 7.2$ Hz, 2H), 7.14-7.19 (m, 3H), 5.38 (d, $J = 3.0$ Hz, 1H; H_4), 5.05 (t, $J = 9.6$ Hz, 1H; H_2), 4.96 (dd, $J = 10.2$ and 3.6 Hz, 1H, H_3), 4.11 (dd, $J = 10.8$ and 7.2 Hz, 1H; H_6), 4.03 (dd, $J = 10.8$ and 6.6 Hz, 1H; H_7), 3.79 (t, $J = 6.6$ Hz, 1H; H_5), 3.35 (dt, $J = 9.6$ and 6.0 Hz, 1H; H_1), 2.58 (t, $J = 7.8$ Hz, 2H), 2.12 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H), 1.94 (s, 3H), 1.80-1.88 (m, 1H), 1.58-1.66 (m, 2H), 1.50-1.54 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.5, 170.4, 170.3, 169.9, 142.1, 128.4, 128.3, 125.8, 78.1, 74.1, 72.3, 69.3, 68.3, 67.7, 61.6, 35.5, 30.8, 26.8, 20.74, 20.70, 20.67, 20.62. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ found 473.173, calcd 473.179 for $\text{C}_{23}\text{H}_{20}\text{O}_9\text{Na}$ (mixture of isomers).

(2*R*, 3*S*, 4*R*, 5*S*, 6*R*)-Acetic acid 3,4,5-triacetoxy-6-(3-phenylpropyl)-tetrahydropyran-2-ylmethyl ester. This compound was obtained as a minor inseparable anomer from the above mixture, and the assignment is from a deconvolution of the mixture. ^1H NMR (600 MHz, CDCl_3): 7.14-7.29 (m, 5H), 5.34 (t, $J = 3.0$ Hz, 1H; H_4), 5.22 (dd, $J = 9.6$ and 5.4 Hz, 1H; H_2), 5.14 (dd, $J = 9.6$ and 3.0 Hz 1H; H_3), 4.18-4.23 (m, 1H; H_1), 4.17 (dd, $J = 11.4$ and 4.2 Hz, 1H, H_6), 4.16 (dd, $J = 11.4$ and 7.2 Hz, 1H; H_7), 3.96 (ddd, $J = 7.2$, 4.2 and 3.0 Hz, 1H; H_5), 2.60-2.67 (m, 2H), 2.09 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.66-1.80 (m, 2H), 1.39-1.46 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 170.6, 170.2, 170.0, 169.9, 141.8, 128.4, 128.3, 125.9, 68.4, 68.0, 67.7, 61.7, 35.2, 29.7, 24.8, 20.74, 20.70, 20.67, 20.62.

(2*S*, 3*S*, 4*R*, 5*R*, 6*R*)-3,4,5-Tris(benzyloxy)-2-benzyloxymethyl-6-(3-phenyl-propyl)-tetrahydropyran. This compound was prepared according to the General Procedure using benzylchloro- α -D-glucose (136 mg, 0.24 mmol, 100 mol%) and phenylpropylzinc bromide (0.73 mL, ~1.0 M, 0.73 mmol,

300 mol%). Flash column chromatography (SiO₂: 5% EtOAc in hexanes) gave the title compound as a colorless oil (60 mg, 0.091 mmol, 38% yield). ¹H NMR (600 MHz, CDCl₃): δ 7.18-7.35 (m, 25H), 4.91 (s, 2H), 4.85 (d, *J* = 10.8 Hz, 1H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.63 (d, *J* = 12 Hz, 1H), 4.59 (d, *J* = 12.6 Hz, 1H), 4.58 (d, *J* = 10.2 Hz, 1H), 4.56 (d, *J* = 10.8 Hz, 1H), 3.74 (dd, *J* = 10.8 and 1.8 Hz, 1H; *H6*), 3.67-3.70 (complex, 2H; *H2*, *H7*), 3.62 (t, *J* = 9.6 Hz, 1H; *H4*), 3.40 (ddd, *J* = 9.6, 4.2 and 1.8 Hz; *H5*), 3.24-3.30 (complex, 2H; *H1*, *H3*), 2.64 (t, *J* = 7.2 Hz, 2H), 1.86-1.93 (m, 2H), 1.68-1.95 (m, 1H), 1.49-1.56 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 142.3, 138.5, 138.1, 138.0, 137.9, 128.34, 128.31, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.59, 127.5, 127.4, 125.5, 87.3, 82.3, 79.2, 78.9, 78.6, 75.5, 75.3, 74.9, 73.4, 69.0, 35.8, 31.2, 27.5. HRMS (ESI): *m/z* [M+Na]⁺ found 665.322, calcd 665.324 for C₄₃H₄₆O₅Na.

(2*R*, 3*S*, 4*R*, 5*R*, 6*R*)-3,4,5-Tris(benzyloxy)-2-benzyloxymethyl-6-(3-phenylpropyl)-tetrahydropyran. This compound was isolated from the above reaction as a colorless oil (41 mg, 0.077 mmol, 32% yield). ¹H NMR (600 MHz, CDCl₃): δ 7.12-7.37 (m, 25H), 4.93 (d, *J* = 10.8, 1H), 4.82 (d, *J* = 10.8 Hz, 1H), 4.80 (d, *J* = 11.4 Hz, 1H), 4.66 (d, *J* = 12 Hz, 1H), 4.63 (d, *J* = 13.2 Hz, 1H), 4.57 (d, *J* = 11.4 Hz, 1H), 4.49 (d, *J* = 12.6 Hz, 1H), 4.47 (d, *J* = 10.8 Hz, 1H), 4.07 (m, 1H; *H1*), 3.77 (t, *J* = 9.6 Hz, 1H), 3.75-3.76 (complex 1H), 3.74 (dd, *J* = 9.6 and 6.0 Hz, 1H; *H2*), 3.69 (dd, *J* = 10.8 and 4.2 Hz, 1H), 3.60-3.66 (complex, 2H), 3.54 (dd, *J* = 10.2 and 3.6 Hz, 1H; *H5*), 2.68 (m, 2H), 1.75-1.81 (m, 2H), 1.69-1.75 (m, 1H), 1.60-1.69 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 142.2, 138.7, 138.2, 138.1, 137.9, 128.34, 128.28, 127.9, 127.8, 127.71, 127.67, 127.57, 127.53, 125.7, 82.5, 80.2, 78.2, 75.4, 75.0, 73.7, 73.4, 73.0, 70.9, 69.0, 35.4, 26.9, 24.1. HRMS (ESI): *m/z* [M+Na]⁺ found 665.327, calcd 665.324 for C₄₃H₄₆O₅Na.

(2*S*, 3*S*, 4*R*, 5*R*, 6*R*)-3,4,5-Tris(benzyloxy)-2-benzyloxymethyl-6-(2-[1,3]dioxolan-2-ylethyl)-tetrahydropyran. This compound was prepared according to the General Procedure using benzyldichloro- α -D-glucose (136 mg, 0.24 mmol, 100 mol%) and acetal ethylzinc bromide (0.73 mL, $\sim$ 1.0 M, 0.73 mmol, 300 mol%). Flash column chromatography (SiO₂: 5% EtOAc in hexanes) gave the title compound as a colorless oil (51 mg, 0.082 mmol, 34% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.19-7.36 (m, 25H), 4.90-4.94 (complex, 3H), 4.87 (d, J = 10.0 Hz, 1H), 4.84 (d, J = 10.8 Hz, 1H), 4.69 (d, J = 10.4 Hz, 1H), 4.65 (d, J = 12.0 Hz, 1H), 4.60 (d, J = 12 Hz, 1H), 4.57 (d, J = 12.8 Hz, 1H), 3.97 (t, J = 6.0 Hz, 2H), 3.86 (t, J = 6.0 Hz, 2H), 3.67-3.77 (m, 3H), 3.64 (t, J = 9.2 Hz, 1H; *H*4), 3.41 (m, 1H; *H*5), 3.26-3.33 (complex, 2H; *H*1, *H*3), 2.64 (t, J = 7.2 Hz, 2H), 1.90-2.10 (m, 2H), 1.72-1.84 (m, 1H), 1.56-1.70 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 138.2, 128.4, 128.38, 128.3, 128.2, 128.0, 127.9, 127.8, 127.4, 100.5, 87.3, 82.4, 78.9, 78.6, 75.6, 74.9, 73.4, 64.9, 64.8, 29.8, 26.0. HRMS (ESI): m/z [M+Na]⁺ found 647.302, calcd 647.298 for C₃₉H₄₄O₇Na.

(2*R*, 3*S*, 4*R*, 5*R*, 6*R*)-3,4,5-Tris(benzyloxy)-2-benzyloxymethyl-6-(2-[1,3]dioxolan-2-ylethyl)-tetrahydropyran. This compound was isolated from the above reaction as a colorless oil (46 mg, 0.074 mmol, 31% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.11-7.37 (m, 25H), 4.87-4.93 (m, 3H), 4.79 (d, J = 10.8 Hz, 1H), 4.77 (d, J = 10.8 Hz, 1H), 4.66 (d, J = 11.6 Hz, 1H), 4.61 (d, J = 11.4 Hz, 1H), 4.45 (d, J = 12.0 Hz, 1H), 4.43 (d, J = 10.4 Hz, 1H), 4.03 (m, 1H), 3.93 (t, J = 6.4 Hz, 2H), 3.85 (t, J = 6.4 Hz, 2H), 3.73-3.81 (complex, 2H), 3.68 (dd, J = 10.0 and 2.4 Hz, 1H), 3.54-3.64 (complex, 3H), 2.68 (m, 2H), 1.75-1.81 (m, 2H), 1.69-1.75 (m, 1H), 1.60-1.69 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 138.8, 138.3, 138.26,

138.1, 128.4, 128.0, 127.9, 127.8, 127.6, 127.58, 118.2, 82.5, 80.2, 78.2, 75.1, 74.0, 73.5, 73.4, 73.0, 70.9, 69.0, 64.94, 64.91, 29.6, 18.9. HRMS (ESI): m/z $[M+Na]^+$ found 647.302, calcd 647.298 for $C_{39}H_{44}O_7Na$.

(2S, 3S, 4R, 5R, 6R)- 4-(3,4,5-Tris(benzyloxy)-6-benzyloxymethyl-tetrahydro-pyran-2-yl)-butyric acid ethyl ester. This compound was prepared according to the General Procedure using benzylchloro- α -D-glucose (136 mg, 0.24 mmol, 100 mol%) and carboethoxy propylzinc bromide (0.73 mL, ~1.0 M, 0.73 mmol, 300 mol%). Flash column chromatography (SiO_2 : 5% EtOAc in hexanes) gave the title compound as a colorless oil (54 mg, 0.085 mmol, 35% yield). 1H NMR (400 MHz, $CDCl_3$): δ 7.26-7.34 (m, 23H), 7.16-7.18 (complex, 2H), 4.90 (s, 2H), 4.88 (d, J = 13.2 Hz, 1H), 4.82 (d, J = 10.8 Hz, 1H), 4.64 (d, J = 10.8 Hz, 1H), 4.63 (d, J = 12.4 Hz, 1H), 4.57 (d, J = 10.0 Hz, 1H), 4.54 (d, J = 12 Hz, 1H), 4.11 (q, J = 7.2 Hz, 2H), 3.66-3.73 (m, 3H), 3.62 (t, J = 9.2 Hz, 1H; *H4*), 3.38 (m, 1H; *H5*), 3.26-3.33 (complex, 2H; *H1*, *H3*), 2.30 (t, J = 7.2 Hz, 2H), 1.80-1.87 (m, 2H), 1.65-1.80 (m, 1H), 1.43-1.54 (m, 1H), 1.23 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 138.6, 138.2, 138.1, 128.4, 128.38, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 127.55, 87.3, 82.1, 78.9, 78.5, 75.5, 75.2, 74.9, 73.5, 69.0, 60.1, 34.3, 31.0, 29.7, 21.2, 14.2. HRMS (ESI): m/z $[M+Na]^+$ found 661.318, calcd 661.314 for $C_{40}H_{46}O_7Na$.

(2R, 3S, 4R, 5R, 6R)-(3,4,5-Tris(benzyloxy)-6-benzyloxymethyl-tetrahydro-pyran-2-yl)-butyric acid ethyl ester. This compound was isolated from the above reaction as a colorless oil (45 mg, 0.071 mmol, 30% yield). 1H NMR (400 MHz, $CDCl_3$): δ 7.26-7.34 (m, 23H), 7.16-7.18 (complex, 2H), 4.91 (d, J = 10.8 Hz, 1H), 4.79 (d, J = 10.4 Hz, 1H), 4.77 (d, J = 10.4 Hz, 1H), 4.67 (d, J = 11.6 Hz, 1H),

4.62 (d, $J = 10.4$ Hz, 1H), 4.59 (d, $J = 11.2$ Hz, 1H), 4.46 (d, $J = 13.6$ Hz, 1H), 4.45 (d, $J = 10.4$ Hz, 1H), 4.10 (q, $J = 7.2$ Hz, 2H), 4.02 (m, 1H), 3.72-3.77 (complex, 2H), 3.69 (dd, $J = 11.2$ and 4.4 Hz, 1H), 3.55-3.61 (complex, 2H), 3.54 (dd, $J = 9.6$ and 3.6 Hz, 1H), 2.32 (ddd, $J = 13.6$, $J = 9.2$ and 6.8 Hz, 2H), 1.53-1.85 (m, 4H), 1.23 (t, $J = 7.2$). ^{13}C NMR (100 MHz, CDCl_3): δ 173.4, 138.8, 138.2, 138.0, 128.4, 128.36, 128.32, 127.9, 127.8, 127.77, 127.7, 127.6, 127.56, 82.5, 80.1, 78.1, 75.5, 75.0, 73.8, 73.5, 73.1, 71.0, 68.9, 60.2, 33.9, 24.0, 20.9, 14.2. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ found 661.318, calcd 661.314 for $\text{C}_{40}\text{H}_{46}\text{O}_7\text{Na}$.

(2R, 3R, 4R, 5R, 6R)-(3,4,5-Tris(benzyloxy)-6-benzyloxymethyl-tetrahydro-pyran-2-yl)-butyric acid ethyl ester. This compound was prepared according to the General Procedure using benzylchloro- α -D-mannose (100 mg, 0.18 mmol, 100 mol%) and carboethoxy propylzinc bromide (0.55 mL, ~ 1.0 M, 0.54 mmol, 300 mol%), $\text{NiCl}_2 \cdot \text{glyme}$ (0.0041 g, 0.018 mmol, 10 mol%), PyBox (0.0059 g, 0.027 mmol, 15 mol%), DMI (0.35 mL). Flash column chromatography (SiO_2 : 5% EtOAc in hexanes) gave the title compound as a colorless oil (88.5 mg, 0.139 mmol, 76% yield). ^1H NMR (600 MHz, CDCl_3): δ 7.25-7.33 (m, 23H), 7.16-7.18 (complex, 2H), 4.68 (d, $J = 11.4$ Hz, 1H), 4.59 (d, $J = 12.0$ Hz, 1H), 4.57 (d, $J = 12.0$ Hz, 1H), 4.56 (d, $J = 12.6$ Hz, 1H), 4.53 (d, $J = 12.0$ Hz, 1H), 4.52 (s, 2H), 4.50 (d, $J = 11.4$ Hz, 1H), 4.09 (q, $J = 7.2$ Hz, 2H), 3.95 (quintet, $J = 4.2$ Hz, 1H; *H1*), 3.84 (q, $J = 6.6$ Hz, 1H; *H4*), 3.76-3.78 (m, 1H; *H5*), 3.74-3.75 (m, 1H; *H6*), 3.73 (dd, $J = 6.6$ and 2.4 Hz, 1H; *H3*), 3.68-3.71 (m, 1H; *H7*), 3.55 (dd, $J = 4.2$ and 3.0 Hz, 1H; *H2*), 2.28 (t, $J = 7.2$ Hz, 2H), 1.73-1.77 (m, 1H), 1.57-1.62 (m, 2H), 1.48-1.51 (m, 1H), 1.21 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 173.3, 138.2, 138.1, 138.05, 128.2, 128.17, 128.1, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 75.8, 74.7, 73.7, 73.2, 73.15, 72.3, 72.0, 71.4, 69.0, 60.1, 33.8, 28.9, 21.1, 14.1. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ found 661.312, calcd 661.314 for $\text{C}_{40}\text{H}_{46}\text{O}_7\text{Na}$.

(2*R*, 3*R*, 4*R*, 5*R*, 6*R*)-3,4,5-Tris(benzyloxy)-2-benzyloxymethyl-6-(2-[1,3]dioxolan-2-yl-ethyl)-tetrahydropyran. This compound was prepared according to the General Procedure using benzylchloro- α -D-mannose (100 mg, 0.18 mmol, 100 mol%) and actal ethylzinc bromide (0.55 mL, $\sim$ 1.0 M, 0.54 mmol, 300 mol%), NiCl₂·glyme (0.0041 g, 0.018 mmol, 10 mol%), PyBox (0.0059 g, 0.027 mmol, 15 mol%), DMI (0.35 mL). Flash column chromatography (SiO₂: 15% EtOAc in hexanes) gave the title compound as a colorless oil (74 mg, 0.118 mmol, 65% yield). ¹H NMR (600 MHz, CDCl₃): δ 7.23-7.35 (m, 23H), 7.16-7.18 (complex, 2H), 4.86 (dd, J = 6.0 and 4.2 Hz, 1H), 4.72 (d, J = 11.4 Hz, 1H), 4.64 (d, J = 12.0 Hz, 1H), 4.60 (d, J = 9.6 Hz, 1H), 4.58 (d, J = 12.6 Hz, 1H), 4.54 (s, 2H), 4.50 (d, J = 11.4 Hz, 2H), 4.00-4.02 (m, 1H), 3.91 (t, J = 7.2 Hz, 2H), 3.88-3.92 (m, 1H; *H1*), 3.80 (t, J = 7.2 Hz, 2H), 3.74-3.78 (complex, 3H; *H5*, *H3* *H6*), 3.72 (dd, J = 7.2 and 1.8 Hz, 1H; *H7*), 3.59 (complex, 1H; *H2*), 1.80-1.86 (m, 1H), 1.70-1.76 (m, 1H), 1.60-1.65 (m, 1H), 1.52-1.60 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 138.4, 138.3, 138.27, 138.2, 128.3, 128.26, 128.24, 127.9, 127.88, 127.74, 127.72, 127.6, 127.5, 127.4, 104.0, 77.9, 75.9, 74.9, 74.1, 73.3, 73.0, 72.9, 72.0, 71.5, 69.2, 64.8, 30.0, 23.6. HRMS (ESI): m/z [M+Na]⁺ found 647.301, calcd 647.298 for C₃₉H₄₄O₇Na.

(2*R*, 3*R*, 4*R*, 5*R*, 6*R*)-3,4,5-Tris(benzyloxy)-2-benzyloxymethyl-6-(2-thiophen-2-yl-ethyl)-tetrahydropyran. This compound was prepared according to the General Procedure using benzylchloro- α -D-mannose (100 mg, 0.18 mmol, 100 mol%) and thiophene ethylzinc bromide (0.55 mL, $\sim$ 1.0 M, 0.54 mmol, 300 mol%), NiCl₂·glyme (0.0041 g, 0.018 mmol, 10 mol%), PyBox (0.0059 g, 0.027 mmol, 15

mol%), DMI (0.35 mL). Flash column chromatography (SiO₂: 4% EtOAc in hexanes) gave the title compound as a colorless oil (49 mg, 0.078 mmol, 43% yield). ¹H NMR (600 MHz, CDCl₃): δ 7.24-7.31 (m, 23H), 7.17-7.19 (complex, 2H), 7.09 (dd, *J* = 4.8 and 1.2 Hz, 1H), 6.88 (dd, *J* = 4.8 and 3.6 Hz, 1H), 6.72 (dt, *J* = 3.6 and 1.2 Hz, 1H), 4.72 (d, *J* = 11.4 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.6 Hz, 1H), 4.59 (d, *J* = 12.6 Hz, 1H), 4.58 (d, *J* = 13.6 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 10.8 Hz, 1H), 4.55 (d, *J* = 11.4 Hz, 1H), 3.98 (quintet, *J* = 4.8 Hz, 1H; *H1*), 3.84 (dd, *J* = 3.6 and 1.2 Hz, 1H; *H4*), 3.79-3.80 (m, 1H; *H5*), 3.77-3.79 (m, 1H; *H6*), 3.77 (dd, *J* = 7.2 and 2.4 Hz, 1H; *H3*), 3.72 (dd, *J* = 10.2 and 3.0 Hz, 1H; *H7*), 3.56 (dd, *J* = 4.8 and 3.0 Hz, 1H; *H2*), 2.66-3.01 (m, 1H), 2.78-2.83 (m, 1H), 1.95-1.99 (m, 1H), 1.82-1.87 (m, 1H), 1.80-1.86 (m, 1H), 1.70-1.76 (m, 1H), 1.60-1.65 (m, 1H), 1.52-1.60 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 144.6, 138.4, 138.2, 138.15, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 127.5, 126.8, 124.4, 123.0, 75.9, 74.8, 73.7, 73.6, 73.3, 72.1, 71.7, 71.5, 69.1, 32.1, 26.0. HRMS (ESI): *m/z* [M+Na]⁺ found 657.265, calcd 657.267 for C₄₀H₄₂O₅SNa.

(2*R*, 3*R*, 4*R*, 5*R*, 6*R*)-2-[3-(3,4,5-Tris(benzyloxy)-6-benzyloxymethyltetrahydropyran-2-yl)-propyl]-isoindole-1,3-dione. This compound was prepared according to the General Procedure using benzylchloro- α -D-mannose (100 mg, 0.18 mmol, 100 mol%) and phthalimide propylzinc bromide (0.55 mL, ~1.0 M, 0.54 mmol, 300 mol%), NiCl₂·glyme (0.0041 g, 0.018 mmol, 10 mol%), PyBox (0.0059 g, 0.027 mmol, 15 mol%), DMI (0.35 mL). Flash column chromatography (SiO₂: 15% EtOAc in hexanes) gave the title compound as a colorless oil (96 mg, 0.11 mmol, 61% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.86 (dd, *J* = 5.2 and 2.8 Hz, 2H), 7.73 (dd, *J* = 4.8 and 2.8 Hz, 2H), 7.24-7.31 (m, 23H), 7.17-7.19 (complex, 2H), 4.67 (d, *J* = 11.4 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 12.6 Hz, 1H), 4.57 (d, *J* = 12.6 Hz, 1H), 4.56 (d, *J* = 13.6 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.54 (d, *J* = 10.8 Hz, 1H), 4.53 (d, *J* =

11.4 Hz, 1H), 3.99 (quintet, $J = 4.8$ Hz, 1H; *H1*), 3.67-3.77 (m, 7H), 3.56 (dd, $J = 4.8$ and 3.0 Hz, 1H; *H2*), 1.80-2.00 (m, 1H), 1.53-1.80 (m, 2H), 1.50-1.53 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 168.4, 138.4, 138.2, 138.19, 138.1, 133.8, 132.1, 128.3, 128.29, 128.25, 128.0, 127.9, 127.8, 127.7, 127.6, 127.56, 127.4, 123.2, 75.9, 74.7, 73.6, 73.4, 73.2, 72.1, 71.8, 71.4, 69.0, 37.7, 27.1, 25.0. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ found 734.316, calcd 734.309 for $\text{C}_{45}\text{H}_{45}\text{NO}_7\text{Na}$.

(2*R*, 3*R*, 4*R*, 5*R*, 6*R*)-3,4,5-Tris(benzyloxy)-2-benzyloxymethyl-6-pent-4-enyl-tetrahydropyran. This compound was prepared according to the General Procedure using benzylchloro- α -D-mannose (100 mg, 0.18 mmol, 100 mol%) and pentenylzinc bromide (0.55 mL, ~ 1.0 M, 0.54 mmol, 300 mol%), $\text{NiCl}_2 \cdot \text{glyme}$ (0.0041 g, 0.018 mmol, 10 mol%), PyBox (0.0059 g, 0.027 mmol, 15 mol%), DMI (0.35 mL). Flash column chromatography (SiO_2 : 4% EtOAc in hexanes) gave the title compound as a colorless oil (43 mg, 0.073 mmol, 40% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.24-7.31 (m, 23H), 7.16-7.18 (complex, 2H), 5.68-5.78 (m, 1H), 4.96 (d, $J = 17.2$ Hz, 1H), 4.92 (d, $J = 10.4$ Hz, 1H), 4.71 (d, $J = 11.6$ Hz, 1H), 4.62 (d, $J = 12.4$ Hz, 1H), 4.59-4.60 (m, 3H), 4.53 (s, 2H), 4.49 (d, $J = 11.2$ Hz, 1H), 3.96 (quintet, $J = 4.0$ Hz, 1H; *H1*), 3.85 (t, $J = 7.2$ Hz, 1H; *H4*), 3.67-3.77 (m, 4H; *H5*, *H6*, *H3*, *H7*), 3.54 (t, $J = 3.2$ Hz, 1H; *H2*), 2.01 (q, $J = 6.8$ Hz, 2H), 1.27-1.60 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 140.5, 138.5, 138.42, 138.33, 138.29, 138.24, 128.34, 128.3, 128.27, 128.0, 128.95, 127.82, 128.7, 127.65, 128.6, 127.4, 114.7, 75.9, 75.1, 74.0, 73.3, 73.27, 73.0, 72.1, 69.3, 33.5, 29.0, 25.0. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ found 615.310, calcd 615.309 for $\text{C}_{39}\text{H}_{44}\text{O}_5\text{Na}$.

NMR spectra for new compounds

Spectral assignment of β -anomer:

^1H NMR (600 MHz, CDCl_3): 7.27 (t, $J = 7.2$ Hz, 2H), 7.14-7.19 (m, 3H), 5.38 (d, $J = 3.0$ Hz, 1H; H_4), 5.05 (t, $J = 9.6$ Hz, 1H; H_2), 4.96 (dd, $J = 10.2$ and 3.6 Hz, 1H, H_3), 4.11 (dd, $J = 10.8$ and 7.2 Hz, 1H; H_6), 4.03 (dd, $J = 10.8$ and 6.6 Hz, 1H; H_7), 3.79 (t, $J = 6.6$ Hz, 1H; H_5), 3.35 (dt, $J = 9.6$ and 6.0 Hz, 1H; H_1), 2.58 (t, $J = 7.8$ Hz, 2H), 2.12 (s, 3H), 2.00 (s, 3H), 1.97 (s, 3H), 1.94 (s, 3H), 1.80-1.88 (m, 1H), 1.58-1.66 (m, 2H), 1.50-1.54 (m, 1H). **^{13}C NMR (100 MHz, CDCl_3):** δ 170.5, 170.4, 170.3, 169.9, 142.1, 128.4, 128.3, 125.8, 78.1, 74.1, 72.3, 69.3, 68.3, 67.7, 61.6, 35.5, 30.8, 26.8, 20.74, 20.70, 20.67, 20.62. HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ found 473.173, calcd 473.179 for $\text{C}_{23}\text{H}_{20}\text{O}_9\text{Na}$ (mixture of isomers).

Spectral assignment of α -anomer:

^1H NMR (600 MHz, CDCl_3): 7.14-7.29 (m, 5H), 5.34 (t, $J = 3.0$ Hz, 1H; H_4), 5.22 (dd, $J = 9.6$ and 5.4 Hz, 1H; H_2), 5.14 (dd, $J = 9.6$ and 3.0 Hz 1H; H_3), 4.18-4.23 (m, 1H; H_1), 4.17 (dd, $J = 11.4$ and 4.2 Hz, 1H, H_6), 4.16 (dd, $J = 11.4$ and 7.2 Hz, 1H; H_7), 3.96 (ddd, $J = 7.2$, 4.2 and 3.0 Hz, 1H; H_5), 2.60-2.67 (m, 2H), 2.09 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.66-1.80 (m, 2H), 1.39-1.46 (m, 2H). **^{13}C NMR (100 MHz, CDCl_3):** δ 170.6, 170.2, 170.0, 169.9, 141.8, 128.4, 128.3, 125.9, 68.4, 68.0, 67.7, 61.7, 35.2, 29.7, 24.8, 20.74, 20.70, 20.67, 20.62.

2D COSY:

1D NOESY:

1. Irradiation on H1 (3.35 ppm): H2 (5.05 ppm, 0.6%), H3 (4.96 ppm, 1.7%), H5 (3.79, 3.0%), H8 (1.5 ppm, 2.2%).

2. Irradiation on H5 (3.79 ppm): H4 (5.38 ppm, 2.1%), H3 (4.96 ppm, 1.6%), H1 (3.35, 3.0%).

1D NOESY:

1. Irradiation on H5 (3.35 ppm): H4 (5.34 ppm, 2.3%), H3 (5.14 ppm, 1.3%), H8/H9 (1.7 ppm, 3.3%).

2. Irradiation on H2 (5.22 ppm): H1 (5.20 ppm, 2.5%).

¹H NMR (600 MHz, CDCl₃): δ 7.18-7.35 (m, 25H), 4.91 (s, 2H), 4.85 (d, *J* = 10.8 Hz, 1H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.63 (d, *J* = 12 Hz, 1H), 4.59 (d, *J* = 12.6 Hz, 1H), 4.58 (d, *J* = 10.2 Hz, 1H), 4.56 (d, *J* = 10.8 Hz, 1H), 3.74 (dd, *J* = 10.8 and 1.8 Hz, 1H; *H*6), 3.67-3.70 (complex, 2H; *H*2, *H*7), 3.62 (t, *J* = 9.6 Hz, 1H; *H*4), 3.40 (ddd, *J* = 9.6, 4.2 and 1.8 Hz; *H*5), 3.24-3.30 (complex, 2H; *H*1, *H*3), 2.64 (t, *J* = 7.2 Hz, 2H), 1.86-1.93 (m, 2H), 1.68-1.95 (m, 1H), 1.49-1.56 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 142.3, 138.5, 138.1, 138.0, 137.9, 128.34, 128.31, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.59, 127.5, 127.4, 125.5, 87.3, 82.3, 79.2, 78.9, 78.6, 75.5, 75.3, 74.9, 73.4, 69.0, 35.8, 31.2, 27.5.

2D COSY:

Data Collected on:
nmrnet6-inova500
Archive directory:
/home/hegui/vnmrsys/data
Sample directory:
File: BnPhPrGlu_gcasy
Pulse Sequence: gCOSY
Solvent: CDCl3
Relax. delay 1.000 sec
Acq. time 0.107 sec
Width 9595.8 Hz
2D Width 9595.8 Hz
4 repetitions
128 increments
OBSERVE H1, 599.7425704 MHz
DATA PROCESSING
Sine bell 0.053 sec
F1 DATA PROCESSING
Sine bell 0.027 sec
FT size 4096 x 4096
Total time 9 min

1D NOESY:

1. Irradiation on H1 and H3 (3.24-3.30 ppm): H2 (3.67-3.70 ppm, 1.2%), H4 (3.62 ppm, 1.0%), H5 (3.40 ppm, 1.4%).

2. Irradiation on H4 (3.62 ppm): H5 (3.40 ppm), H3 (3.24-3.30 ppm).

3. Irradiation on H6, H7 (3.67-3.70 ppm): H5 (3.40 ppm).

4. Irradiation on H5 (3.40 ppm): H1 and H3 (3.24-3.40 ppm, 2.8%).

¹H NMR (600 MHz, CDCl₃): δ 7.12-7.37 (m, 25H), 4.93 (d, J = 10.8, 1H), 4.82 (d, J = 10.8 Hz, 1H), 4.80 (d, J = 11.4 Hz, 1H), 4.66 (d, J = 12 Hz, 1H), 4.63 (d, J = 13.2 Hz, 1H), 4.57 (d, J = 11.4 Hz, 1H), 4.49 (d, J = 12.6 Hz, 1H), 4.47 (d, J = 10.8 Hz, 1H), 4.07 (m, 1H; *H1*), 3.77 (t, J = 9.6 Hz, 1H), 3.75-3.76 (complex 1H), 3.74 (dd, J = 9.6 and 6.0 Hz, 1H; *H2*), 3.69 (dd, J = 10.8 and 4.2 Hz, 1H), 3.60-3.66 (complex, 2H), 3.54 (dd, J = 10.2 and 3.6 Hz, 1H; *H5*), 2.68 (m, 2H), 1.75-1.81 (m, 2H), 1.69-1.75 (m, 1H), 1.60-1.69 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 142.2, 138.7, 138.2, 138.1, 137.9, 128.34, 128.28, 127.9, 127.8, 127.71, 127.67, 127.57, 127.53, 125.7, 82.5, 80.2, 78.2, 75.4, 75.0, 73.7, 73.4, 73.0, 70.9, 69.0, 35.4, 26.9, 24.1.

2D COSY:

STANDARD PROTON PARAMETERS

Data Collected on:
nmrnet6-inova600
Archive directory:
/home/hegui/vnmrsys/data
Sample directory:

File: BnPhPralphGlu_gcosy

Pulse Sequence: gCOSY
Solvent: CDC13

Relax. delay 1.000 sec
Acq. time 0.107 sec
Width 9595.8 Hz
2D Width 9595.8 Hz
6 repetitions
128 increments
OBSERVE H1, 599.7425704 MHz
DATA PROCESSING
Sine bell 0.053 sec
F1 DATA PROCESSING
Sine bell 0.027 sec
FT size 4096 x 4096
Total time 14 min

1D NOE:

1. irradiation on H1: H2 (3.74 ppm), H8/ H9 (1.60-1.90 ppm)

2. Irradiation on H5: (3.60-3.66 ppm, H3), H8/ H9 (1.70-1.78 ppm)

¹H NMR (400 MHz, CDCl₃): δ 7.26-7.34 (m, 23H), 7.16-7.18 (complex, 2H), 4.90 (s, 2H), 4.88 (d, *J* = 13.2 Hz, 1H), 4.82 (d, *J* = 10.8 Hz, 1H), 4.64 (d, *J* = 10.8 Hz, 1H), 4.63 (d, *J* = 12.4 Hz, 1H), 4.57 (d, *J* = 10.0 Hz, 1H), 4.54 (d, *J* = 12 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.66-3.73 (m, 3H), 3.62 (t, *J* = 9.2 Hz, 1H; *H*4), 3.38 (m, 1H; *H*5), 3.26-3.33 (complex, 2H; *H*1, *H*3), 2.30 (t, *J* = 7.2 Hz, 2H), 1.80-1.87 (m, 2H), 1.65-1.80 (m, 1H), 1.43-1.54 (m, 1H), 1.23 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 173.6, 138.6, 138.2, 138.1, 128.4, 128.38, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 127.55, 87.3, 82.1, 78.9, 78.5, 75.5, 75.2, 74.9, 73.5, 69.0, 60.1, 34.3, 31.0, 29.7, 21.2, 14.2.

¹H NMR (400 MHz, CDCl₃): δ 7.26-7.34 (m, 23H), 7.16-7.18 (complex, 2H), 4.91 (d, J = 10.8 Hz, 1H), 4.79 (d, J = 10.4 Hz, 1H), 4.77 (d, J = 10.4 Hz, 1H), 4.67 (d, J = 11.6 Hz, 1H), 4.62 (d, J = 10.4 Hz, 1H), 4.59 (d, J = 11.2 Hz, 1H), 4.46 (d, J = 13.6 Hz, 1H), 4.45 (d, J = 10.4 Hz, 1H), 4.10 (q, J = 7.2 Hz, 2H), 4.02 (m, 1H), 3.72-3.77 (complex, 2H), 3.69 (dd, J = 11.2 and 4.4 Hz, 1H), 3.55-3.61 (complex, 2H), 3.54 (dd, J = 9.6 and 3.6 Hz, 1H), 2.32 (ddd, J = 13.6, J = 9.2 and 6.8 Hz, 2H), 1.53-1.85 (m, 4H), 1.23 (t, J = 7.2).

¹³C NMR (100 MHz, CDCl₃): δ 173.4, 138.8, 138.2, 138.0, 128.4, 128.36, 128.32, 127.9, 127.8, 127.77, 127.7, 127.6, 127.56, 82.5, 80.1, 78.1, 75.5, 75.0, 73.8, 73.5, 73.1, 71.0, 68.9, 60.2, 33.9, 24.0, 20.9, 14.2.

¹H NMR (400 MHz, CDCl₃): δ 7.19-7.36 (m, 25H), 4.90-4.94 (complex, 3H), 4.87 (d, J = 10.0 Hz, 1H), 4.84 (d, J = 10.8 Hz, 1H), 4.69 (d, J = 10.4 Hz, 1H), 4.65 (d, J = 12.0 Hz, 1H), 4.60 (d, J = 12 Hz, 1H), 4.57 (d, J = 12.8 Hz, 1H), 3.97 (t, J = 6.0 Hz, 2H), 3.86 (t, J = 6.0 Hz, 2H), 3.67-3.77 (m, 3H), 3.64 (t, J = 9.2 Hz, 1H; *H*4), 3.41 (m, 1H; *H*5), 3.26-3.33 (complex, 2H; *H*1, *H*3), 2.64 (t, J = 7.2 Hz, 2H), 1.90-2.10 (m, 2H), 1.72-1.84 (m, 1H), 1.56-1.70 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 138.2, 128.4, 128.38, 128.3, 128.2, 128.0, 127.9, 127.8, 127.4, 104.5, 87.3, 82.4, 78.9, 78.6, 75.6, 74.9, 73.4, 64.9, 64.8, 29.8, 26.0.

¹H NMR (400 MHz, CDCl₃): δ 7.11-7.37 (m, 25H), 4.87-4.93 (m, 3H), 4.79 (d, *J* = 10.8 Hz, 1H), 4.77 (d, *J* = 10.8 Hz, 1H), 4.66 (d, *J* = 11.6 Hz, 1H), 4.61 (d, *J* = 11.4 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.43 (d, *J* = 10.4 Hz, 1H), 4.03 (m, 1H), 3.93 (t, *J* = 6.4 Hz, 2H), 3.85 (t, *J* = 6.4 Hz, 2H), 3.73-3.81 (complex, 2H), 3.68 (dd, *J* = 10.0 and 2.4 Hz, 1H), 3.54-3.64 (complex, 3H), 2.68 (m, 2H), 1.75-1.81 (m, 2H), 1.69-1.75 (m, 1H), 1.60-1.69 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 138.8, 138.3, 138.18, 138.0, 128.4, 128.3, 127.9, 127.88, 127.82, 127.7, 127.6, 127.55, 104.1, 82.5, 80.2, 78.1, 77.3, 75.5, 75.1, 74.0, 73.5, 73.0, 70.8, 68.9, 64.9, 29.6, 18.8.

¹H NMR (600 MHz, CDCl₃): δ 7.25-7.33 (m, 23H), 7.16-7.18 (complex, 2H), 4.68 (d, *J* = 11.4 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.6 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.52 (s, 2H), 4.50 (d, *J* = 11.4 Hz, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.95 (quintet, *J* = 4.2 Hz, 1H; *H1*), 3.84 (q, *J* = 6.6 Hz, 1H; *H4*), 3.76-3.78 (m, 1H; *H5*), 3.74-3.75 (m, 1H; *H6*), 3.73 (dd, *J* = 6.6 and 2.4 Hz, 1H; *H3*), 3.68-3.71 (m, 1H; *H7*), 3.55 (dd, *J* = 4.2 and 3.0 Hz, 1H; *H2*), 2.28 (t, *J* = 7.2 Hz, 2H), 1.73-1.77 (m, 1H), 1.57-1.62 (m, 2H), 1.48-1.51 (m, 1H), 1.21 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 173.3, 138.2, 138.1, 138.05, 128.2, 128.17, 128.1, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 75.8, 74.7, 73.7, 73.2, 73.15, 72.3, 72.0, 71.4, 69.0, 60.1, 33.8, 28.9, 21.1, 14.1.

2D COSY:

STANDARD PROTON PARAMETERS

Data Collected on:
nmrnet5-inova500
Archive directory:
/home/hegui/vnmrsys/data
Sample directory:

File: BnEsterMann_gcosy

Pulse Sequence: gCOSY
Solvent: CDC13

Relax. delay 1.000 sec
Acq. time 0.107 sec
Width 9595.8 Hz
2D Width 9595.8 Hz
3 repetitions
128 increments
OBSERVE H1, 599.7425704 MHz
DATA PROCESSING
Sine bell 0.053 sec
F1 DATA PROCESSING
Sine bell 0.027 sec
FT size 4096 x 4096
Total time 7 min

1D NOESY:

1. Irradiation on H1 (3.97 ppm): H6 (3.74-3.75, 1.3%), H7 (3.68-3.71 ppm, 0.5%), H2 (3.55 ppm, 1.1%).

2. Irradiation on H2 (3.55 ppm): H1 (3.97 ppm, 1.3%), H3 (3.73 ppm, 2.5%), H8 and H9 (1.4-1.6 ppm, 2.4%).

3. Irradiation on H8 and H9 (1.4-1.6 ppm): H1 (3.97 ppm, 2.0%), H3 and H5 (3.73-3.78 ppm, 1.5%), H2 (3.55 ppm, 1.3%).

¹H NMR (400 MHz, CDCl₃): δ 7.86 (dd, $J = 5.2$ and 2.8 Hz, 2H), 7.73 (dd, $J = 4.8$ and 2.8 Hz, 2H), 7.24-7.31 (m, 23H), 7.17-7.19 (complex, 2H), 4.67 (d, $J = 11.4$ Hz, 1H), 4.61 (d, $J = 12.0$ Hz, 1H), 4.60 (d, $J = 12.6$ Hz, 1H), 4.57 (d, $J = 12.6$ Hz, 1H), 4.56 (d, $J = 13.6$ Hz, 1H), 4.55 (d, $J = 12.0$ Hz, 1H), 4.54 (d, $J = 10.8$ Hz, 1H), 4.53 (d, $J = 11.4$ Hz, 1H), 3.99 (quintet, $J = 4.8$ Hz, 1H; *H1*), 3.67-3.77 (m, 7H), 3.56 (dd, $J = 4.8$ and 3.0 Hz, 1H; *H2*), 1.80-2.00 (m, 1H), 1.53-1.80 (m, 2H), 1.50-1.53 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 168.4, 138.4, 138.2, 138.19, 138.1, 133.8, 132.1, 128.3, 128.29, 128.25, 128.0, 127.9, 127.8, 127.7, 127.6, 127.56, 127.4, 123.2, 75.9, 74.7, 73.6, 73.4, 73.2, 72.1, 71.8, 71.4, 69.0, 37.7, 27.1, 25.0.

¹H NMR (400 MHz, CDCl₃): δ 7.24-7.31 (m, 23H), 7.16-7.18 (complex, 2H), 5.68-5.78 (m, 1H), 4.96 (d, *J* = 17.2 Hz, 1H), 4.92 (d, *J* = 10.4 Hz, 1H), 4.71 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 12.4 Hz, 1H), 4.59-4.60 (m, 3H), 4.53 (s, 2H), 4.49 (d, *J* = 11.2 Hz, 1H), 3.96 (quintet, *J* = 4.0 Hz, 1H; *H*1), 3.85 (t, *J* = 7.2 Hz, 1H; *H*4), 3.67-3.77 (m, 4H; *H*5, *H*6, *H*3, *H*7), 3.54 (t, *J* = 3.2 Hz, 1H; *H*2), 2.01 (q, *J* = 6.8 Hz, 2H), 1.27-1.60 (m, 4H).

¹³C NMR (100 MHz, CDCl₃): δ 138.5, 138.4, 138.3, 138.26, 138.2, 128.34, 128.29, 128.26, 128.0, 127.95, 127.8, 128.7, 127.65, 127.6, 127.4, 114.7, 77.7, 75.8, 75.0, 74.1, 73.3, 73.2, 73.0, 72.1, 71.5, 69.3, 33.5, 28.9, 25.0.

¹H NMR (600 MHz, CDCl₃): δ 7.23-7.35 (m, 23H), 7.16-7.18 (complex, 2H), 4.86 (dd, *J* = 6.0 and 4.2 Hz, 1H), 4.72 (d, *J* = 11.4 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 9.6 Hz, 1H), 4.58 (d, *J* = 12.6 Hz, 1H), 4.54 (s, 2H), 4.50 (d, *J* = 11.4 Hz, 2H), 4.00-4.02 (m, 1H), 3.91 (t, *J* = 7.2 Hz, 2H), 3.88-3.92 (m, 1H; *H1*), 3.80 (t, *J* = 7.2 Hz, 2H), 3.74-3.78 (complex, 3H; *H5*, *H3*, *H6*), 3.72 (dd, *J* = 7.2 and 1.8 Hz, 1H; *H7*), 3.59 (complex, 1H; *H2*), 1.80-1.86 (m, 1H), 1.70-1.76 (m, 1H), 1.60-1.65 (m, 1H), 1.52-1.60 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 138.4, 138.3, 138.27, 138.2, 128.3, 128.26, 128.24, 127.9, 127.88, 127.74, 127.72, 127.6, 127.5, 127.4, 104.0, 77.9, 75.9, 74.9, 74.1, 73.3, 73.0, 72.9, 72.0, 71.5, 69.2, 64.8, 30.0, 23.6.

2D COSY:

STANDARD PROTON PARAMETERS

Data Collected on:
nmrnet6-incva600
Archive directory:
/home/hegui/vnmrsys/data
Sample directory:

File: BnAcetalMann_gcasy

Pulse Sequence: gCOSY
Solvent: CDCl₃

Relax. delay 1.000 sec
Acq. time 0.107 sec
Width 9595.8 Hz
2D Width 9595.8 Hz
4 repetitions
128 increments
OBSERVE H1, 599.7425704 MHz
DATA PROCESSING
Sine bell 0.075 sec
F1 DATA PROCESSING
Sine bell 0.013 sec
FT size 4096 x 4096
Total time 9 min

¹H NMR (600 MHz, CDCl₃): δ 7.24-7.31 (m, 23H), 7.17-7.19 (complex, 2H), 7.09 (dd, J = 4.8 and 1.2 Hz, 1H), 6.88 (dd, J = 4.8 and 3.6 Hz, 1H), 6.72 (dt, J = 3.6 and 1.2 Hz, 1H), 4.72 (d, J = 11.4 Hz, 1H), 4.63 (d, J = 12.0 Hz, 1H), 4.62 (d, J = 12.6 Hz, 1H), 4.59 (d, J = 12.6 Hz, 1H), 4.58 (d, J = 13.6 Hz, 1H), 4.57 (d, J = 12.0 Hz, 1H), 4.56 (d, J = 10.8 Hz, 1H), 4.55 (d, J = 11.4 Hz, 1H), 3.98 (quintet, J = 4.8 Hz, 1H; *H1*), 3.84 (dd, J = 3.6 and 1.2 Hz, 1H; *H4*), 3.79-3.80 (m, 1H; *H5*), 3.77-3.79 (m, 1H; *H6*), 3.77 (dd, J = 7.2 and 2.4 Hz, 1H; *H3*), 3.72 (dd, J = 10.2 and 3.0 Hz, 1H; *H7*), 3.56 (dd, J = 4.8 and 3.0 Hz, 1H; *H2*), 2.66-3.01 (m, 1H), 2.78-2.83 (m, 1H), 1.95-1.99 (m, 1H), 1.82-1.87 (m, 1H), 1.80-1.86 (m, 1H), 1.70-1.76 (m, 1H), 1.60-1.65 (m, 1H), 1.52-1.60 (m, 1H).

¹³C NMR (100 MHz, CDCl₃): δ 144.6, 138.4, 138.2, 138.15, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 127.5, 126.8, 124.4, 123.0, 75.9, 74.8, 73.7, 73.6, 73.3, 72.1, 71.7, 71.5, 69.1, 32.1, 26.0.

^1H NMR (400 MHz, CDCl_3): δ 7.27 (t, $J = 7.2$ Hz, 2H), 7.14-7.19 (m, 3H), 5.27 (t, $J = 9.2$ Hz, 1H; *H*3), 5.04 (dd, $J = 9.6$ and 5.6, Hz, 1H; *H*2), 4.94 (t, $J = 9.2$ Hz, 1H; *H*4), 4.19 (dd, $J = 12.0$ and 5.2 Hz, 1H; *H*7), 4.17-4.21 (m, 1H; *H*1), 4.04 (dd, $J = 12.0$ and 2.0 Hz, 1H; *H*6), 3.73 (ddd, $J = 9.2$, 5.2, and 2.0 Hz, 1H; *H*5), 2.55-2.69 (m, 2H), 2.06 (s, 3H), 2.034 (s, 3H), 2.027 (s, 3H), 2.02 (s, 3H), 1.70-1.90 (m, 2H), 1.40-1.70 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 170.7, 170.2, 169.7, 169.6, 141.7, 128.4, 128.3, 126.0, 72.3, 70.4, 68.9, 68.6, 62.4, 35.2, 26.5, 24.5, 20.71, 20.66.

2D COSY:

Spectral assignment of β -anomer:

^1H NMR (600 MHz, CDCl_3): δ 7.10-7.28 (m, 5H), 5.30 (d, $J = 3.6$, 1H), 5.21 (d, $J = 3.6$ Hz, 2H), 5.01 (dd, $J = 10.2$ and 3.0 Hz, 1H), 4.23 (dd, $J = 6.6$ and 3.0 Hz, 1H), 3.54-3.58 (m, 2H), 2.54-2.58 (m, 2H), 2.09 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.96 (s, 3H), 1.74-1.83 (m, 2H), 1.62-1.72 (m, 1H), 154-1.62 (m, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 170.7, 170.5, 170.2, 169.6, 141.7, 128.4, 128.3, 125.8, 76.2, 75.2, 74.6, 72.5, 69.4, 66.2, 62.9, 35.4, 29.8, 29.6, 20.9, 20.8, 20.6, 20.4.

Spectral assignment of α -anomer:

^1H NMR (600 MHz, CDCl_3): δ 7.27 (t, $J = 7.6$ Hz, 2H), 7.15-7.19 (m, 3H), 5.21 (dd, $J = 9.0$ and 3.6 Hz, 1H; $H3$), 5.18 (t, $J = 9.0$ Hz, 1H; $H4$), 5.14 (t, $J = 3.0$ Hz, 1H; $H2$), 4.29 (dd, $J = 12.0$ and 6.0 Hz, 1H; $H6$), 4.07 (dd, $J = 12.0$ and 2.4 Hz, 1H; $H7$), 3.97 (dt, $J = 9.6$ and 3.6 Hz, 1H; $H1$), 3.78 (ddd, $J = 9.0$, 6.0 and 3.0 Hz, 1H; $H5$), 2.59-2.69 (m, 2H), 2.11 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.74-1.83 (m, 2H), 1.62-1.72 (m, 1H), 154-1.62 (m, 1H).

^{13}C NMR (100 MHz, CDCl_3): δ 170.6, 170.2, 170.0, 169.6, 141.6, 128.4, 128.3, 125.9, 74.9, 70.7, 70.1, 69.0, 66.9, 62.5, 35.1, 27.8, 27.0, 20.9, 20.68, 20.65.

2D COSY:

1D NOESY:

1. Irradiation on H1 (3.97 ppm): H2 (5.14 ppm, 1.4%), H6/H7 (4.29 ppm, 0.6%).

2. Irradiation on H5 (3.78 ppm): H3 and H4 (5.18-5.21 ppm, 2.0%), H8/H9 (1.74-1.83 ppm, 2.8%).

Spectral assignment of α -anomer:

^1H NMR (400 MHz, CDCl_3): δ 5.13-5.23 (complex, 3H), 4.85-4.90 (bs, 1H), 4.29 (dd, $J = 6.0$ Hz, $J = 12$ Hz, 1H), 4.03-4.07 (complex, 1H), 3.90-4.00 (complex, 3H), 3.78-3.88 (complex, 3H), 2.74 (m, 2H), 2.12 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.60-1.90 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 170.7, 170.2, 170.0, 169.6, 103.4, 74.8, 70.8, 70.0, 68.9, 65.0, 64.9, 62.4, 45.0, 29.4, 22.4, 20.9, 20.7, 20.67.

Spectral assignment of α -anomer:

^1H NMR (400 MHz, CDCl_3): δ 5.21 (dd, $J = 8.8$ and 3.0 Hz, 1H; H_3), 5.17 (t, $J = 8.8$ Hz, 1H; H_4), 5.12 (t, $J = 3.0$ Hz, 1H; H_2), 4.31 (dd, $J = 12.0$ and 6.0 Hz, 1H; H_6), 4.11 (q, $J = 7.2$ Hz, 2H), 4.07 (dd, $J = 9.6$ and 2.4 Hz, 1H; H_7), 3.93 (dt, $J = 10$ Hz and 3.2 Hz, 1H; H_1), 3.85 (ddd, $J = 8.8$, 6.0 and 2.4 Hz, 1H; H_5), 2.40-2.25 (m, 2H), 2.10 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H), 1.72-1.88 (m, 2H), 1.52-1.67 (m, 2H).

^{13}C NMR (100 MHz, CDCl_3): δ 172.8, 170.5, 170.1, 169.8, 169.5, 74.5, 70.5, 70.1, 68.8, 66.7, 62.2, 60.2, 33.2, 27.6, 20.8, 20.6, 20.5, 14.0.