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Stereodivergent Syntheses at the Glucose Backbone

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General methods: Solvents and commercially available chemicals were purified by standard methods or used as purchased. TLC was performed on aluminium sheets coated with silica gel $60F_{254}$ (Merck, Darmstadt). Silica gel (63-200 □m, Woelm, Erlangen) was used for column chromatography. Optical rotations were measured on a JASCO P-1020 digital polarimeter at 589 nm. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. NMR spectra were measured on a Bruker AC 300 or Avance 500 with $CDCl_3$ as the internal standard. Elemental analyses were performed on an ELEMENTAR vario EL analysator.

Methylation of malonate 1: A solution of malonate **1**[1] (580 mg, 1.0 mmol) in dry tetrahydrofuran (15 mL) was cooled to 0 °C under an argon atmosphere, and sodium hydride (80 mg, 2.0 mmol) was added. After 45 min, methyl iodide (0.32 mL, 5.0 mmol) was added dropwise within 10 min. The solution was stirred until tlc showed complete conversion of the starting material. Water (10 mL) and ethyl acetate (10 mL) were added, and the mixture was extracted with dichloromethane (3 x 10 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated. The crude product was purified by flash chromatography (cylohexane/ethyl acetate 9:1).

Methyl 3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[1,1-bis-(methoxycarbonyl)-ethyl]-ß-D-glucopyranoside (2): Colorless sirup (520 mg, 88%). R_f = 0.43 (cyclohexane/ethyl acetate 4:1); $[\alpha]_D^{20}$ = –56.7 (c = 0.79 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.40 (s, 3 H, CH_3), 2.93 (dd, J = 10.8, 7.8 Hz, 1 H, 2-H), 3.20 (s, 3 H, OMe), 3.31 (s, 3 H, COOMe), 3.49 (ddd, J = 9.3, 6.3, 3.0 Hz, 1 H, 5-H), 3.56 (s, 3 H, COOMe), 3.57 (dd, J = 9.3, 8.7 Hz, 1 H, 4-H), 3.62–3.68 (m, 2 H, 6-H), 3.58 (dd, J = 10.8, 8.7 Hz, 1 H, 3-H), 4.22 (d, J = 7.8 Hz, 1 H, 1-H), 4.39 (d, J = 11.4 Hz, 1 H, CH_2-Ph), 4.47 (d, J = 10.8 Hz, 1 H, CH_2-Ph), 4.48 (d, J = 12.0 Hz, 1 H, CH_2-Ph), 4.58 (d, J = 12.0 Hz, 1 H, CH_2-Ph), 4.60 (d, J = 10.8 Hz, 1 H, CH_2-Ph), 4.94 (d, J = 11.4 Hz, 1 H, CH_2-Ph), 6.94 – 7.31 (m, 15 H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.4 (q, CH_3), 51.1 (d, C-2), 52.2, 52.4 (2q, COO*Me*), 53.4 (s, C-7), 57.0 (q, OMe), 69.4 (t, C-6), 73.5, 74.1, 74.3 (3t, *C*H_2-Ph), 75.7, 79.1, 80.8 (3d, C-3, C-4, C-5), 102.5 (d, C-1), 127.2, 127.3, 127.6, 127.8, 128.1, 128.3 (6d, arom, C-H), 137.7, 138.1, 138.3 (3s, arom. *C*-CH_2O), 171.0, 171.7 (2s, *C*OOMe); IR (film): ν = 3697, 3032, 2947, 2845, 1738, 1453, 1262,

1211, 1098 cm^{-1}; elemental analysis calcd (%) for $C_{34}H_{40}O_9$ (592.68): C 68.90, H 6.80; found: C 69.06, H 6.53.

Decarboxylation of malonate 2: A solution of malonate **2** (295 mg, 0.5 mmol) and lithium iodide (100 mg, 0.75 mmol) in DMSO (3 mL) was heated to 100 °C with a microwave oven (power: 200 W; pressure: 10 bar). After 15 min DMSO was removed at 0.01 mbar and the crude product was directly analyzed by NMR spectroscopy, showing a 52:48 ratio of two epimers **3a**. Purification by flash chromatography (cyclohexane/ethyl acetate 9:1) afforded the 7*S* isomer (100 mg, 38%) and the 7*R* isomer (90 mg, 34%) in analytically pure form (data see next sections).

General procedure for the deprotonation of ester 4 and lactone 6, and subsequent trapping with electrophiles: A solution of ester **4**[1] (258 mg, 0.5 mmol) or lactone **6**[2] (235 mg, 0.5 mmol) in dry tetrahydrofuran (10 mL) was cooled to –78 °C under an argon atmosphere. At this temperature potassium hexamethyldisilazide (1.5 mL, 0.75 mmol) was added slowly. After 45 min, iodomethane (0.16 mL, 2.5 mmol), 2-phenylsulfonyl-3-phenyloxaziridine[3] (Davis reagent, 265 mg, 1.0 mmol) or trisyl azide[4] (310 mg, 1.0 mmol) was added dropwise within 10 min. The solution was stirred until tlc showed complete conversion of the starting material. A saturated solution of ammonium chloride (10 mL) was added, and the mixture was extracted with dichloromethane (3 x 10 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated. The crude products **3** and **7** were analyzed by NMR spectroscopy and purified by flash chromatography (cylohexane/ethyl acetate 7:1).

Methyl (7*R*)-3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[(methoxycarbonyl)-ethyl]-ß-D-glucopyranoside (7*R*-3a): Colorless sirup (239 mg, 90%). R_f = 0.37 (cyclohexane/ethyl acetate 3:1); $[\alpha]_D^{20}$ = –8.7 (*c* = 1.11 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (d, *J* = 7.2 Hz, 3 H, CH_3), 2.35 (ddd, *J* = 11.4, 8.7, 2.1 Hz, 1 H, 2-H), 2.79 (qd, *J* = 7.2, 2.1 Hz, 1 H, 7-H), 3.33 (ddd, *J* = 9.0, 6.3, 3.6 Hz, 1 H, 5-H), 3.34 (s, 3 H, OMe), 3.42 (dd, *J* = 9.0, 9.3 Hz, 1 H, 4-H), 3.48 (dd, *J* = 12.6, 3.6 Hz, 1 H, 6'-H), 3.56 (s, 3 H, COOMe), 3.61 (dd, *J* = 12.6, 6.3 Hz, 1 H, 6-H), 3.67 (dd, *J* = 11.4, 9.3 Hz, 1 H, 3-H), 4.12 (d, *J* = 8.7 Hz, 1 H, 1-H), 4.48 (d, *J* = 12.0 Hz, 1 H, C*H*$_2$-Ph), 4.52 (d, *J* = 10.8 Hz, 1 H, C*H*$_2$-Ph), 4.56 (d, *J* = 11.1 Hz, 1 H, C*H*$_2$-Ph), 4.58 (d, *J* = 12.0 Hz, 1 H, C*H*$_2$-Ph), 4.72 (d, *J* = 10.8 Hz, 1 H, C*H*$_2$-Ph), 4.86 (d, *J* = 11.1 Hz, 1 H, C*H*$_2$-Ph), 7.11 – 7.29 (m, 15 H, arom. H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.0 (q, CH_3), 35.3 (d, C-7), 48.7 (d, C-2), 51.5 (q, COO*Me*), 57.0 (q, OMe), 69.1 (t, C-6), 73.5, 74.3, 74.7 (3t, *C*H_2-Ph), 75.1, 79.5, 80.2 (3d, C-3, C-4, C-5), 102.0 (d, C-1), 127.6, 127.8,

127.9, 128.0, 128.3, 128.4, 128.5 (7d, arom, C-H), 138.0, 138.1, 138.2 (3s, arom. *C*-CH_2O), 175.7 (s, *C*OOMe); IR (film): ν = 3456, 3024, 2922, 2858, 1801, 1738, 1490, 1453, 1358, 1270, 1064 cm^{-1}; elemental analysis calcd (%) for $C_{32}H_{38}O_7$ (534.64): C 71.89, H 7.16; found: C 72.05, H 7.23.

Methyl (7*R*)-3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[(hydroxy)-(methoxycarbonyl)-methyl]-ß-D-glucopyranoside (7*R*-3b): Colorless sirup (219 mg, 82%). R_f = 0.28 (cyclohexane/ethyl acetate 2:1); $[\alpha]_D^{20}$ = –6.8 (*c* = 1.11 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.14 (ddd, *J* = 11.1, 8.7, 1.8 Hz, 1 H, 2-H), 3.32 (s, 3 H, OMe), 3.38 (ddd, *J* = 9.6, 6.3, 2.4 Hz, 1 H, 5-H), 3.58 (dd, *J* = 9.6, 8.7 Hz, 1 H, 4-H), 3.65 (dd, *J* = 12.3, 6.3 Hz, 1 H, 6'-H), 3.66 (s, 3 H, COOMe), 3.68 (dd, *J* = 12.3, 2.4 Hz, 1 H, 6-H), 3.76 (dd, *J* = 11.1, 8.7 Hz, 1 H, 3-H), 4.33 (d, *J* = 8.7 Hz, 1 H, 1-H), 4.39 (d, *J* = 1.8 Hz, 1 H, 7-H), 4.47 (d, *J* = 12.0 Hz, 1 H, C*H*$_2$-Ph), 4.52 (d, *J* = 11.1 Hz, 1 H, C*H*$_2$-Ph), 4.56 (d, *J* = 12.0 Hz, 1 H, C*H*$_2$-Ph), 4.65 (d, *J* = 11.1 Hz, 1 H, C*H*$_2$-Ph), 4.75 (d, *J* = 11.1 Hz, 1 H, C*H*$_2$-Ph), 4.87 (d, *J* = 11.1 Hz, 1 H, C*H*$_2$-Ph), 7.10 – 7.28 (m, 15 H, arom. H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 50.6 (d, C-2), 52.4 (q, COO*Me*), 57.3 (q, OMe), 66.3 (d, C-7), 69.0 (t, C-6), 73.5, 74.7, 75.4 (3t, *C*H_2-Ph), 75.0, 79.6, 79.7 (3d, C-3, C-4, C-5), 100.8 (d, C-1), 127.5, 127.7, 127.8, 128.3, 128.4 (5d, arom, C-H), 138.1, 138.2, 138.3 (3s, arom. *C*-CH_2O), 175.7 (s, *C*OOMe); IR (film): ν = 3028, 2921, 2853, 1735, 1497, 1453, 1358, 1294, 1250, 1213, 1183 cm^{-1}; HR-MS(ES) ($C_{31}H_{36}O_8$): calcd for [*M*+H] 537.2488; found 537.2477.

Methyl (7*R*)-3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[(azido)-(methoxycarbonyl)-methyl]-ß-D-glucopyranoside (7*R*-3c): Colorless sirup (238 mg, 85%). R_f = 0.37 (cyclohexane/ethyl acetate 3:1); $[\alpha]_D^{20}$ = +12.0 (*c* = 0.81 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (ddd, *J* = 11.1, 8.4, 2.1 Hz, 1 H, 2-H), 3.32 (dd, *J* = 12.0, 3.0 Hz, 1 H, 6'-H), 3.33 (s, 3 H, OMe), 3.56 (ddd, *J* = 9.3, 6.3, 3.0 Hz, 1 H, 5-H), 3.58 (dd, *J* = 9.3, 7.5 Hz, 1 H, 4-H), 3.64 (s, 3 H, COOMe), 3.65 (dd, *J* = 12.0, 6.3 Hz, 1 H, 6-H), 4.20 (dd, *J* = 11.1, 7.5 Hz, 1 H, 3-H), 4.21 (d, *J* = 10.8 Hz, 1 H, C*H*$_2$-Ph), 4.47 (d, *J* = 12.0 Hz, 1 H, C*H*$_2$-Ph), 4.53 (d, *J* = 2.1 Hz, 1 H, 7-H), 4.56 (d, *J* = 11.4 Hz, 1 H, C*H*$_2$-Ph), 4.56 (d, *J* = 8.4 Hz, 1 H, 1-H), 4.57 (d, *J* = 12.0 Hz, 1 H, C*H*$_2$-Ph), 4.73 (d, *J* = 10.8 Hz, 1 H, C*H*$_2$-Ph), 4.88 (d, *J* = 11.4 Hz, 1 H, C*H*$_2$-Ph), 7.09 – 7.32 (m, 15 H, arom. H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 49.2 (d, C-2), 52.3 (q, COO*Me*), 57.3 (d, C-7), 58.5 (q, OMe), 68.8 (t, C-6), 73.6, 74.7, 75.1 (3t, *C*H_2-Ph), 74.9, 78.8, 79.9 (3d, C-3, C-4, C-5), 101.0 (d, C-1), 127.6, 127.8, 128.0, 128.1, 128.3, 128.4, 128.6 (7d, arom, C-H), 137.9, 138.0, 138.1 (3s, arom. *C*-CH_2O), 170.4 (s, *C*OOMe); IR (film): ν = 3437, 3058, 3028, 2951, 1801, 1738, 1494, 1454, 1439, 1264, 1213 cm^{-1}; HR-MS(ES) ($C_{31}H_{35}N_3O_7$): calcd for

[*M*+Na] 584.2373; found 584.2336.

(3*S*, 3a*S*, 4*R*, 5*S*, 6*R*, 7a*R*)-4,5-Dibenzyloxy-6-benzyloxymethyl-3-methyl-2-oxo-hexahydro-furo[2,3-b]pyran (7*S*-7a): Colorless sirup (215 mg, 90%). R_f = 0.36 (cyclohexane/ethyl acetate 3:1); $[\alpha]_D^{20}$ = –2.4 (*c* = 0.63 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16 (d, *J* = 7.5 Hz, 3 H, CH_3), 2.33 (dt, *J* = 11.7, 5.7 Hz, 1 H, 2-H), 2.68 (qd, *J* = 7.5, 5.7 Hz, 1 H, 7-H), 3.48 (ddd, *J* = 10.5, 4.8, 3.0 Hz, 1 H, 5-H), 3.60–3.70 (m, 2 H, 3-H, 4-H), 3.69 (dd, *J* = 12.9, 4.8 Hz, 1 H, 6'-H), 3.72 (dd, *J* = 12.9, 3.0 Hz, 1 H, 6-H), 4.42 (d, *J* = 11.4 Hz, 1 H, *CH*$_2$-Ph), 4.44 (d, *J* = 12.0 Hz, 1 H, *CH*$_2$-Ph), 4.48 (d, *J* = 12.0 Hz, 1 H, *CH*$_2$-Ph), 4.53 (d, *J* = 11.4 Hz, 1 H, *CH*$_2$-Ph), 4.54 (d, *J* = 12.0 Hz, 1 H, *CH*$_2$-Ph), 4.67 (d, *J* = 12.0 Hz, 1 H, *CH*$_2$-Ph), 5.76 (d, *J* = 5.7 Hz, 1 H, 1-H), 7.08 – 7.31 (m, 15 H, arom. H);^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.4 (q, CH_3), 38.9 (d, C-7), 46.6 (d, C-2), 68.7 (t, C-6), 73.2, 73.3, 73.5 (3t, *C*H$_2$-Ph), 72.3, 75.8, 77.5 (3d, C-3, C-4, C-5), 99.3 (d, C-1), 127.7, 127.8, 128.0, 128.4, 128.5, 128.6 (6d, arom, C-H), 137.6, 137.7, 137.8 (3s, arom. *C*-CH_2O), 177.1 (s, *C*OOR); IR (film): ν = 3452, 3032, 1963, 1771, 1710, 1624, 1490, 1447, 1345, 1094 cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{32}O_6$ (488.57): C 73.75, H 6.60; found: C 74.05, H 6.76.

(3*S*, 3a*S*, 4*R*, 5*S*, 6*R*, 7a*R*)-4,5-Dibenzyloxy-6-benzyloxymethyl-3-hydroxy-2-oxo-hexahydro-furo[2,3-b]pyran (7*S*-7b): Colorless sirup (213 mg, 87%); R_f = 0.25 (cyclohexane/ethyl acetate 2:1); $[\alpha]_D^{20}$ = –0.6 (*c* = 0.86 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.71 (ddd, *J* = 11.1, 6.9, 5.7 Hz, 1 H, 2-H), 3.57 (dd, *J* = 9.3, 9.0 Hz, 1 H, 4-H), 3.56 – 3.66 (m, 2 H, 6-H, 6'-H), 3.61 (ddd, *J* = 9.3, 5.7, 2.7 Hz, 1 H, 5-H), 3.63 (dd, *J* = 11.1, 9.0 Hz, 1 H, 3-H), 3.73 (d, *J* = 6.9 Hz, 1 H, 7-H), 4.37 (d, *J* = 12.0 Hz, 1 H, *CH*$_2$-Ph), 4.40 (d, *J* = 11.4 Hz, 1 H, *CH*$_2$-Ph), 4.44 (d, *J* = 12.0 Hz, 1 H, *CH*$_2$-Ph), 4.51 (d, *J* = 11.4 Hz, 1 H, *CH*$_2$-Ph), 4.52 (d, *J* = 12.0 Hz, 1 H, *CH*$_2$-Ph), 4.61 (d, *J* = 12.0 Hz, 1 H, *CH*$_2$-Ph), 5.94 (d, *J* = 5.7 Hz, 1 H, 1-H), 7.08 – 7.32 (m, 15 H, arom. H);^{13}C NMR (75 MHz, $CDCl_3$): δ = 46.1 (d, C-2), 68.8 (t, C-6), 70.1 (d, C-7), 72.7, 73.0, 73.5 (3t, *C*H$_2$-Ph), 72.7, 74.9, 75.3 (3d, C-3, C-4, C-5), 99.6 (d, C-1), 127.8, 127.9, 128.1, 128.4, 128.6, 128.6 (6d, arom, C-H), 137.3, 137.5, 137.8 (3s, arom. *C*-CH_2O), 174.5 (s, *C*OOR); IR (film): ν = 3029, 2863, 1748, 1496, 1453, 1361, 1208, 1027 cm^{-1}; HR-MS(ES) ($C_{29}H_{30}O_7$): calcd for [*M*+Na] 513.1889; found 513.1874.

(3*S*, 3a*S*, 4*R*, 5*S*, 6*R*, 7a*R*)-3-Azido-4,5-dibenzyloxy-6-benzyloxymethyl-2-oxo-hexahydro-furo[2,3-b] pyran (7*S*-7c): Colorless sirup (228 mg, 88%); R_f = 0.38 (cyclohexane/ethyl acetate 3:1); $[\alpha]_D^{20}$ = –2.6 (*c* = 0.89 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.44 (ddd, *J*

= 11.7, 5.4, 4.8 Hz, 1 H, 2-H), 3.48 (ddd, *J* = 10.5, 4.5, 2.4 Hz, 1 H, 5-H), 3.60 (dd, *J* = 12.9, 4.5 Hz, 1 H, 6'-H), 3.64 (dd, *J* = 11.7, 8.1 Hz, 1 H, 3-H), 3.68 (dd, *J* = 10.5, 8.1 Hz, 1 H, 4-H), 3.72 (dd, *J* = 12.9, 2.4 Hz, 1 H, 6-H), 3.98 (d, *J* = 4.8 Hz, 1 H, 7-H), 4.43 (d, *J* = 11.4 Hz, 1 H, *CH*$_2$-Ph), 4.46 (d, *J* = 11.7 Hz, 1 H, *CH*$_2$-Ph), 4.47 (d, *J* = 12.0 Hz, 1 H, *CH*$_2$-Ph), 4.51 (d, *J* = 12.0 Hz, 1 H, *CH*$_2$-Ph), 4.54 (d, *J* = 11.4 Hz, 1 H, *CH*$_2$-Ph), 4.65 (d, *J* = 11.7 Hz, 1 H, *CH*$_2$-Ph), 5.83 (d, *J* = 5.4 Hz, 1 H, 1-H), 7.09 – 7.33 (m, 15 H, arom. H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 45.2 (d, C-2), 60.3 (d, C-7), 68.3 (t, C-6), 73.3, 73.4, 73.5 (3t, *C*H$_2$-Ph), 72.8, 75.2, 75.3 (3d, C-3, C-4, C-5), 99.8 (d, C-1), 127.8, 127.9, 128.0, 128.1, 128.3, 128.4, 128.5, 128.7 (8d, arom, C-H), 137.2, 137.3, 137.7 (3s, arom. *C*-CH$_2$O), 170.4 (s, *C*OOR); IR (film): ν = 3424, 3058, 3032, 2952, 1738, 1456, 1438, 1149, 1087, 1021 cm^{-1}; HR-MS(ES) ($C_{29}H_{29}N_3O_6$): calcd for [*M*+Na] 538.1954; found 538.1945.

General procedure for the opening of lactones 7: A mixture of lactone **7** (0.5 mmol) and Drierite® (20-40 mesh) (680 mg) in dry methanol (10 mL) was stirred at 0 °C under argon atmosphere. At this temperature Sc(OTf)$_3$ (370 mg, 0.75 mmol, 1.5 eq) was added and after 30 min tlc showed complete conversion. The reaction was quenched with saturated sodium hydrogen carbonate solution (10 mL) and the mixture was extracted with dichloromethane (3 × 20 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated and the crude products **3** were purified by flash chromatography (cylohexane/ethyl acetate 7:1).

Methyl (7*S*)-3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[(methoxycarbonyl)-ethyl]-ß-D-glucopyranoside (7*S*-3a): Colorless sirup (235 mg, 89%). R_f = 0.37 (cyclohexane/ethyl acetate 3:1); $[\alpha]_D^{20}$ = –3.5 (*c* = 0.88 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.13 (d, *J* = 7.2 Hz, 3 H, CH_3), 2.25 (ddd, *J* = 11.1, 8.7, 5.8 Hz, 1 H, 2-H), 2.89 (qd, *J* = 7.2, 5.8 Hz, 1 H, 7-H), 3.35 (dt, *J* = 9.3, 3.3 Hz, 1 H, 5-H), 3.37 (s, 3 H, OMe), 3.43 (s, 3 H, COOMe), 3.58 (dd, *J* = 9.3, 8.7 Hz, 1 H, 4-H), 3.60 (dd, *J* =11.1, 8.7 Hz, 1 H, 3-H), 3.69 (d, *J* = 3.3 Hz, 2 H, 6-H), 4.18 (d, *J* = 8.7 Hz, 1 H, 1-H), 4.50 (d, *J* = 12.0 Hz, 1 H, C*H*$_2$-Ph), 4.52 (d, *J* = 10.8 Hz, 1 H, C*H*$_2$-Ph), 4.57 (d, *J* = 10.8 Hz, 1 H, C*H*$_2$-Ph), 4.59 (d, *J* = 12.0 Hz, 1 H, C*H*$_2$-Ph), 4.67 (d, *J* = 10.8 Hz, 1 H, C*H*$_2$-Ph), 4.84 (d, *J* = 10.8 Hz, 1 H, C*H*$_2$-Ph), 7.04 – 7.31 (m, 15 H, arom. H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.3 (q, CH_3), 35.6 (d, C-7), 49.5 (d, C-2), 51.4 (q, COO*Me*), 56.7 (q, OMe), 69.0 (t, C-6), 73.5, 74.5, 74.6 (3t, *C*H$_2$-Ph), 75.1, 79.5, 80.6 (3d, C-3, C-4, C-5), 102.5 (d, C-1), 127.4, 127.6, 127.7, 127.8, 128.2, 128.3, 128.4 (7d, arom, C-H), 138.0, 138.2, 138.4 (3s, arom. *C*-CH$_2$O), 175.3 (s, *C*OOMe); IR (film): ν = 3463, 3024, 2926, 2949, 1738, 1456, 1362, 1217, 1054 cm^{-1}; elemental analysis calcd (%) for $C_{32}H_{38}O_7$ (534.64): C 71.89, H 7.16; found: C 71.77, H 6.96.

Methyl (7*S*)-3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[(hydroxy)-(methoxycarbonyl)-methyl]-ß-D-glucopyranoside (7*S*-3b): Colorless sirup (218 mg, 81%). R_f = 0.28 (cyclohexane/ethyl acetate 2:1); $[\alpha]_D^{20}$ = –3.1 (*c* = 0.79 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.21 (ddd, *J* = 11.1, 8.7, 6.6 Hz, 1 H, 2-H), 3.35 (s, 3 H, OMe), 3.36 (ddd, *J* = 10.5, 5.1, 3.6 Hz, 1 H, 5-H), 3.49 (s, 3 H, COOMe), 3.64 (dd, *J* = 10.5, 9.0 Hz, 1 H, 4-H), 3.68–3.72 (m, 2 H, 6-H,), 3.80 (dd, *J* = 11.1, 9.0 Hz, 1 H, 3-H), 4.32 (d, *J* = 8.7 Hz, 1 H, 1-H), 4.42 (d, *J* = 10.8 Hz, 1 H, C*H*$_2$-Ph), 4.50 (d, *J* = 12.3 Hz, 1 H, C*H*$_2$-Ph), 4.51 (d, *J* = 6.6 Hz, 1 H, 7-H), 4.52 (d, *J* = 10.8 Hz, 1 H, C*H*$_2$-Ph), 4.60 (d, *J* = 12.3 Hz, 1 H, C*H*$_2$-Ph), 4.68 (d, *J* = 10.8 Hz, 1 H, C*H*$_2$-Ph), 4.85 (d, *J* = 10.8 Hz, 1 H, C*H*$_2$-Ph), 7.03 – 7.30 (m, 15 H, arom. H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 50.8 (d, C-2), 52.4 (q, COO*Me*), 57.0 (q, OMe), 66.6 (d, C-7), 68.8 (t, C-6), 73.5, 74.7, 74.9 (3t, *C*H$_2$-Ph), 74.3, 74.8, 80.4 (3d, C-3, C-4, C-5), 101.6 (d, C-1), 127.4, 127.6, 127.7, 127.8, 128.1, 128.3, 128.4 (7d, arom, C-H), 137.9, 138.2, 138.3 (3s, arom. *C*-CH$_2$O), 175.3 (s, *C*OOMe); IR (film): ν = 3441, 3030, 2869, 1723, 1605, 1496, 1453, 1361, 1261, 1207, 1055 cm^{-1}; HR-MS(ES) ($C_{31}H_{36}O_8$): calcd for [*M*+H] 537.2488; found 537.2478.

Methyl (7*S*)-3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[(azido)-(methoxycarbonyl)-methyl]-ß-D-glucopyranoside (7*S*-3c): Colorless sirup (231 mg, 82%). R_f = 0.37 (cyclohexane/ethyl acetate 3:1); $[\alpha]_D^{20}$ = +4.9 (*c* = 1.09 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (ddd, *J* = 11.4, 8.7, 6.0 Hz, 1 H, 2-H), 3.29 (s, 3 H, OMe), 3.36 (ddd, *J* = 9.9, 5.7, 2.7 Hz, 1 H, 5-H), 3.47 (s, 3 H, COOMe), 3.58 (dd, *J* = 9.9, 8.1 Hz, 1 H, 4-H), 3.58 (dd, *J* = 12.6, 5.7 Hz, 1 H, 6'-H), 3.66 (dd, *J* = 12.6, 2.7 Hz, 1 H, 6-H), 4.05 (dd, *J* = 11.4, 8.1 Hz, 1 H, 3-H), 4.44 (d, *J* = 11.4 Hz, 1 H, C*H*$_2$-Ph), 4.50 (d, *J* = 12.0 Hz, 1 H, C*H*$_2$-Ph), 4.51 (d, *J* = 6.0 Hz, 1 H, 7-H), 4.59 (d, *J* = 12.0 Hz, 1 H, C*H*$_2$-Ph), 4.63 (d, *J* = 8.7 Hz, 1 H, 1-H), 4.65 (d, *J* = 11.4 Hz, 1 H, C*H*$_2$-Ph), 4.80 (d, *J* = 11.1 Hz, 1 H, C*H*$_2$-Ph), 4.84 (d, *J* = 11.1 Hz, 1 H, C*H*$_2$-Ph), 7.00 – 7.26 (m, 15 H, arom. H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 45.9 (d, C-2), 52.3 (q, COO*Me*), 57.1 (d, C-7), 60.4 (q, OMe), 69.1 (t, C-6), 71.1, 73.4, 73.5 (3t, *C*H$_2$-Ph), 72.1, 74.3, 78.0 (3d, C-3, C-4, C-5), 100.9 (d, C-1), 127.4, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.4 (8d, arom, C-H), 137.8, 137.9, 138.6 (3s, arom. *C*-CH$_2$O), 176.3 (s, *C*OOMe); IR (film): ν = 3435, 3079, 3053, 2924, 2849, 1737, 1631, 1494, 1452, 1204, 1065 cm^{-1}; HR-MS(ES) ($C_{31}H_{35}N_3O_7$): calcd for [*M*+Na] 584.2373; found 584.2349.

Reduction of azides (7*R*)- or (7*S*)-3c: To a solution of azido-sugars (7*R*)-**3c** or (7*S*)-**3c** (280 mg, 0.5 mmol) in freshly distilled tetrahydrofuran (10 mL) were added water (0.11 mL, 6

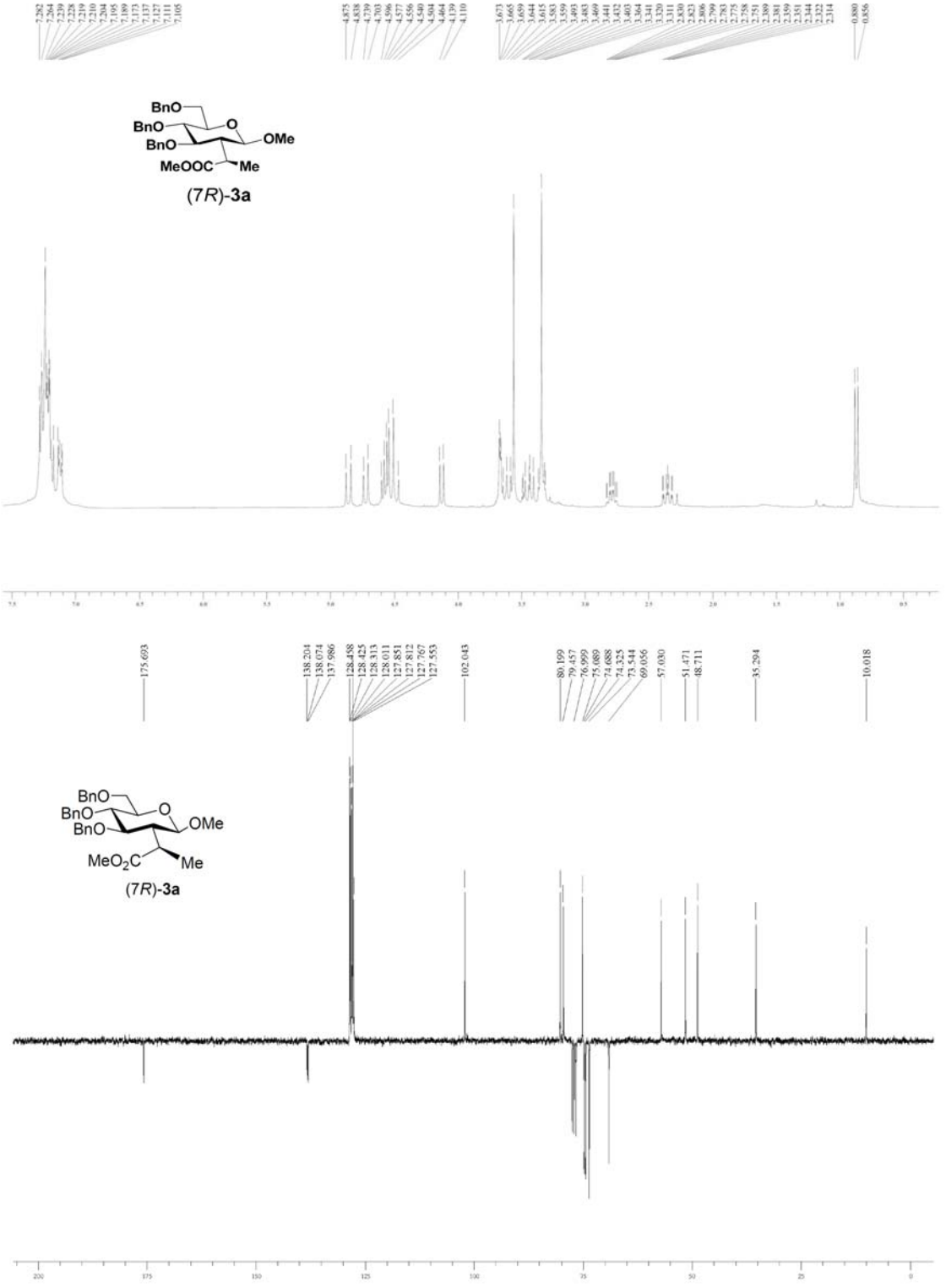
mmol) and triphenylphosphine (395 mg, 1.5 mmol) under argon atmosphere. The mixture was stirred at room temperature until tlc showed complete conversion of the starting material. The solvent was removed, and the residue was purified by flash chromatography (cylohexane/ethyl acetate 1:1) to afford the corresponding protected amino acids **8**.

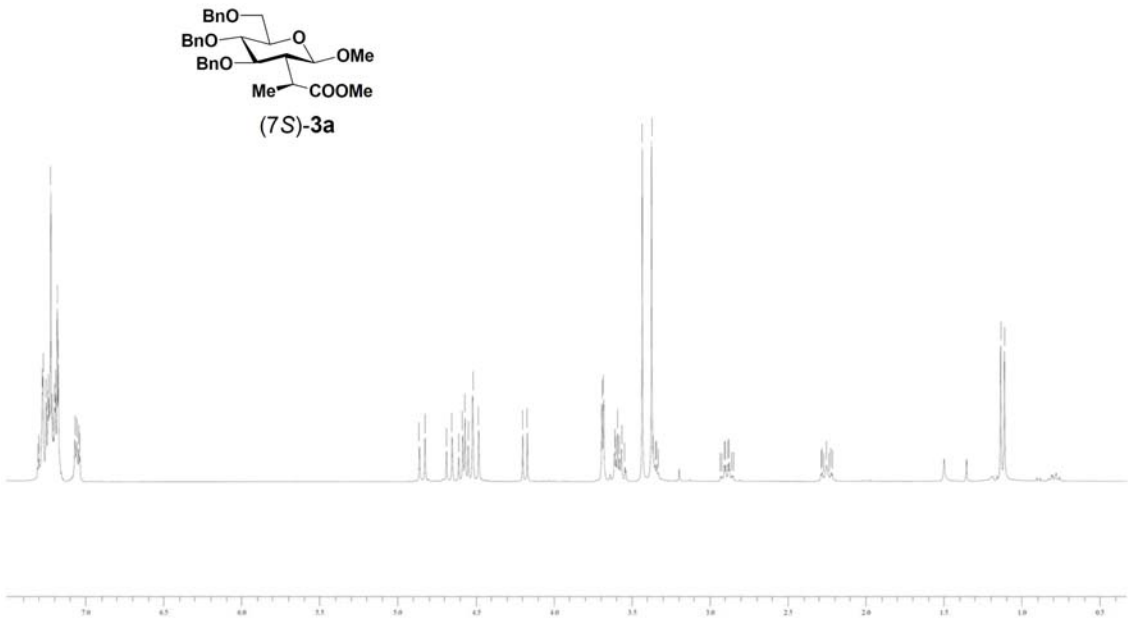
Methyl (7*R*)-3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[(amino)-(methoxycarbonyl)-methyl]-ß-D-glucopyranoside (7*R*-8): Colorless sirup (230 mg, 86%). R_f = 0.21 (cyclohexane/ethyl acetate 1:2); $[\alpha]_D^{20}$ = –12.5 (*c* = 1.04 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.17 (ddd, *J* = 10.8, 8.7, 2.1 Hz, 1 H, 2-H), 3.31 (s, 3 H, OMe), 3.36 (ddd, *J* = 9.3, 6.6, 3.6 Hz, 1 H, 5-H), 3.58 (s, 3 H, COOMe), 3.59 (dd, *J* = 9.3, 9.0 Hz, 1 H, 4-H), 3.60 (d, *J* = 2.1 Hz, 1 H, 7-H), 3.61–3.68 (m, 2 H, 6-H), 3.73 (dd, *J* = 10.8, 9.0 Hz, 1 H, 3-H), 4.26 (d, *J* = 8.7 Hz, 1 H, 1-H), 4.47 (d, *J* = 12.0 Hz, 1 H, C*H*$_2$-Ph), 4.53 (d, *J* = 10.8 Hz, 1 H, C*H*$_2$-Ph), 4.57 (d, *J* = 12.0 Hz, 1 H, C*H*$_2$-Ph), 4.63 (d, *J* = 11.7 Hz, 1 H, C*H*$_2$-Ph), 4.75 (d, *J* = 10.8 Hz, 1 H, C*H*$_2$-Ph), 4.86 (d, *J* = 11.7 Hz, 1 H, C*H*$_2$-Ph), 7.12 – 7.29 (m, 15 H, arom. H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 50.1, 50.4 (2d, C-2, C-7), 51.9 (q, COO*Me*), 57.0 (q, OMe), 69.0 (t, C-6), 73.4, 73.5, 73.6 (3t, *C*H$_2$-Ph), 74.9, 78.5, 80.2 (3d, C-3, C-4, C-5), 101.2 (d, C-1), 127.5, 127.7, 127.8, 128.3, 128.4, 128.5 (6d, arom, C-H), 138.1, 138.2, 138.3 (3s, arom. *C*-CH$_2$O), 176.1 (s, *C*OOMe); IR (film): ν = 3434, 3083, 3062, 3027, 2922, 1728, 1709, 1496, 1453, 1362, 1102, 1028 cm^{-1}; HR-MS(ES) ($C_{31}H_{37}NO_7$): calcd for [*M*+H] 536.2648; found 536.2653.

Methyl (7*S*)-3,4,6-tri-*O*-benzyl-2-deoxy-2-*C*-[(amino)-(methoxycarbonyl)-methyl]-ß-D-glucopyranoside (7*S*-8): Colorless sirup (235 mg, 88%). R_f = 0.22 (cyclohexane/ethyl acetate 1:2); $[\alpha]_D^{20}$ = –19.2 (*c* = 0.92 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (ddd, *J* = 11.4, 8.7, 6.0 Hz, 1 H, 2-H), 3.29 (s, 3 H, OMe), 3.36 (ddd, *J* = 9.9, 5.7, 2.7 Hz, 1 H, 5-H), 3.47 (s, 3 H, COOMe), 3.58 (dd, *J* = 9.9, 8.1 Hz, 1 H, 4-H), 3.58 (dd, *J* = 12.6, 5.7 Hz, 1 H, 6'-H), 3.66 (dd, *J* = 12.6, 2.7 Hz, 1 H, 6-H), 4.05 (dd, *J* = 11.4, 8.1 Hz, 1 H, 3-H), 4.44 (d, *J* = 11.4 Hz, 1 H, C*H*$_2$-Ph), 4.50 (d, *J* = 12.0 Hz, 1 H, C*H*$_2$-Ph), 4.51 (d, *J* = 6.0 Hz, 1 H, 7-H), 4.59 (d, *J* = 12.0 Hz, 1 H, C*H*$_2$-Ph), 4.63 (d, *J* = 8.7 Hz, 1 H, 1-H), 4.65 (d, *J* = 11.4 Hz, 1 H, C*H*$_2$-Ph), 4.80 (d, *J* = 11.1 Hz, 1 H, C*H*$_2$-Ph), 4.84 (d, *J* = 11.1 Hz, 1 H, C*H*$_2$-Ph), 7.00 – 7.26 (m, 15 H, arom. H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 44.7, 44.8 (2d, C-2, C-7), 51.4 (q, COO*Me*), 56.9 (q, OMe), 69.0 (t, C-6), 73.5, 74.7, 74.8 (3t, *C*H$_2$-Ph), 75.2, 79.9, 82.0 (3d, C-3, C-4, C-5), 103.4 (d, C-1), 127.5, 127.6, 127.7, 127.8, 128.3, 128.4 (6d, arom, C-H), 138.0, 138.1, 138.2 (3s, arom. *C*-CH$_2$O), 176.6 (s, *C*OOMe); IR (film): ν = 3471, 3088, 3062, 3028, 2952, 1738, 1494, 1453, 1435, 1358, 1213, 1153 cm^{-1}; HR-MS(ES) ($C_{31}H_{37}NO_7$): calcd for [*M*+H] 536.2648; found 536.2633.

Determination of the configurations

All products were thoroughly investigated by NMR spectroscopy. The *R* and *S* isomers showed distinctive different chemical shifts and coupling constants (see selected examples):





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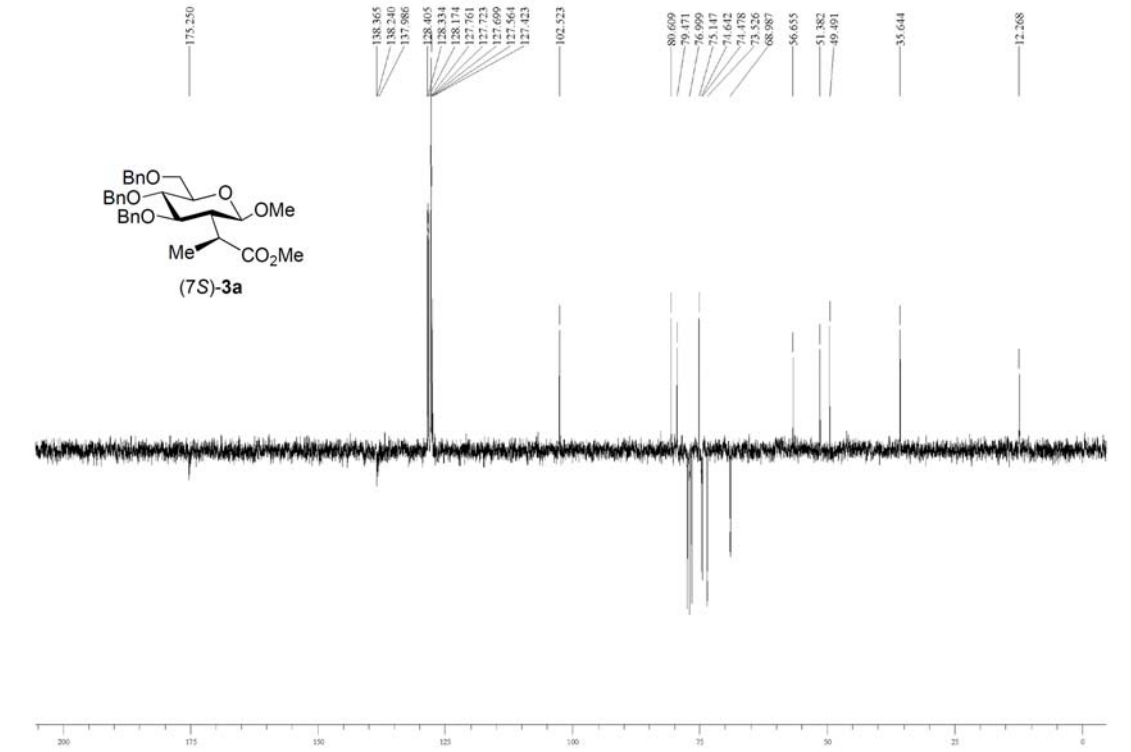

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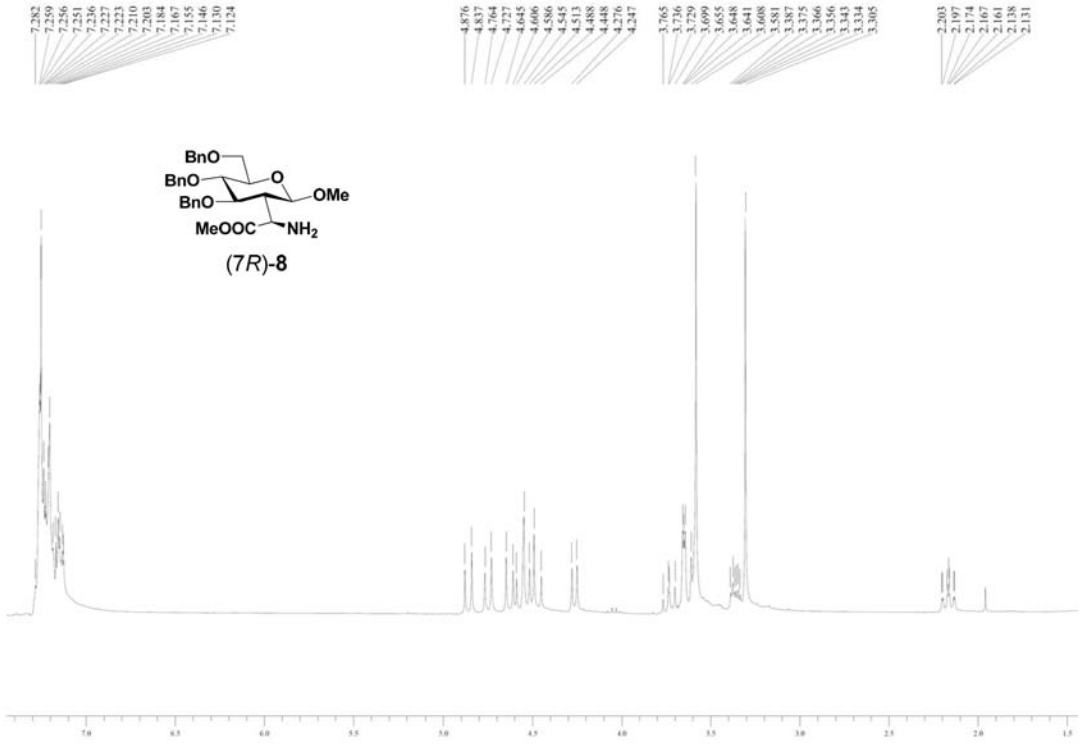
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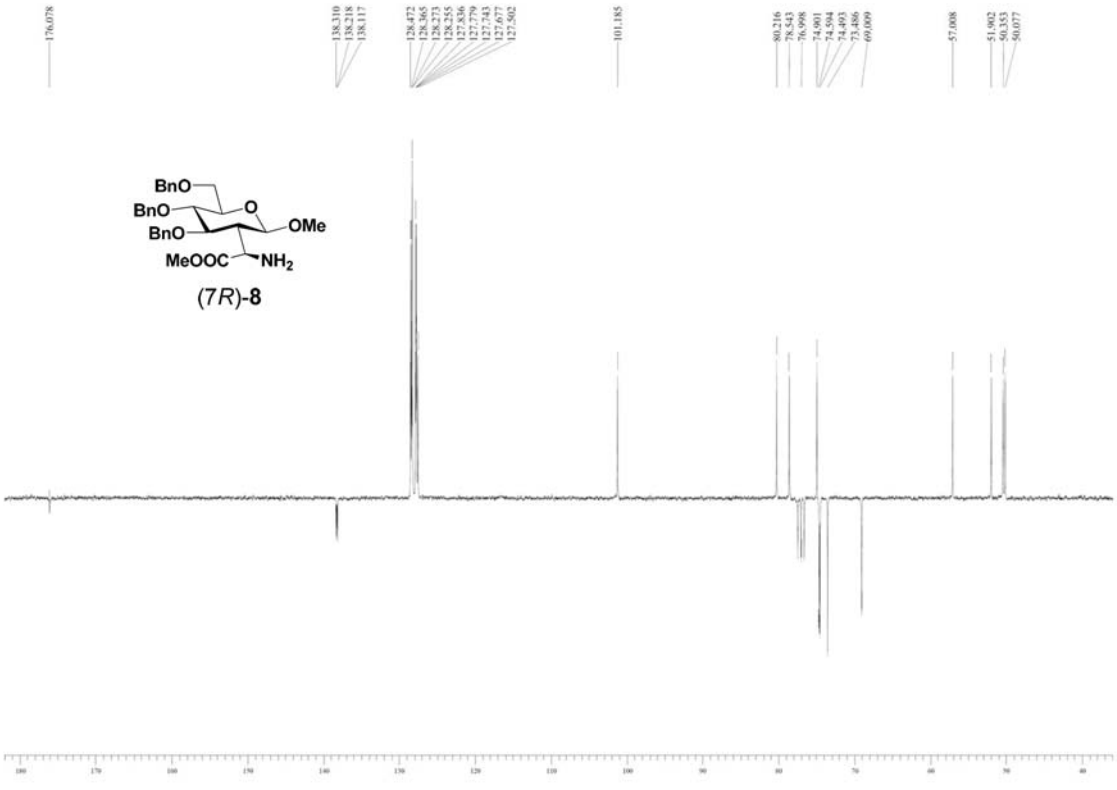
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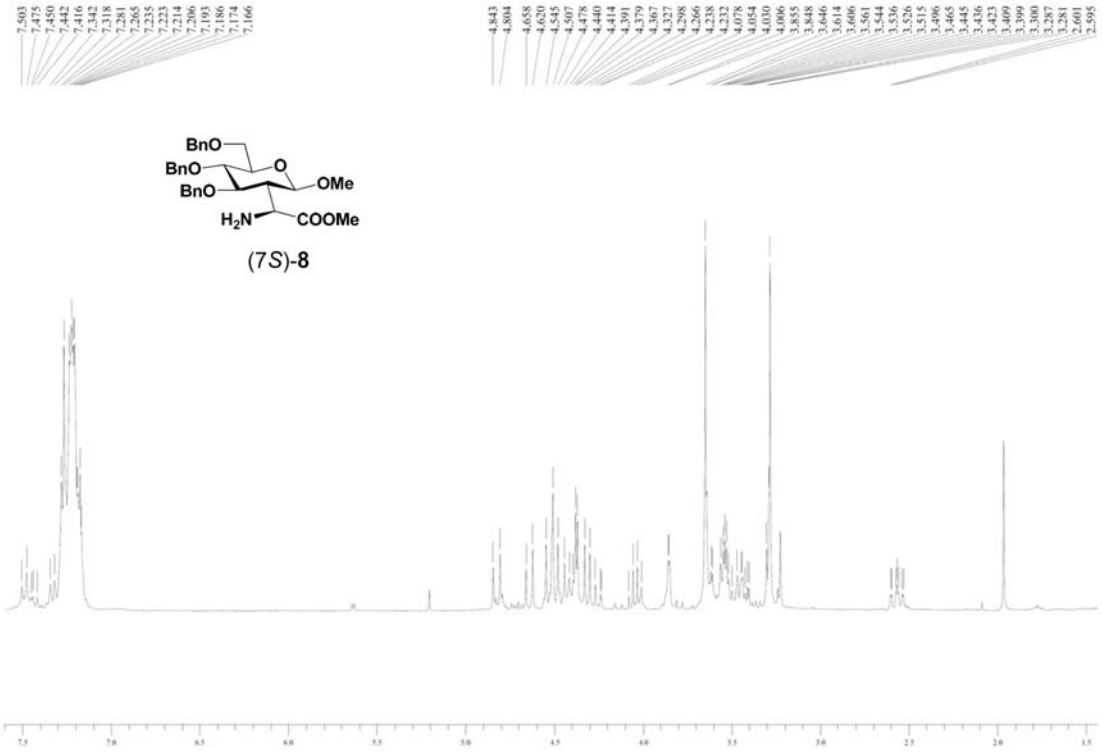
(7R)-8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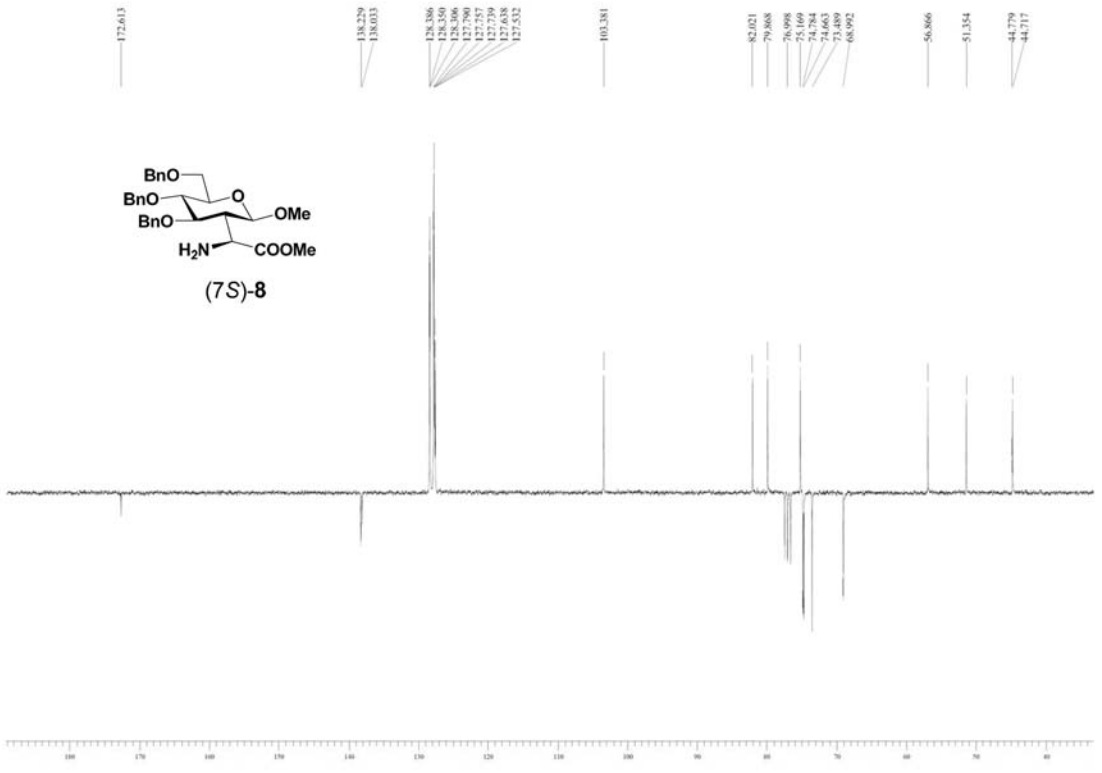
COOMe
(7S)-8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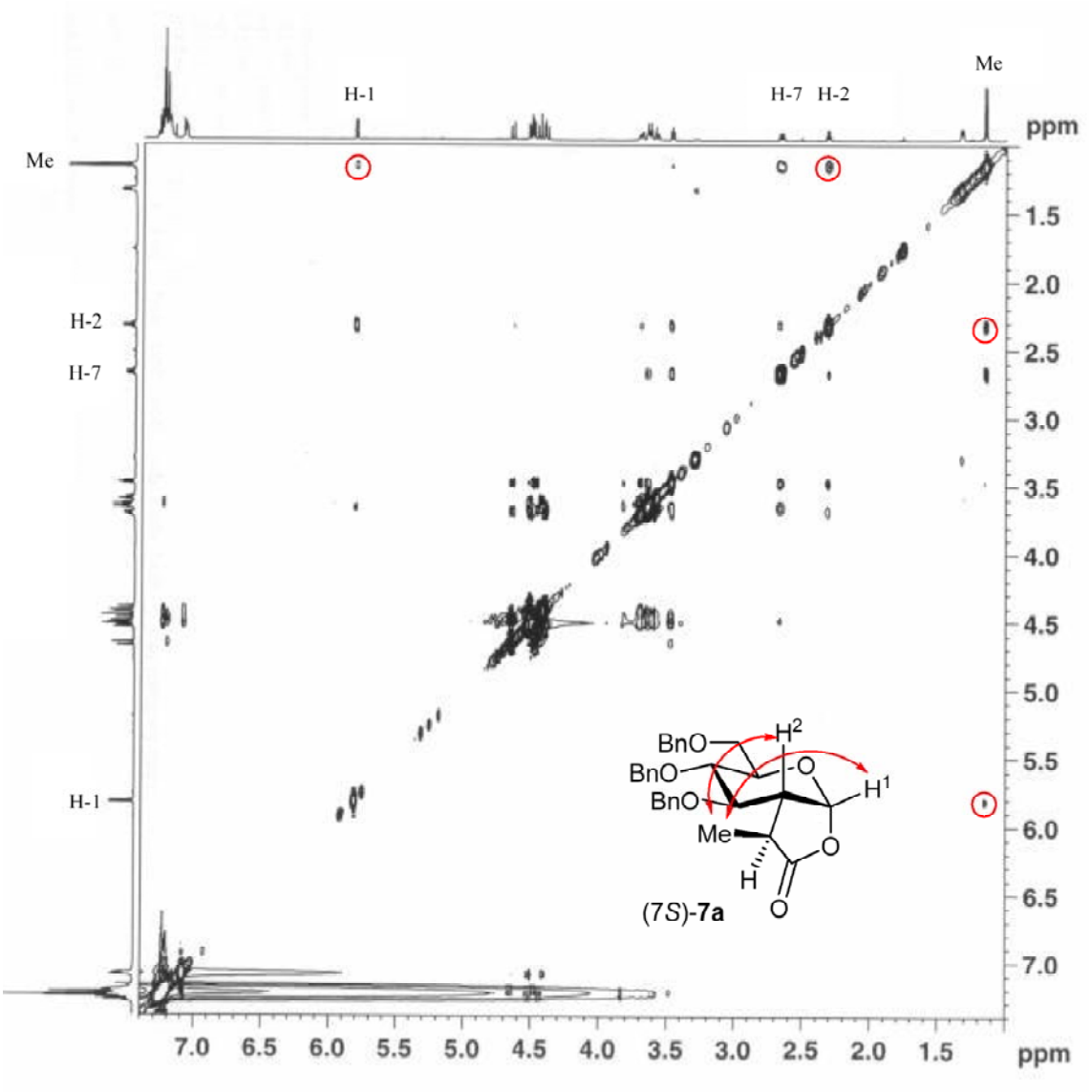
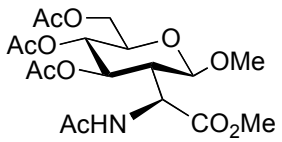
44.717
BnO
BnO
BnO
O
OMe
H2N
COOMe
(7S)-8

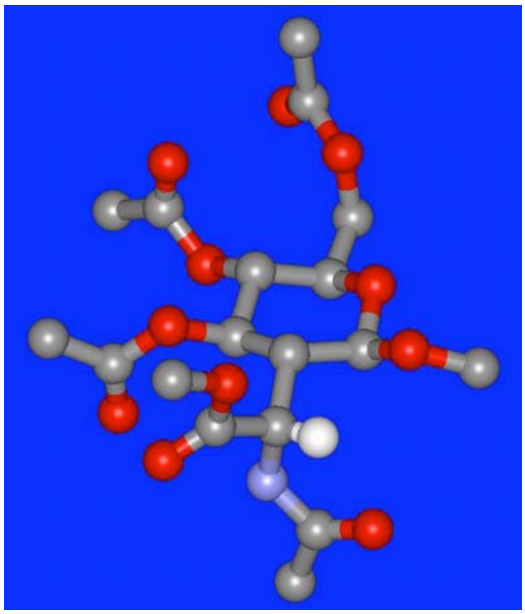
The lactone 7*S*-**7a** allowed detailed NOE studies. Thus, the methyl group showed distinctive cross-peaks with 2-H and even 1-H, clearly proving the *S* configuration.



Finally, the analytical data of amino acid derivative (7*R*)-**8** are in complete accordance to the literature,[5] and epimer (7*S*)-**8** was converted by removal of the benzyl groups and acetylation into the known compound (7*S*)-**9**, which was already characterized by X-ray structure analysis.[6]



(7*S*)-**9**



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