

Supplementary Information

Simple synthesis of 2-*C*-branched glyco-acetic acids

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General procedure for the demethoxycarbonylation of carbohydrates **3**.

A solution of the carbohydrate **3** (1.0 mmol) and lithium iodide (201 mg, 1.5 mmol) in DMSO (12 mL) was heated to 180 °C in a Kugelrohrföfen and kept under rotation at this temperature for several hours (Table 1). DMSO was removed at 0.01 mbar directly in the Kugelrohrföfen and the crude product was purified by flash chromatography (*n*-hexane/ethyl acetate 4:1→3:1).

4a (*gluco* configuration) (4.5 hours):

Yield: 92%; $[\alpha]_D^{20} = +20.3$ (*c* 1.20, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ =2.01, 2.02, 2.08 (3s, 3H each, OAc), 2.27 (dddd, *J* = 11.1, 8.7, 5.7, 2.4 Hz, 1 H, 2-H), 2.39 – 2.43 (m, 2 H, 7-H, 7'-H), 3.51 (s, 3 H, OMe), 3.67 (s, 3 H, COOMe), 3.70 (ddd, *J* = 9.6, 4.5, 2.4 Hz, 1 H, 5-H), 4.13 (dd, *J* = 12.3, 2.4 Hz, 1 H, 6-H), 4.30 (dd, *J* = 12.3, 4.5 Hz, 1 H, 6'-H), 4.47 (d, *J* = 8.7 Hz, 1 H, 1-H), 4.99 (dd, *J* = 9.6, 9.3 Hz, 1 H, 4-H), 5.12 (dd, *J* = 11.1, 9.3 Hz, 1 H, 3-H); ¹³C NMR (75 MHz, CDCl₃): δ =20.5, 20.6 (3q, OAc), 31.5 (t, C-7), 43.2 (d, C-2), 51.6 (q, COOMe), 57.1 (q, OMe), 62.2 (t, C-6), 69.6, 71.6, 72.9 (3d, C-3, C-4, C-5), 103.0 (d, C-1), 169.7, 170.3, 170.6, 171.6 (4s, OAc, COOMe); IR (film): ν = 3002, 2972, 1751, 1372, 1237 cm⁻¹; elemental analysis (%) calcd for C₁₆H₂₄O₁₀: C 51.06, H 6.43; found: C 51.03, H 6.57.

4b (*galacto* configuration) (4.5 hours):

Yield: 81%; $[\alpha]_{\text{D}}^{20} = -0.84$ (*c* 1.02, CHCl_3); ^1H NMR (300 MHz, CDCl_3): $\delta=1.99, 2.05, 2.14$ (3s, 3H each, OAc), 2.42 (dddd, $J = 11.1, 8.4, 4.8, 3.0$ Hz, 1 H, 2-H), 2.36 – 2.49 (m, 2 H, 7-H, 7'-H), 3.52 (s, 3 H, OMe), 3.67 (s, 3 H, COOMe), 3.87 (ddd, $J = 6.9, 6.6, 0.9$ Hz, 1 H, 5-H), 4.12 (dd, $J = 11.1, 6.9$ Hz, 1 H, 6-H), 4.20 (dd, $J = 11.1, 6.6$ Hz, 1 H, 6'-H), 4.40 (d, $J = 8.4$ Hz, 1 H, 1-H), 4.92 (dd, $J = 11.4, 3.3$ Hz, 1 H, 3-H), 5.29 (dd, $J = 3.3, 0.9$ Hz, 1 H, 4-H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=20.5, 20.6$ (3q, OAc), 31.4 (t, C-7), 38.6 (d, C-2), 51.6 (q, COOMe), 57.2 (q, OMe), 61.6 (t, C-6), 65.8, 70.6, 71.3 (3d, C-3, C-4, C-5), 103.6 (d, C-1), 170.0, 170.3, 170.4, 171.9 (4s, OAc, COOMe); IR (film): $\nu = 2956, 2849, 1747, 1372, 1244$ cm^{-1} ; elemental analysis (%) calcd for $\text{C}_{16}\text{H}_{24}\text{O}_{10}$: C 51.06, H 6.43; found: C 51.54, H 6.53.

4c (*xylo* configuration) (5.0 hours):

Yield: 81%; $[\alpha]_{\text{D}}^{20} = +26.82$ (*c* 1.08, CHCl_3); ^1H NMR (300 MHz, CDCl_3): $\delta=2.03, 2.05$ (2s, 3H each, OAc), 2.25 (dddd, $J = 10.2, 7.8, 4.2, 1.2$ Hz, 1 H, 2-H), 2.43 (d, $J = 6.0$, 2H, 6-H), 3.36 (dd, $J = 11.7, 8.7$ Hz, 1 H, 5-H), 3.46 (s, 3 H, OMe), 3.67 (s, 3 H, COOMe), 4.11 (dd, $J = 11.7, 5.4$ Hz, 1 H, 5'-H), 4.39 (d, $J = 7.8$ Hz, 1 H, 1-H), 4.89 (ddd, $J = 8.7, 8.4, 5.4$ Hz, 1 H, 4-H), 5.05 (dd, $J = 10.2, 8.4$ Hz, 1 H, 3-H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=20.7, 20.8$ (2q, OAc), 32.2 (t, C-6), 42.2 (d, C-2), 51.7 (q, COOMe), 56.8 (q, OMe), 62.3 (t, C-5), 70.2, 72.1 (2d, C-3, C-4), 103.2 (d, C-1), 170.0, 170.2, 171.8 (3s, OAc, COOMe); IR (film): $\nu = 2955, 2849, 1747, 1372, 1244$ cm^{-1} ; elemental analysis (%) calcd for $\text{C}_{13}\text{H}_{20}\text{O}_8$: C 51.31, H 6.62; found: C 51.72, H 6.73.

4d (*arabino* configuration) (5.5 hours):

Yield: 79%; $[\alpha]_D^{20} = -26.85$ (*c* 1.22, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ =2.02, 2.14 (2s, 3H each, OAc), 2.42 (t, *J* = 5.7, 2H, 6-H), 2.52 (dddd, *J* = 11.4, 8.4, 3.6, 1.5 Hz, 1 H, 2-H), 3.50 (s, 3 H, OMe), 3.65 (dd, *J* = 13.2, 1.2 Hz, 1 H, 5-H), 3.67 (s, 3 H, COOMe), 4.05 (dd, *J* = 13.2, 2.4 Hz, 1 H, 5'-H), 4.30 (d, *J* = 8.4 Hz, 1 H, 1-H), 4.91 (dd, *J* = 11.4, 3.3 Hz, 1 H, 3-H), 5.17 (ddd, *J* = 3.3, 2.4, 1.2 Hz, 1 H, 4-H); ¹³C NMR (75 MHz, CDCl₃): δ =20.6, 20.9 (2q, OAc), 31.7 (t, C-6), 39.0 (d, C-2), 51.6 (q, COOMe), 57.0 (q, OMe), 64.2 (t, C-5), 66.8, 71.0 (2d, C-3, C-4), 103.8 (d, C-1), 170.1, 170.4, 172.0 (3s, OAc, COOMe); IR (film): ν = 2955, 2847, 1742, 1373, 1249 cm⁻¹; elemental analysis (%) calcd for C₁₃H₂₀O₈: C 51.31, H 6.62; found: C 51.40, H 6.60.

4e (*malto* configuration) (6.0 hours):

Yield: 73%; $[\alpha]_D^{20} = +72.8$ (*c* 1.07, CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ =2.00, 2.03, 2.06, 2.10, 2.14 (6s, 3H each, OAc), 2.07 (dddd, *J* = 11.1, 8.7, 5.7, 5.4 Hz, 1 H, 2-H), 2.31 (dd, *J* = 16.4, 5.7 Hz, 1 H, 13-H), 2.41 (dd, *J* = 16.4, 5.4 Hz, 1 H, 13'-H), 3.48 (s, 3 H, OMe), 3.66 (s, 3 H, COOMe), 3.68 (ddd, *J* = 9.3, 4.5, 2.7 Hz, 1 H, 5-H), 3.90 (dd, *J* = 9.3, 8.7 Hz, 1 H, 4-H), 3.98 (ddd, *J* = 10.2, 3.6, 2.4 Hz, 1 H, 11-H), 4.05 (dd, *J* = 12.3, 2.1 Hz, 1 H, 12-H), 4.26 (dd, *J* = 12.3, 4.5 Hz, 1 H, 12'-H), 4.26 (dd, *J* = 12.0, 4.5 Hz, 1 H, 6-H), 4.47 (dd, *J* = 12.0, 2.7 Hz, 1 H, 6'-H), 4.49 (d, *J* = 8.7 Hz, 1 H, 1-H), 4.89 (dd, *J* = 10.5, 3.9 Hz, 1 H, 8-H), 5.05 (dd, *J* = 10.5, 9.3 Hz, 1 H, 10-H), 5.20 (dd, *J* = 11.1, 8.7 Hz, 1 H, 3-H), 5.35 (d, *J* = 3.9 Hz, 1 H, 7-H), 5.35 (dd, *J* = 10.5, 9.3 Hz, 1 H, 9-H); ¹³C NMR (75 MHz, CDCl₃): δ =20.6, 20.8, 20.9 (6q, OAc), 31.4 (t, C-13), 43.9 (d, C-2), 51.6 (q, COOMe), 57.1 (q, OMe), 61.6, 63.2 (2t, C-6, C-12), 68.1, 68.4, 69.4, 70.0, 72.2, 74.0, 75.3 (7d, C-3,

C-4, C-5, C-8, C-9, C-10, C-11), 95.5, 102.7 (2d, C-1, C-7), 169.4, 169.8, 170.4, 170.5, 171.7 (7s, OAc, COOMe). IR (film): $\nu = 2960, 1746, 1371, 1230, 1042 \text{ cm}^{-1}$; elemental analysis (%) calcd for $\text{C}_{30}\text{H}_{42}\text{O}_{18}$: C 50.60, H 6.07; found: C 50.34, H 6.08.

4f (*lacto* configuration) (6.0 hours):

Yield: 72%; $[\alpha]_{\text{D}}^{20} = +13.7$ (*c* 1.03, CHCl_3); ^1H NMR (300 MHz, CDCl_3): $\delta=1.96, 2.05, 2.06, 2.07, 2.12, 2.15$ (6s, 3H each, OAc), 2.22 (dddd, $J = 10.8, 8.7, 5.7, 2.4$ Hz, 1 H, 2-H), 2.38 (dd, $J = 5.7, 3.0$ Hz, 2 H, 13-H), 3.34 (dd, $J = 10.8, 0.9$ Hz, 1 H, 4-H), 3.47 (s, 3 H, OMe), 3.57 (ddd, $J = 9.9, 5.1, 2.1$ Hz, 1 H, 5-H), 3.66 (s, 3 H, COOMe), 3.67 – 3.73 (m, 1 H, 11-H), 3.84 – 3.91 (m, 1 H, 12-H), 4.04 – 4.20 (m, 2 H, 6-H, 12'-H), 4.38 (d, $J = 8.7$ Hz, 1 H, 1-H), 4.44 – 4.52 (m, 1 H, 6'-H), 4.45 (dd, $J = 7.8, 2.4$ Hz, 1 H, 8-H), 4.95 (dd, $J = 10.5, 3.3$ Hz, 1 H, 10-H), 5.07 (d, $J = 7.8$ Hz, 1 H, 7-H), 5.07 (dd, $J = 2.4, 1.2$ Hz, 1 H, 9-H), 5.35 (dd, $J = 3.3, 0.9$ Hz, 1 H, 3-H); ^{13}C NMR (75 MHz, CDCl_3): $\delta=20.6, 20.8, 21.0$ (6q, OAc), 31.9 (t, C-13), 43.6 (d, C-2), 51.6 (q, COOMe), 57.1 (q, OMe), 60.3, 60.8 (2t, C-6, C-12), 62.3, 66.7, 69.2, 70.6, 71.0, 72.7, 76.9 (7d, C-3, C-4, C-5, C-8, C-9, C-10, C-11), 101.0, 103.1 (2d, C-1, C-7), 169.0, 170.0, 170.1, 170.3, 170.4, 171.8 (7s, OAc, COOMe); IR (film): $\nu = 2957, 1751, 1372, 1229, 1050 \text{ cm}^{-1}$; elemental analysis (%) calcd for $\text{C}_{30}\text{H}_{42}\text{O}_{18}$: C 50.60, H 6.07; found: C 50.67, H 6.20.

Addition of dimethyl malonate (2) to tri-*O*-benzyl-*D*-glucal (1g).

A solution of tri-*O*-benzyl-*D*-glucal (**1g**) (2.08 g, 5.0 mmol), dimethyl malonate (**2**) (5.8 mL, 50 mmol) and NaHCO_3 (1.68 g, 20 mmol) in dry methanol (20 mL) was cooled to 0 °C under an argon atmosphere. At this temperature, a solution of ceric(IV) ammonium nitrate (CAN) (10.96 g, 4

equiv) in methanol (30 mL) was added dropwise over a period of 5.5 h until TLC showed complete conversion of the starting material. After stirring for 30 min at 0 °C, an ice-cold diluted solution of sodium thiosulfate (200 mL) was added, and the mixture was extracted with dichloromethane (4 x 80 mL). The combined organic extracts were dried (Na₂SO₄) and concentrated, and the excess of malonate was removed at 0.01 mbar in a Kugelrohrfen. The crude product was purified by column chromatography (*n*-hexane /ethyl acetate 10:1 → 8:1).

Gluco isomer **3g**:

Yield: 78%; $[\alpha]_{\text{D}}^{20} = +5.0$ (*c* 1.10, CHCl₃); ¹H-NMR (500 MHz, CDCl₃): δ =2.43 (ddd, *J*=12.5, 9.0, 4.0 Hz, 1 H, 2-H), 3.38 (s, 3 H, OMe), 3.43 (ddd, *J*=11.5, 4.0, 3.0 Hz, 1 H, 5-H), 3.50 (s, 3 H, CO₂Me), 3.58 (dd, *J*= 12.5, 8.5 Hz, 1 H, 3-H), 3.62 (s, 3 H, CO₂Me), 3.68 (d, *J*= 3.0 Hz, 2 H, 6-H), 3.73 (dd, *J*= 11.5, 8.5 Hz, 1 H, 4-H), 3.85 (d, *J*= 4.0 Hz, 1 H, 7-H), 4.46 (d, *J*= 11.0 Hz, 1 H, CH₂-Ph), 4.49 (d, *J*= 12.0 Hz, 1 H, CH₂-Ph), 4.52 (d, *J*= 10.5 Hz, 1 H, CH₂-Ph), 4.59 (d, *J*= 12.0 Hz, 1 H, CH₂-Ph), 4.66 (d, *J*= 9.0 Hz, 1 H, 1-H), 4.69 (d, *J*= 11.0 Hz, 1 H, CH₂-Ph), 4.82 (d, *J*= 10.5 Hz, 1 H, CH₂-Ph), 7.06 – 7.30 (m, 15 H, arom. H); ¹³C NMR (125 MHz, CDCl₃): δ =48.0, 48.2 (2d, C-2, C-7), 52.1, 52.2 (2q, COOMe), 57.2 (q, OMe), 68.9 (t, C-6), 73.5, 74.6, 74.7 (3t, CH₂-Ph), 75.0, 80.0, 80.4 (3d, C-3, C-4, C-5), 101.9 (d, C-1), 127.6, 127.7, 127.8, 128.3, 128.4 (15d, arom, C-H), 137.9, 138.1, 138.2 (3s, arom. C-CH₂O), 169.0, 169.5 (2s, COOMe); IR (film): ν = 3025, 2947, 2860, 1729, 1435, 1237 cm⁻¹; elemental analysis (%) calcd for C₃₃H₃₈O₉: C 68.50, H 6.62; found: C 68.75, H 6.58.

Manno isomer 3h:

Yield: 13%; $[\alpha]_D^{20} = +3.4$ (c 0.92, CHCl_3); $^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta=3.14$ (ddd, $J=10.5, 5.0, 1.5$ Hz, 1 H, 2-H), 3.27 (s, 3 H, OMe), 3.36 (s, 3 H, CO_2Me), 3.58 (ddd, $J=9.5, 6.0, 3.5$ Hz, 1 H, 5-H), 3.64 (s, 3 H, CO_2Me), 3.65 – 3.70 (m, 2 H, 6-H, 6'-H), 3.65 – 3.70 (m, 2 H, 6-H, 6'-H), 3.67 (d, $J=5.0$ Hz, 1 H, 7-H), 3.77 (dd, $J=9.5, 4.5$ Hz, 1 H, 4-H), 4.08 (dd, $J=10.5, 4.5$ Hz, 1 H, 3-H), 4.35 (d, $J=11.0$ Hz, 1 H, $\underline{\text{CH}_2\text{-Ph}}$), 4.38 (d, $J=11.0$ Hz, 1 H, $\underline{\text{CH}_2\text{-Ph}}$), 4.42 (d, $J=12.5$ Hz, 1 H, $\underline{\text{CH}_2\text{-Ph}}$), 4.50 (d, $J=11.0$ Hz, 1 H, $\underline{\text{CH}_2\text{-Ph}}$), 4.54 (d, $J=12.5$ Hz, 1 H, $\underline{\text{CH}_2\text{-Ph}}$), 4.65 (d, $J=1.5$ Hz, 1 H, 1-H), 4.73 (d, $J=11.0$ Hz, 1 H, $\underline{\text{CH}_2\text{-Ph}}$), 7.06 – 7.31 (m, 15 H, arom. H); ^{13}C NMR (125 MHz, CDCl_3): $\delta=42.2, 49.4$ (2d, C-2, C-7), 52.4, 52.7 (2q, COOMe), 55.1 (q, OMe), 69.1 (t, C-6), 72.2, 73.3, 74.6 (3t, $\text{CH}_2\text{-Ph}$), 71.4, 73.3, 78.7 (3d, C-3, C-4, C-5), 99.8 (d, C-1), 127.5, 127.6, 127.7, 128.0, 128.2, 128.3 (15d, arom, C-H), 138.0, 138.3 (3s, arom. C- CH_2O), 168.9, 169.1 (2s, COOMe); IR (film): $\nu = 3060, 3028, 2951, 2864, 1733, 1435, 1267$ cm^{-1} ; elemental analysis (%) calcd for $\text{C}_{33}\text{H}_{38}\text{O}_9$: C 68.50, H 6.62; found: C 68.75, H 6.90.

Demethoxycarbonylation of addition product 3g under microwave irradiation.

A solution of the *gluco* isomer **3g** (578 mg, 1.0 mmol) and lithium iodide (201 mg, 1.5 mmol) in DMSO (6 mL) was heated to 100 °C with a microwave oven (power: 200 W; pressure: 10 bar) and kept stirred for 10 minutes. DMSO was removed at 0.01 mbar and the crude product was purified by flash chromatography (*n*-hexane/ethyl acetate 10:1→8:1).

2-*C-gluco*-acetic ester **4g:**

Yield: 92%; $[\alpha]_D^{20} = +14.2$ (c 0.97, CHCl_3); $^1\text{H-NMR}$ (300 MHz, CDCl_3): $\delta=2.09$ (dddd, $J=10.8, 8.7, 5.7, 5.4$ Hz, 1 H, 2-H), 2.39 (dd, $J=15.3, 5.7$ Hz, 1 H, 7-H), 2.47 (dd, $J=15.3, 5.4$ Hz, 1 H, 7'-H), 3.41 (s, 3 H, OMe), 3.43 (ddd, $J=9.3, 5.4, 3.9$ Hz, 1 H, 5-H), 3.45 (dd, $J=10.8, 2.1$ Hz, 1 H, 3-H), 3.49 (s, 3 H, CO_2Me), 3.56 (dd, $J=9.3, 2.1$ Hz, 1 H, 4-H), 3.67 – 3.70 (m, 2 H, 6-H, 6'-H), 4.22 (d, $J=8.7$ Hz, 1 H, 1-H), 4.50 (d, $J=12.3$ Hz, 1 H, $\underline{\text{CH}_2\text{-Ph}}$), 4.51 (d, $J=11.1$ Hz, 1 H, $\underline{\text{CH}_2\text{-Ph}}$), 4.54 (d, $J=11.7$ Hz, 1 H, $\underline{\text{CH}_2\text{-Ph}}$), 4.59 (d, $J=12.0$ Hz, 1 H, $\underline{\text{CH}_2\text{-Ph}}$), 4.71 (d, $J=10.8$ Hz, 1 H, $\underline{\text{CH}_2\text{-Ph}}$), 4.84 (d, $J=11.1$ Hz, 1 H, $\underline{\text{CH}_2\text{-Ph}}$), 7.09 – 7.30 (m, 15 H, arom. H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): $\delta=31.9$ (t, C-7), 44.8 (d, C-2), 51.4 (q, COOMe), 56.9 (q, OMe), 69.0 (t, C-6), 73.5, 74.7, 74.8 (3t, $\text{CH}_2\text{-Ph}$), 75.2, 79.9, 82.1 (3d, C-3, C-4, C-5), 103.4 (d, C-1), 127.6, 127.7, 127.8, 128.3, 128.4 (15d, arom, C-H), 138.0, 138.2, 138.3 (3s, arom. C- CH_2O), 172.6 (s, COOMe); IR (film): $\nu = 3030, 2949, 1736, 1452, 1260$ cm^{-1} ; elemental analysis (%) calcd for $\text{C}_{31}\text{H}_{36}\text{O}_7$: C 71.52, H 6.97; found: C 71.45, H 7.16.

Saponification procedure.

A solution of the 2-*C-gluco*-acetic ester **4g** (520 mg, 1.0 mmol) and $\text{LiOH}\cdot\text{H}_2\text{O}$ (420 mg, 10.0 mmol) in $\text{MeOH}/\text{H}_2\text{O}$ (4/1, 10 mL) was stirred at reflux for 2 hours. After cooling to room temperature, the pH value was adjusted to 5-6 with ion exchanger, and the solvent was removed under high vacuum. The crude product was purified by flash chromatography (*n*-hexane/ethyl acetate 2:3→4:7).

2-*C*-gluco-acetic acid **5g:**

Yield: 98%; $[\alpha]_D^{20} = +1.4$ (*c* 1.07, CHCl₃); ¹H-NMR (300 MHz, CDCl₃): δ =2.16 (ddt, *J*=10.8, 8.7, 5.4 Hz, 1 H, 2-H), 2.48 (dd, *J*=15.6, 5.4 Hz, 1 H, 7-H), 2.55 (dd, *J*=15.6, 5.4 Hz, 1 H, 7'-H), 3.48 (s, 3 H, OMe), 3.50 (ddd, *J*=9.3, 5.4, 3.9 Hz, 1 H, 5-H), 3.56 (dd, *J*=10.8, 9.0 Hz, 1 H, 3-H), 3.64 (dd, *J*=9.3, 9.0 Hz, 1 H, 4-H), 3.76 (d, *J*=2.4 Hz, 2 H, 6-H), 4.30 (d, *J*=8.7 Hz, 1 H, 1-H), 4.56 (d, *J*=12.3 Hz, 1 H, CH₂-Ph), 4.58 (d, *J*=10.8 Hz, 1 H, CH₂-Ph), 4.64 (d, *J*=11.1 Hz, 1 H, CH₂-Ph), 4.65 (d, *J*=12.3 Hz, 1 H, CH₂-Ph), 4.77 (d, *J*=10.5 Hz, 1 H, CH₂-Ph), 4.91 (d, *J*=11.1 Hz, 1 H, CH₂-Ph), 7.16 – 7.37 (m, 15 H, arom. H); ¹³C NMR (75 MHz, CDCl₃): δ =31.6 (t, C-7), 44.5 (d, C-2), 56.9 (q, OMe), 68.8 (t, C-6), 73.4, 74.7, 75.0 (3t, CH₂-Ph), 74.6, 79.7, 81.6 (3d, C-3, C-4, C-5), 103.2 (d, C-1), 127.5, 127.7, 127.8, 128.3, 128.4 (15d, arom, C-H), 137.9, 138.0 (3s, arom. C-CH₂O), 178.3 (s, COOH); IR (film): ν = 3027, 2947, 1735, 1462, 1263 cm⁻¹; elemental analysis (%) calcd for C₃₀H₃₄O₇: C 71.73, H 6.76; found: C 71.42, H 7.09.

Reduction with lithium aluminium hydride.

A suspension of the 2-*C*-gluco-acetic ester **4g** (520 mg, 1.0 mmol) and LiAlH₄ (114 mg, 3 mmol) in 1,4-dioxane (10 mL) was stirred at reflux for 3 hours until TLC showed complete conversion of the starting material. Ethyl acetate and water were added sequentially. The mixture was filtered over Celite and was extracted with dichloromethane (4 x 10 mL). The combined organic extracts were dried (Na₂SO₄) and concentrated, the crude product was purified by column chromatography (*n*-hexane /ethyl acetate 1:1→2:3).

2-C-*gluco*-ethanol 7g:

Yield: 83%; $[\alpha]_D^{20} = +0.3$ (*c* 0.87, CHCl₃); ¹H-NMR (500 MHz, CDCl₃): δ =1.63 (dddd, *J* = 10.0, 8.5, 6.0, 2.0 Hz, 1 H, 2-H), 1.76 – 1.88 (m, 2 H, 7-H), 3.32 – 3.38 (m, 2 H, 8-H), 3.46 (ddd, *J* = 10.0, 4.5, 3.0 Hz, 1 H, 5-H), 3.52 (s, 3 H, OMe), 3.62 – 3.68 (m, 2 H, 3-H, 4-H), 3.75 (t, *J* = 2.8 Hz, 2 H, 6-H), 4.14 (d, *J* = 8.5 Hz, 1 H, 1-H), 4.57 (d, *J* = 12.5 Hz, 1 H, CH₂-Ph), 4.59 (d, *J* = 10.5 Hz, 1 H, CH₂-Ph), 4.64 (d, *J* = 12.5 Hz, 1 H, CH₂-Ph), 4.65 (d, *J* = 11.0 Hz, 1 H, CH₂-Ph), 4.77 (d, *J* = 11.0 Hz, 1 H, CH₂-Ph), 4.95 (d, *J* = 11.5 Hz, 1 H, CH₂-Ph), 7.17 – 7.36 (m, 15 H, arom. H); ¹³C NMR (125 MHz, CDCl₃): δ =30.7 (t, C-7), 45.9 (d, C-2), 56.7 (q, OMe), 61.8 (t, C-8), 69.0 (t, C-6), 73.5, 74.6, 75.0 (3t, CH₂-Ph), 75.2, 79.7, 83.2 (3d, C-3, C-4, C-5), 104.7 (d, C-1), 127.6, 127.8, 127.9, 128.3, 128.4 (15d, arom, C-H), 138.0, 138.2 (3s, arom. C-CH₂O); IR (film): ν = 3088, 2893, 2360, 1496, 1361, 1054 cm⁻¹; elemental analysis (%) calcd for C₃₀H₃₆O₆: C 73.15, H 7.37; found: C 73.15, H 7.33.

Reduction with di-isobutyl aluminium hydride.

A solution of the 2-C-*gluco*-acetic ester **4g** (520 mg, 1.0 mmol) in dry CH₂Cl₂ (10 mL) was cooled to -78 °C under an argon atmosphere. Then DIBAL (1.2 mL, 1.2mmol) was added to the solution, which was stirred at low temperature for 3 hours. Isopropanol was added to quench the reaction and water and CH₂Cl₂ were added sequentially. The combined organic extracts were dried (Na₂SO₄) and concentrated, and the crude product was purified by column chromatography (*n*-hexane /ethyl acetate 10:1→8:1).

2-C-*gluco*-acetaldehyde 6g:

Yield: 82%; $[\alpha]_D^{20} = +8.6$ (c 1.05, CHCl_3); $^1\text{H-NMR}$ (500 MHz, CDCl_3): $\delta=2.21$ (dddd, $J=10.5, 8.5, 6.0, 2.5$ Hz, 1 H, 2-H), 2.31 (ddd, $J=16.0, 6.0, 2.5$ Hz, 1 H, 7-H), 2.39 (ddd, $J=16.0, 6.0, 2.5$ Hz, 1 H, 7'-H), 3.31 (dd, $J=10.5, 9.0$ Hz, 1 H, 3-H), 3.38 (s, 3 H, OMe), 3.38 – 3.41 (m, 1 H, 6'-H), 3.40 (dt, $J=9.5, 3.5$ Hz, 1 H, 5-H), 3.61 (dd, $J=9.5, 9.0$ Hz, 1 H, 4-H), 3.69 (d, $J=3.5$ Hz, 2 H, 6-H), 4.08 (d, $J=8.5$ Hz, 1 H, 1-H), 4.47 (d, $J=11.0$ Hz, 1 H, $\underline{\text{CH}_2\text{-Ph}}$), 4.49 (d, $J=12.5$ Hz, 1 H, $\underline{\text{CH}_2\text{-Ph}}$), 4.50 (d, $J=11.0$ Hz, 1 H, $\underline{\text{CH}_2\text{-Ph}}$), 4.58 (d, $J=12.5$ Hz, 1 H, $\underline{\text{CH}_2\text{-Ph}}$), 4.72 (d, $J=10.5$ Hz, 1 H, $\underline{\text{CH}_2\text{-Ph}}$), 4.80 (d, $J=11.5$ Hz, 1 H, $\underline{\text{CH}_2\text{-Ph}}$), 7.09 – 7.30 (m, 15 H, arom. H), 9.47 (t, $J=2.5$ Hz, 1 H, CHO); $^{13}\text{C NMR}$ (125 MHz, CDCl_3): $\delta=42.2$ (t, C-7), 43.8 (d, C-2), 56.8 (q, OMe), 68.8 (t, C-6), 73.5, 74.7, 74.9 (3t, $\text{CH}_2\text{-Ph}$), 75.2, 79.8, 82.3 (3d, C-3, C-4, C-5), 103.7 (d, C-1), 127.6, 127.7, 127.8, 127.9, 128.0, 128.3, 128.4, 128.5 (15d, arom, C-H), 137.7, 137.9, 138.1 (3s, arom. C- CH_2O), 201.0 (s, CHO); IR (film): $\nu = 3029, 2863, 1721, 1496, 1050$ cm^{-1} ; elemental analysis (%) calcd for $\text{C}_{30}\text{H}_{34}\text{O}_6$: C 73.45, H 6.99; found: C 72.98, H 7.04.