Supporting Information

for

Synthesis and NMR studies of malonyl-linked glycoconjugates of N-(2-aminoethyl)glycine.
Building blocks for the construction of combinatorial glycopeptide libraries

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Experimental data

General

All solvents were dried according to standard procedures, distilled and stored over molecular sieves 3 Å under an atmosphere of nitrogen prior to their use. All non-aqueous reactions were performed in oven-dried glassware under an atmosphere of nitrogen unless otherwise stated. NMR spectra were recorded on a Bruker Avance 400 spectrometer or Bruker Avance 600 spectrometer (temperature-dependent investigations) and calibrated for the solvent signal (\textsuperscript{1}H CDCl\textsubscript{3}: 7.26 ppm; \textsuperscript{13}C CDCl\textsubscript{3}: 77.16 ppm; \textsuperscript{1}H DMSO-\textit{d}\textsubscript{6}: 2.50 ppm; \textsuperscript{13}C DMSO-\textit{d}\textsubscript{6}: 39.52 ppm; \textsuperscript{1}H DMF-\textit{d}\textsubscript{7}: 8.03 ppm, 2.92 ppm, 2.75 ppm; \textsuperscript{13}C DMF-\textit{d}\textsubscript{7}: 163.2 ppm, 34.9 ppm, 29.8 ppm; \textsuperscript{1}H chlorobenzene-\textit{d}\textsubscript{6}: 7.14 ppm, 6.99 ppm, 6.96 ppm; \textsuperscript{13}C chlorobenzene-\textit{d}\textsubscript{6}: 134.19 ppm, 129.26 ppm, 128.25 ppm, 125.96 ppm; \textsuperscript{1}H-D\textsubscript{2}O: 4.79 ppm). ESI-HRMS were
measured on a Bruker Apex II FT-ICR-MS spectrometer, FAB-spectra were measured on a Finnigan model TSQ 70. Elemental analysis was performed on a HEKAtech Euro 3000 CHN analyzer. IR spectra were recorded on a Bruker Tensor 27 spectrometer. Optical rotations were measured at 589 nm (Na D-line) with a Perkin-Elmer Polarimeter 341 in a 10 cm cuvette at 20 °C. Melting points were determined with a Büchi Melting Point M-560 apparatus. Reactions were monitored by TLC on Polygram Sil G/UV silica gel plates from Machery&Nagel. Detection of spots was effected by charring with H₂SO₄ (5% in EtOH), staining by spraying the plates with an alkaline aqueous solution of potassium permanganate or by inspection of the TLC plates under UV light. Preparative chromatography was performed on silica gel (0.032–0.063 mm) from Machery&Nagel with different mixtures of solvents as eluents. All yields given below are isolated yields determined after purification of the product either by silica gel column chromatography or crystallization and were not optimized unless noted otherwise.

**Starting materials**

Known compounds were prepared according to literature procedures: tert-butyl N-[2-(N-9H-fluoren-9-ylmethoxycarbonylamino)ethyl]glycinat hydrochloride (5) [1], 3-oxo-3-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylamino)propanoic acid (6a) [2], 3-oxo-3-(β-D-galactopyranosylamino)propanoic acid (6b) [2], 3-oxo-3-(2-acetamido-2-deoxy-3,4,6-tetra-O-acetyl-β-D-glucopyranosylamino)propanoic acid (6c) [2], 3-oxo-3-(2-acetamido-2-deoxy-3,4,6-tetra-O-acetyl-β-D-galactopyranosylamino)propanoic acid (6d) [2].
**General procedure for the synthesis of compounds 1a–d**

Analogous as described in [14] building blocks 1a–d were prepared according to the following procedure.

In a 25 mL round bottom flask equipped with a gas inlet and a stirring bar, 6a–d (1 equiv) was dissolved in 12 mL dry DMF under an atmosphere of nitrogen. The solution was cooled to 0°C and HBTU (1.5 equiv) (Method A) or EDCI·HCl (1.3 equiv) and HOBt (1.3-1.5 equiv) (Method B), and DIPEA (3.9 equiv) were added. The mixture was stirred at 0°C for 10 min. Afterwards tert-butyl N-[2-(N-9H-fluoren-9-yl-methoxycarbonylamino)ethyl]glycinat hydrochloride (5) (1 equiv) was added and the resulting solution was stirred at 0 °C for 2 h and at rt for 72 h. The solvent was removed under reduced pressure, the residue dissolved in ethyl acetate (70 mL) and successively washed with an aqueous solution of citric acid (10%) (2 × 20 mL), satd. aqueous NaHCO₃ solution, (3 × 20 mL), satd. aqueous NaCl solution (20 mL), dried over Na₂SO₄, filtered and concentrated. Purification of the residue by column chromatography afforded the pure title compounds 1a–d as white amorphous solid.
**tert-Butyl [N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylamino)malonyl]-N-2-[2-(9H-fluoren-9-ylmethoxycarbonylamino)ethyl]glycinate (1a)**

Method A: according to the general procedure, 6a (100 mg, 0.23 mmol), HBTU (1.5 equiv), HOBt (1.5 equiv), DIPEA (3.9 equiv) and column chromatography (PE/EA 1:3) gave 1a (149 mg, 79%).

Method B: according to the general procedure, 6a (100 mg, 0.23 mmol), EDCI·HCl (1.3 equiv), HOBt (1.3 equiv), DIPEA (3.9 equiv) and column chromatography (CHCl₃/MeOH 200:1→50:1) gave 1a (83 mg, 40%).

Rf: 0.36 (PE/EA 1:3); [α]D⁰20: +0.6 (c 1.0, CHCl₃).

**1H-NMR (CDCl₃):** δ 8.19, (d, 0.5H, J₁,NH = 9.1 Hz, H-1N₄CO trans-rotamer), 7.99 (d, 0.5H, J₁,NH = 9.0 Hz, H-1NHCO cis-rotamer), 7.77-7.75 (m, 2H, H-aryl), 7.61-7.58 (m, 2H, H-aryl), 7.42-7.38 (m, 2H, H-aryl), 7.33-7.29 (m, 2H, H-aryl), 5.74, 5.45 (t, t, J₆ = 5.9 Hz, J₇ = 5.7 Hz, CONHCH₂ cis-/trans-rotamer), 5.28-5.22 (m, 2H, H-1, H-3), 5.09-4.97 (m, 2H, H-4, H-2), 4.44-4.39 (m, 2H, Fmoc-CH₂), 4.26-4.18 (m, 2H, H-6a, Fmoc-CH), 4.09-4.03 (m, 1H, H-6b), 3.98-3.89 (m, 2H, NCH₂CO₂Bu), 3.80-3.72 (m, 1H, H-5), 3.54-3.46 (m, 2H, NHCH₂CH₂N), 3.40-3.16 (m, 4H, COCH₂CO), 2.05, 2.04, 2.03, 2.02, 2.01, 2.00 (8s, 12H, CH₃), 1.48, 1.47 (2s, 9H, CO₂C(CH₃)₃); **13C NMR (CDCl₃):** δ 170.1, 169.6, 168.9, 168.3, 168.1, 166.9, 166.6 (7C, CO), 156.8, 156.7 (1C, Fmoc-CO cis-/trans-rotamer), 144.0, 143.9, 141.4, 127.8, 127.8, 127.2, 125.1, 120.1 (8C, C-aryl), 83.6, 82.7 (1C, CO₂C(CH₃)₃ cis-/trans-rotamer), 78.0 (1C, C-1), 73.7, 73.6 (1C, C-5 cis-/trans-rotamer), 73.1, 72.9 (1C, C-3...
cis-/trans-rotamer), 70.4, 70.3 (1C, C-4 cis-/trans-rotamer), 68.2 (1C, C-2), 66.8, 66.9 (1C, Fmoc-CH₂ cis-/trans-rotamer), 61.7, 60.5 (1C, C-6 cis-/trans-rotamer), 52.3, 50.0 (1C, NCH₂CO₂Bu cis-/trans-rotamer), 48.9 (1C, COCH₂CO), 47.3 (1C, Fmoc-CH), 40.5, 40.2, 39.0, 38.7 (2C, NHCH₂CH₂N cis-/trans-rotamer), 28.1, 28.1 (3C, CO₂C(CH₃)₃ cis-/trans-rotamer), 21.1, 20.8, 20.7, 20.7 (4C, CH₃); Due to the rotameric structure the signals can be exchanged. ESI-TOF-MS: Anal. Calcd. for C₄₀H₄₉N₃O₁₅ [M+Na]^+: m/z 834.305589; found: m/z 834.305244.

![Chemical Structure](image)

**tert-Butyl [N-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosylamino)malonyl]-N-2-[2-(9H-fluoren-9-ylmethoxycarbonylamino)ethyl]glycinate (1b)**

Method A: according to the general procedure 6b (100 mg, 0.23 mmol), HBTU (1.5 equiv), HOBt (1.5 equiv), DIPEA (3.9 equiv) and column chromatography (PE/EA 1:3) gave 1b (148 mg, 79%).

Method B: according to the general procedure 6b (100 mg, 0.23 mmol), EDCI·HCl (1.3 equiv), HOBt (1.3 equiv), DIPEA (3.9 equiv) and column chromatography (CHCl₃/MeOH 100:1) gave 1b (87 mg, 47%).

Rᵣ: 0.21 (PE/EA 1:3); [α]ᵣ²⁰: +7.0 (c 1.0, CHCl₃). $^1$H-NMR (CDCl₃): δ 8.26 (d, 0.5H, $J_{1,NH} = 8.6$ Hz, H-1NHCO trans-rotamer), 7.99 (d, 0.5H, $J_{1,NH} = 8.4$ Hz, H-1NHCO cis-rotamer), 7.77-7.75 (m, 2H, H-aryl), 7.62-7.58 (m, 2H, H-aryl), 7.41-7.37 (m, 2H, H-
aryl), 7.34-7.29 (m, 2H, H-aryl), 5.76, 5.50 (t, t, 1H, $J_a = 6.0$ Hz, $J_b = 5.5$ Hz, CONHCH$_2$ cis-/trans-rotamer), 5.40 (dd, 1H, $J_{3,4} = 3.3$ Hz, $J_{4,5} = 11.6$ Hz, H-4), 5.26-5.16 (m, 2H, H-1, H-2), 5.11-5.05 (m, 1H, H-3), 4.44-4.39 (m, 2H, Fmoc-CH$_2$), 4.23-4.19 (m, 1H, Fmoc-CH), 4.13-3.90 (m, 5H, H-6a, H-6b, NCH$_2$CO$_2$Bu, H-5), 3.56-2.83 (m, 6H, NHCH$_2$CH$_2$N, COCH$_2$CO), 2.14, 2.14, 2.13, 2.12, 2.10, 2.06, 2.02, 1.99, 1.98, 1.97 (10s, 12H, H$_3$), 1.48, 1.47 (2s, 9H, CO$_2$C(CH$_3$)$_3$ cis-/trans-rotamer), 144.1, 144.0, 143.9, 141.4, 127.9, 127.8, 127.2, 127.1, 125.2, 125.1, 120.1 (11C, C-aryl), 83.7, 82.8 (1C, CO$_2$C(CH$_3$)$_3$ cis-/trans-rotamer b), 78.4 (1C, C-1), 72.5, 72.4 (1C, C-5 cis-/trans-rotamer), 71.3, 71.2 (1C, C-3 cis-/trans-rotamer), 68.2, 68.1 (1C, C-2 cis-/trans-rotamer), 67.3, 67.2 (1C, C-4 cis-/trans-rotamer), 67.0, 66.8 (1C, Fmoc-CH$_2$ cis-/trans-rotamer), 61.4 (1C, C-6), 52.4, 49.2 (1C, NCH$_2$CO$_2$Bu cis-/trans-rotamer), 49.2 (1C, COCH$_2$CO), 47.4, 47.3 (1C, Fmoc-CH cis-/trans-rotamer), 40.4, 40.2, 39.2, 39.6 (2C, NHCH$_2$CH$_2$N cis-/trans-rotamer), 28.2, 28.1 (3C, CO$_2$C(CH$_3$)$_3$ cis-/trans-rotamer), 20.8, 20.8, 20.7, 20.7 (4C, CH$_3$); Due to the rotameric structure the signals can be exchanged. FT-ICR-MS: Anal. Calcd. for C$_{40}$H$_{49}$N$_3$O$_{15}$ [M+Na]$^+$: m/z 834.305589; found: m/z 834.304890.

Method A: according to the general procedure 6c (100 mg, 0.23 mmol), HBTU (1.5 equiv), HOBt (1.5 equiv), DIPEA (3.9 equiv) and column chromatography (CHCl₃/MeOH 100:1→50:1) gave 1c (141 mg, 75%).

Method B: according to the General Procedure 6c (100 mg, 0.23 mmol), EDCI-HCl (1.3 equiv), HOBt (1.3 equiv), DIPEA (3.9 equiv) and column chromatography (CHCl₃/MeOH 100:1→50:1) gave 1c (106 mg, 57%).

Rₚ: 0.61 (CHCl₃/MeOH 25:1); \([\alpha]_{D}^{20}=-0.7\) (c 1.0, CHCl₃). ¹H-NMR (CDCl₃): δ 7.82 (d, 0.5H, \(J_{1,NH}=8.4\) Hz, H-1NHCOCH₂\textit{trans-rotamer}), 7.76-7.74 (m, 2H, H-aryl), 7.64-7.58 (m, 2H, H-aryl), 7.53 (d, 1H, \(J_{1,NH}=8.3\) Hz, H-1NHCOCH₂\textit{cis-rotamer}), 7.41-7.37 (m, 2H, H-aryl), 7.32-7.28 (m, 2H, H-aryl), 7.11, 6.54-6.50 (d, m, 1H, \(J=8.8\) Hz, NH \textit{cis-/trans-rotamer}), 6.54-6.50, 5.99 (m, t, 1H, \(J=5.4\) Hz, CONHCH₂\textit{cis-/trans-rotamer}), 5.49, 5.28-5.20 (t, m, 1H, \(J=9.9\) Hz, H-3 \textit{cis-/trans-rotamer}), 5.39 (t, 0.5H, \(J=9.0\) Hz, H-1 \textit{cis-rotamer}), 5.28-5.20 (m, 1H, H-1 \textit{trans-rotamer}), 5.07, 4.96 (t, t, 1H, \(J_a=9.7\) Hz, \(J_b=9.5\) Hz, H-4 \textit{cis-/trans-rotamer}), 4.63-4.35 (m, 2H, Fmoc-CH₂), 4.27-3.99 (m, 5H, Fmoc-CH, H-6a, H-2, H-6b, H-5), 3.89-3.80 (m, 2H, NCH₂CO₂Bu), 3.55-2.96 (m, 6H, NHCH₂CH₂, COCH₂CO), 2.05, 2.00, 1.97, 1.96, 1.93, 1.91, 1.90 (7s, 12H, CH₃), 1.47, 1.43 (2s, 9H, CO₂(CH₃)₃); ¹³C NMR (CDCl₃):
δ 173.2, 172.4, 171.5, 171.2, 170.8, 169.6, 169.5, 168.8, 168.5, 168.3, 168.1, 167.3, 167.1, 156.8 (14C, C=O), 144.0, 143.8, 141.4, 127.9, 127.8, 127.2, 127.1, 125.3, 125.2, 120.1, 120.0 (11C, C-aryl), 83.5, 82.4 (1C, CO₂C(CH₃)₃ cis-/trans-rotamer), 80.1, 79.9 (1C, C-1 cis-/trans-rotamer), 73.4, 73.0 (1C, C-5 cis-/trans-rotamer), 72.7, 72.3 (1C, C-3 cis-/trans-rotamer), 68.7, 68.3 (1C, C-4 cis-/trans-rotamer), 67.1, 66.6 (1C, Fmoc-CH₂ cis-/trans-rotamer), 62.0, 61.9 (1C, C-6 cis-/trans-rotamer), 53.0, 52.6 (1C, C-2 cis-/trans-rotamer), 49.9, 49.6 (1C, NCH₂CO₂Bu cis-/trans-rotamer), 47.4, 47.3 (1C, Fmoc-CH cis-/trans-rotamer), 41.8, 41.7 (1C, COCH₂CO cis-/trans-rotamer), 39.6, 39.0 (2C, NHCH₂CH₂), 28.1 (3C, CO₂C(CH₃)₃), 23.0, 22.9, 20.8, 20.7, 20.6 (5C, CH₃); Due to the rotameric structure the signals can be exchanged. FT-ICR-MS: Calcd. for C₄₀H₅₀N₄O₁₄ [M+Na]^+: m/z 833.321573; found: m/z 833.321147.

tert-Butyl [N-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-galactopyranosylamino)malonylamino]-N-2-[2-(9H-fluoren-9-
ylmethoxycarbonylamino)ethyl]glycinate (1d)

Method A: according to the general procedure 6d (100 mg, 0.23 mmol), HBTU (1.5 equiv), HOBT (1.5 equiv), DIPEA (3.9 equiv) and column chromatography (CHCl₃/MeOH 100:1→50:1) gave 1d (145 mg, 77%).
Method B: according to the general procedure 6d (100 mg, 0.23 mmol), EDCI·HCl (1.3 equiv), HOBT (1.3 equiv), DIPEA (3.9 equiv) and column chromatography (CHCl₃/MeOH 100:1→50:1) gave 1d (78 mg, 42%).

Rᵣ: 0.50 (CHCl₃/MeOH 25:1); [α]Dº20: -5.7 (c 1.0, CHCl₃). ¹H-NMR (CDCl₃): δ 7.87 (d, 0.5H, J₁,NH = 8.3 Hz, H-1NHCOCH₂ trans-rotamer), 7.76-7.73 (m, 2H, H-aryl), 7.71 (d, 0.5H, J₁,NH = 7.4 Hz, H-1NHCOCH₂ cis-rotamer), 7.61-7.56 (m, 2H, H-aryl), 7.40-7.36 (m, 2H, H-aryl), 7.33-7.30 (m, 2H, H-aryl), 7.33-7.30, 6.64 (m, d, 1H, J₅ = 8.9 Hz, NH cis-/trans-rotamer), 6.73, 6.09 (s, s, 1H, CONHCH₂ cis-/trans-rotamer), 5.58 (dd, 1H, J₃,₄ = 2.7 Hz, J₄,₅ = 11.0 Hz, H-4), 5.43 (t, 0.5H, J = 8.8 Hz, H-1 cis-rotamer), 5.36-5.25 (m, 1H, H-3), 5.21 (t, 0.5H, J = 9.9 Hz, H-1 trans-rotamer), 4.64-2.88 (m, 15H, Fmoc-CH₂, Fmoc-CH, H-6a, H-2, H-6b, H-5, NCH₂CO₂Bu, NHCH₂CH₂N, COCH₂CO), 2.11, 1.98, 1.96, 1.92, 1.90, 1.78 (6s, 12H, CH₃), 1.47, 1.43 (2s, 9H, CO₂C(CH₃)₃); ¹³C NMR (CDCl₃): δ 173.7, 171.0, 170.8, 170.5, 170.4, 170.3, 169.0, 168.9, 168.3, 167.7, 167.3, 167.1, 156.9 (13C, CO), 144.5, 144.0, 143.6, 141.4, 141.3, 127.9, 127.8, 127.3, 127.2, 125.6, 125.2, 120.1, 120.0, (13C, C-aryl), 83.6, 82.4 (1C, CO₂C(CH₃)₃ cis-/trans-rotamer), 80.6, 80.4 (1C, C-1 cis-/trans-rotamer), 72.2, 71.9 (1C, C-5 cis-/trans-rotamer), 70.4, 69.8 (1C, C-4 cis-/trans-rotamer), 67.4, 66.9 (1C, Fmoc-CH₂ cis-/trans-rotamer), 66.8, 66.7 (1C, C-3 cis-/trans-rotamer), 61.5, 61.4 (1C, C-6 cis-/trans-rotamer), 49.7, 49.6 (2C, NHCH₂CH₂N), 49.4, 49.2 (1C, C-2 cis-/trans-rotamer), 47.4, 47.0 (1C, Fmoc-CH cis-/trans-rotamer), 41.7 (1C, COCH₂CO), 39.5 (1C, NCH₂CO₂Bu), 28.1 (3C, CO₂C(CH₃)₃), 23.1, 20.9, 20.8, 20.7, 20.3 (5C, CH₃); Due to the rotameric structure the signals can be exchanged. FT-ICR-MS: Calcd. for C₄₀H₅₀N₄O₁₄ [M+Na]⁺: m/z 833.321573; found: m/z 833.321729.
General procedure for tert-butyl ester hydrolysis

In almost the same way as described in [14] building blocks 1a-d were converted into their free carbon acids 2a-d according to following procedure.

Compounds 1a–d (1 equiv) were dissolved in a mixture of formic acid and DCM (2:1) and stirred at rt for 38 h. DCM and formic acid were removed by passing a stream of N₂ through the solution. The residue was repeatedly dissolved in toluene and concentrated in vacuo (5 × 20 mL) in order to remove remaining traces of formic acid. Chromatography of the residue afforded compounds 2a–d as white amorphous solids.

\[ N\text{-}(2,3,4,6\text{-Tetra-O-acetyl}\text{-}\beta\text{-D-glucopyranosylamino})\text{malonyl]}\text{-}N\text{-}2\text{-}[2\text{-}(9\text{H-fluoren-9-ylmethoxycarbonylamino})\text{ethyl}]\text{glycine (2a)} \]

According to the general procedure, 1a (294 mg, 0.36 mmol) in 12 mL HCO₂H/DCM afforded after column chromatography (CHCl₃/MeOH 50:1 + 1 % HCO₂H→CHCl₃/MeOH 25:1 + 1 % HCO₂H) 2a (269 mg, 98%).

Rₚ: 0.52 (CHCl₃/MeOH 25:1 + 1 % HCO₂H); [α]_{D}^{20}: -2.0 (c 1.0, CHCl₃); \(^1\)H-NMR (DMSO-d₆) δ 12.89 (s, 1H, CO₂H), 8.84 (t, 1H, J₁,NH = 10.3 Hz, H-1NHCO), 7.89-7.88 (m, 2H, H-aryl), 7.68-7.66 (m, 2H, H-aryl), 7.41 (t, 2H, J = 7.4 Hz, H-aryl), 7.35-7.31 (m, 3H, H-aryl, NH), 5.42-5.32 (m, 2H, H-1, H-3), 4.89 (t, 1H, J₃,₄ = 9.6 Hz, H-4),
4.84-4.77 (m, 1H, H-2), 4.32-4.27 (m, 2H, Fmoc-CH₂), 4.21 (t, 1H, J = 6.4 Hz, Fmoc-CH), 4.16-4.07 (m, 3H, H-6a, H-6b, H-5), 3.98-3.89 (m, 2H, CH₂CO₂H), 3.48-3.10 (m, 6H, NHCH₂CH₂, COCH₂CO), 1.99, 1.97, 1.92 (3s, 12H, CH₃); ¹³C-NMR (DMSO-d₆) δ 170.8, 170.1, 169.5, 169.4, 169.3, 169.2, 167.7, 167.2, 167.0, 166.8 (10C, C=O), 156.3, 156.1 (1C, Fmoc-C=O cis-/trans-rotamer), 143.9, 143.9, 140.7, 140.7, 127.7, 127.1, 125.2, 125.1, 120.2 (9C, C-aryl), 76.8 (C-1), 72.8 (C-3), 72.2 (C-5), 70.5 (C-2), 67.9 (C-4), 65.5 (1C, Fmoc-CH₂), 61.8 (C-6), 48.1 (1C, CH₂CO₂H), 47.8 (1C, COCH₂CO), 46.7 (1C, Fmoc-CH), 40.8 (1C, NHCH₂CH₂), 20.5, 20.4, 20.4, 20.3 (4C, CH₃); Due to the rotameric structure the signals can be exchanged. FT-ICR-MS: Calcd. for C₃₅H₄₁N₃O₁₅Na [M+Na]⁺: m/z 778.242989; found: m/z 778.242857.

\[ \text{[N-(2,3,4,6-Tetra-O-acetyl-\(\beta\)-D-galactopyranosylamino)malonyl]-N-2-[2-(9H-fluoren-9-ylmethoxycarbonylamo\(\text{no}?)\text{ethyl]}\text{glycine (2b) }\] \]

According to the general procedure, 1b (243 mg, 0.30 mmol) in 12 mL HCO₂H/DCM afforded after column chromatography (CHCl₃/MeOH 50:1 + 1 % HCO₂H→CHCl₃/MeOH 25:1 + 1 % HCO₂H) 2b (219 mg, 97%).

Rᵣ: 0.50 (CHCl₃/MeOH 25:1 + 1 % HCO₂H); [α]D²⁰: +6.3 (c 1.0, CHCl₃); ¹H-NMR (DMSO-d₆) δ 12.92 (s, 1H, CO₂H), 8.89 (t, 1H, H[NH = 8.5 Hz, H-1NCO], 7.89-7.87 (m, 2H, H-aryl), 7.68-7.66 (m, 2H, H-aryl), 7.41 (t, 1H, J = 7.4 Hz, H-aryl), 7.35-7.31 (m, 3H, H-aryl, NH), 5.37-5.28 (m, 3H, H-1, H-4, H-3), 5.03-4.99 (m, 1H, H-2), 4.84-4.77 (m, 1H, H-2), 4.32-4.27 (m, 2H, Fmoc-CH₂), 4.21 (t, 1H, J = 6.4 Hz, Fmoc-CH), 4.16-4.07 (m, 3H, H-6a, H-6b, H-5), 3.98-3.89 (m, 2H, CH₂CO₂H), 3.48-3.10 (m, 6H, NHCH₂CH₂, COCH₂CO), 1.99, 1.97, 1.92 (3s, 12H, CH₃); ¹³C-NMR (DMSO-d₆) δ 170.8, 170.1, 169.5, 169.4, 169.3, 169.2, 167.7, 167.2, 167.0, 166.8 (10C, C=O), 156.3, 156.1 (1C, Fmoc-C=O cis-/trans-rotamer), 143.9, 143.9, 140.7, 140.7, 127.7, 127.1, 125.2, 125.1, 120.2 (9C, C-aryl), 76.8 (C-1), 72.8 (C-3), 72.2 (C-5), 70.5 (C-2), 67.9 (C-4), 65.5 (1C, Fmoc-CH₂), 61.8 (C-6), 48.1 (1C, CH₂CO₂H), 47.8 (1C, COCH₂CO), 46.7 (1C, Fmoc-CH), 40.8 (1C, NHCH₂CH₂), 20.5, 20.4, 20.4, 20.3 (4C, CH₃); Due to the rotameric structure the signals can be exchanged. FT-ICR-MS: Calcd. for C₃₅H₄₁N₃O₁₅Na [M+Na]⁺: m/z 778.242989; found: m/z 778.242857.

\[ \text{[N-(2,3,4,6-Tetra-O-acetyl-\(\beta\)-D-galactopyranosylamino)malonyl]-N-2-[2-(9H-fluoren-9-ylmethoxycarbonylamo\(\text{no}?)\text{ethyl]}\text{glycine (2b) }\] \]

According to the general procedure, 1b (243 mg, 0.30 mmol) in 12 mL HCO₂H/DCM afforded after column chromatography (CHCl₃/MeOH 50:1 + 1 % HCO₂H→CHCl₃/MeOH 25:1 + 1 % HCO₂H) 2b (219 mg, 97%).

Rᵣ: 0.50 (CHCl₃/MeOH 25:1 + 1 % HCO₂H); [α]D²⁰: +6.3 (c 1.0, CHCl₃); ¹H-NMR (DMSO-d₆) δ 12.92 (s, 1H, CO₂H), 8.89 (t, 1H, H[NH = 8.5 Hz, H-1NCO], 7.89-7.87 (m, 2H, H-aryl), 7.68-7.66 (m, 2H, H-aryl), 7.41 (t, 1H, J = 7.4 Hz, H-aryl), 7.35-7.31 (m, 3H, H-aryl, NH), 5.37-5.28 (m, 3H, H-1, H-4, H-3), 5.03-4.99 (m, 1H, H-2), 4.84-4.77 (m, 1H, H-2), 4.32-4.27 (m, 2H, Fmoc-CH₂), 4.21 (t, 1H, J = 6.4 Hz, Fmoc-CH), 4.16-4.07 (m, 3H, H-6a, H-6b, H-5), 3.98-3.89 (m, 2H, CH₂CO₂H), 3.48-3.10 (m, 6H, NHCH₂CH₂, COCH₂CO), 1.99, 1.97, 1.92 (3s, 12H, CH₃); ¹³C-NMR (DMSO-d₆) δ 170.8, 170.1, 169.5, 169.4, 169.3, 169.2, 167.7, 167.2, 167.0, 166.8 (10C, C=O), 156.3, 156.1 (1C, Fmoc-C=O cis-/trans-rotamer), 143.9, 143.9, 140.7, 140.7, 127.7, 127.1, 125.2, 125.1, 120.2 (9C, C-aryl), 76.8 (C-1), 72.8 (C-3), 72.2 (C-5), 70.5 (C-2), 67.9 (C-4), 65.5 (1C, Fmoc-CH₂), 61.8 (C-6), 48.1 (1C, CH₂CO₂H), 47.8 (1C, COCH₂CO), 46.7 (1C, Fmoc-CH), 40.8 (1C, NHCH₂CH₂), 20.5, 20.4, 20.4, 20.3 (4C, CH₃); Due to the rotameric structure the signals can be exchanged. FT-ICR-MS: Calcd. for C₃₅H₄₁N₃O₁₅Na [M+Na]⁺: m/z 778.242989; found: m/z 778.242857.
4.32-4.22 (m, 4H, Fmoc-CH₂, H-5, Fmoc-CH), 4.06-3.94 (m, 4H, H-6a, H-6b, CH₂CO₂H), 3.36-3.09 (m, 6H, NHCH₂CH₂, COCH₂CO), 2.09, 1.99, 1.98, 1.96, 1.91 (5s, 12H, CH₃); ¹³C-NMR (DMSO-d₆) δ 170.7, 169.9, 169.9, 169.5, 169.4, 167.8, 167.3, 167.0, 166.9 (9C, C=O), 156.3, 156.1 (1C, Fmoc-C=O cis-/trans-rotamer), 143.9, 143.9, 140.8, 140.7, 127.7, 127.1, 125.2, 125.2, 120.2 (9C, C-aryl), 77.2 (C-1), 71.4 (C-5), 70.8 (C-3), 68.1 (C-2), 67.6 (C-4), 65.5 (1C, Fmoc-CH₂), 61.5 (C-6), 48.1 (1C, CH₂CO₂H), 47.8 (1C, COCH₂CO), 46.7 (1C, Fmoc-CH), 41.2, 40.7 (2C, NHCH₂CH₂), 20.5, 20.5, 20.4, 20.4 (4C, CH₃); Due to the rotameric structure the signals can be exchanged. FT-ICR-MS: Calcd. for C₃₅H₄₁N₃O₁₅Na [M+Na]+: m/z 778.242989; found.: m/z 778.243134.

![Chemical Structure](image)

[N-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosylamino)malonyl]-N-2-[2-(9H-fluoren-9-ylmethoxycarbonylamino)ethyl]glycine (2c)

According to the general procedure, 1c (273 mg, 0.34 mmol) in 12 mL HCO₂H/DCM afforded after column chromatography (CHCl₃/MeOH 50:1 + 1 % HCO₂H→CHCl₃/MeOH 25:1 + 1 % HCO₂H) 2c (245 mg, 97%).

Rf: 0.28 (CHCl₃/MeOH 25:1 + 1 % HCO₂H); [α]D²⁰: +0.7 (c 1.0, CHCl₃); ¹H-NMR (DMSO-d₆) δ 12.84 (s, 1H, CO₂H), 8.77-8.73 (m, 1H, H-1NHC=O cis-/trans-rotamer), 7.95-7.92 (m, 1H, NH), 7.89-7.87 (m, 2H, H-aryl), 7.68-7.66 (m, 2H, H-aryl), 7.43-7.39 (m, 2H, H-aryl), 7.35-7.31 (m, 3H, H-aryl, CONHCH₂), 5.22-5.09 (m, 2H, H-1, H-
3), 4.82 (t, 1H, J_{3,4} = 9.8 Hz, H-4), 4.32-4.26 (m, 2H, Fmoc-CH\textsubscript{2}), 4.23-4.14 (m, 2H, Fmoc-CH \textit{cis-/trans}-rotamer, H-6a), 4.04-3.81 (m, 5H, H-2, H-6b, H-5, COCH\textsubscript{2}CO), 3.42-3.26 (m, 4H, CH\textsubscript{2}COH, NHCH\textsubscript{2}CH\textsubscript{2}), 3.22-3.07 (m, 2H, NHCH\textsubscript{2}CH\textsubscript{2}), 1.99, 1.98, 1.96, 1.90, 1.76, 1.73 (6s, 12H, CH\textsubscript{3}); \textsuperscript{13}C-NMR (DMSO-d\textsubscript{6}) δ 171.3, 170.9, 170.1, 169.7, 169.6, 169.4, 167.7, 167.2, 167.0, 166.9 (10C, C=O), 156.3, 156.1 (1C, Fmoc-C=O \textit{cis-/trans}-rotamer), 143.9, 143.8, 140.8, 140.7, 127.7, 127.1, 125.3, 125.1, 120.2 (9C, C-aryl), 78.0, 78.0 (1C, C-1 \textit{cis-/trans}-rotamer), 73.3 (C-3), 72.3 (C-5), 68.4 (C-4), 65.5 (1C, Fmoc-CH\textsubscript{2}), 61.8 (C-6), 52.1, 52.0 (1C, C-2 \textit{cis-/trans}-rotamer), 50.9 (1C, COCH\textsubscript{2}CO), 48.1, (1C, CH\textsubscript{2}COH\textsubscript{2}H), 47.8, 46.7 (1C, Fmoc-CH \textit{cis-/trans}-rotamer), 41.2, 40.8 (2C, NHCH\textsubscript{2}CH\textsubscript{2}), 22.6, 20.6, 20.4, 20.4 (4C, CH\textsubscript{3}); Due to the rotameric structure the signals can be exchanged. FT-ICR-MS: Calcd. for C\textsubscript{36}H\textsubscript{42}N\textsubscript{4}O\textsubscript{14}Na [M+Na]\textsuperscript{+}: m/z 777.258973; found: m/z 777.258435.

![Structure of 2d]


According to the General Procedure 1d (124 mg, 0.15 mmol) in 6 mL HCO\textsubscript{2}H/DCM afforded after column chromatography (CHCl\textsubscript{3}/MeOH 50:1 + 1 % HCO\textsubscript{2}H→CHCl\textsubscript{3}/MeOH 10:1 + 1 % HCO\textsubscript{2}H) 2d (111 mg, 97%).
Rf: 0.23 (CHCl₃/MeOH 25:1 + 1 % HCO₂H); [α]D²⁰: +1.3 (c 1.0, CHCl₃); ¹H-NMR (DMSO-d₆) δ 12.88 (s, 1H, CO₂H), 8.69-8.67 (m, 1H, H-1NHCO cis-/trans-rotamer), 7.92-7.88 (m, 3H, NH, H-aryl), 7.69-7.66 (m, 2H, H-aryl), 7.43-7.31 (m, 5H, H-aryl, CONHCH₂), 5.26-5.25 (m, 1H, H-3), 5.13-5.07 (m, 1H, H-1), 5.05-5.01 (m, 1H, H-4), 4.32-4.22 (m, 3H, Fmoc-CH₂, Fmoc-CH), 4.06-3.91 (m, 6H, H-5, H-6a, H-6b, H-2, COCH₂CO), 3.35-3.10 (m, 8H, NHCH₂CH₂, CH₂CO₂H), 2.09, 2.08, 1.98, 1.97, 1.89, 1.78, 1.75 (7s, 12H, CH₃); ¹³C-NMR (DMSO-d₆) δ 170.1, 170.0, 169.6, 167.8, 167.2, 167.1, 166.9 (8C, C=O), 156.3, 156.1 (1C, Fmoc-C=O, cis-/trans-rotamer), 143.9, 143.9, 140.8, 140.7, 127.7, 127.1, 120.2, 120.1 (8C, C-aryl), 78.8, 78.7 (1C, C-1 cis-/trans-rotamer), 71.4 (C-5), 70.8 (C-4), 66.7 (C-3), 65.5 (1C, Fmoc-CH₂), 61.6 (C-6), 51.7 (C-2), 48.3 (1C, COCH₂CO), 48.2 (CH₂CO₂H), 46.7 (1C, Fmoc-CH), 40.7 (2C, NHCH₂CH₂), 22.7, 20.6, 20.5, 20.5 (4C, CH₃); Due to the rotameric structure the signals can be exchanged. ESI-TOF-MS: Calcd. for C₃₆H₄₁N₄O₁₄ [M-H]: m/z 753.26248; found: m/z 753.26314.

tert-Butyl [N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosylamino)malonyl]-N-2-[2-(acetylamino)ethyl]glycinate (7)

Compound 1a (105 mg, 0.13 mmol) was dissolved in a 1:1 mixture of Et₃N/DMF (6 mL) and the mixture was stirred for 3 ½ h at rt until TLC indicated complete
consumption of the starting material. Ac₂O (4 mL) was added and the mixture was stirred at rt for 30 min. The solvent was removed under reduced pressure, the residue dissolved in ethyl acetate (70 mL) and successively washed with an aqueous solution of citric acid (10%) (2 × 20 mL), satd. aqueous NaHCO₃ solution. (3 × 20 mL), satd. aqueous NaCl solution (20 mL), dried over Na₂SO₄, filtered and concentrated. Purification of the residue by column chromatography (CHCl₃/MeOH 100:1→50:1) afforded the pure title compound 7 (49 mg, 60%) as amorphous solid.

Rf: 0.26 (CHCl₃/MeOH 50:1); [α]D²⁰: -2.0 (c 1.0, CHCl₃); ¹H-NMR (CDCl₃) δ 8.19 (d, 0.5H, J₁,NH = 9.1 Hz, H-1NHCOC₂H₂ trans-rotamer), 7.99 (d, 0.5H, J₁,NH = 9.1 Hz, H-1NHCOC₂H₂ cis-rotamer), 6.73 (t, 0.5H, J = 5.7 Hz, NH cis-rotamer), 6.42 (t, 0.5H, J = 5.1 Hz, NH trans-rotamer), 5.28-5.21 (m, 2H, H-1, H-3), 5.06-4.94 (m, 2H, H-2, H-4), 4.25-4.19 (m, 1H, H-6a), 4.07-4.01 (m, 2H, H-6b), 3.96-3.85 (m, 2H, NCH₂CO₂tBu cis-/trans-rotamer), 3.79-3.76 (m, 1H, H-5), 3.56-3.11 (m, 6H, NCH₂CH₂CO₂tBu cis-/trans-rotamer), 2.04, 2.03, 2.01, 1.99, 1.98, 1.97, 1.95, 1.92 (10s, 12H, CH₃), 1.44 (s, 9H, CO₂C(CH₃)₃); ¹³C-NMR (CDCl₃) δ 170.9, 170.8, 170.7, 170.7, 170.4, 170.0, 170.0, 169.6, 169.2, 169.1, 168.4, 168.0, 167.0, 166.6 (8C, C=O cis-/trans-rotamer), 83.7, 82.7 (1C, CO₂C(CH₃)₃ cis-/trans-rotamer), 78.0, 78.0 (1C, C-1 cis-/trans-rotamer), 73.7 (C-5), 73.1, 73.0 (1C, C-3 cis-/trans-rotamer), 70.4, 70.3 (1C, C-4 cis-/trans-rotamer), 68.2 (C-2), 61.8 (C-6), 52.0, 49.9 (1C, NCH₂CO₂tBu cis-/trans-rotamer), 49.7, 48.5 (1C, NHCH₂CH₂N cis-/trans-rotamer), 40.4, 40.2 (1C, COCH₂CO cis-/trans-rotamer), 37.8, 37.7 (NHCH₂CH₂N cis-/trans-rotamer), 28.0, 28.0 (3C, CO₂C(CH₃)₃ cis-/trans-rotamer), 23.2, 23.1, 20.8, 20.7, 20.6 (5C, CH₃); Due to the rotameric structure the signals can be exchanged. ESI-TOF-MS: Calcd. for C₂₇H₄₃N₃O₁₄Na [M+Na]⁺: m/z 654.24807; found: m/z 654.24871.
*tert*-Butyl [N-(β-D-glucopyranosylamino)malonyl]-N-2-[(acetylaminoethyl)glycinate (3)

Compound 7 (46 mg, 0.07 mmol) was dissolved in a 6:1 mixture of MeOH/NH$_3$ in MeOH (7 N) (7 mL) for 1 h at rt until the TLC indicated complete consumption of the starting material. The solvent was removed under reduced pressure to afford the pure title compound 3 (34 mg, 100%) as amorphous solid.

R$_f$: 0.41 (CHCl$_3$/MeOH 2:1); [α]$_D^{20}$ -2.0 (c 1.0, H$_2$O); $^1$H-NMR (D$_2$O) δ 5.01-4.97 (m, 1H, H-1cis-/trans-rotamer), 4.25 (s, 1H, NCH$_2$CO$_2^-$Bu trans-rotamer), 4.06 (s, 1H, NCH$_2$CO$_2^-$Bu cis-rotamer), 3.89 (dd, 1H, $J_{5,6a}$ = 1.9 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 3.73 (dd, 1H, $J_{5,6b}$ = 5.3 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6b), 3.68-3.35 (m, 10H, COC$_2$H$_5$, NHCH$_2$CH$_2$N, H-2, H-3, H-4, H-5), 2.01 (s, 2H, CH$_3$ cis-rotamer), 1.98 (s, 1H, CH$_3$ trans-rotamer), 1.50 (s, 3H, CO$_2$C(CH$_3$)$_3$ trans-rotamer), 1.48 (s, 6H, CO$_2$C(CH$_3$)$_3$ cis-rotamer); $^{13}$C-NMR (D$_2$O) δ 175.3, 175.1, 171.0, 170.7, 170.6, 170.6, 170.4 (7C, C=O cis-/trans-rotamer), 85.5, 84.8 (1C, CO$_2$C(CH$_3$)$_3$ cis-/trans-rotamer), 80.1 (C-1), 78.3 (C-5), 77.1 (C-3), 72.5 (C-4), 69.9 (C-2), 61.2 (C-6), 52.2 (1C, NCH$_2$CO$_2^-$Bu trans-rotamer), 50.6 (1C, NCH$_2$CO$_2^-$Bu cis-rotamer), 49.6, 47.4 (1C, NHCH$_2$CH$_2$N cis-/trans-rotamer), 42.1 (1C, COCH$_2$CO trans-rotamer), 41.6 (1C, COCH$_2$CO cis-rotamer), 38.2, 37.6 (1C, NHCH$_2$CH$_2$N cis-/trans-rotamer), 27.9 (3C, CO$_2$C(CH$_3$)$_3$), 22.6 (1C, CH$_3$); Due to the rotameric structure the signals can be exchanged. ESI-TOF-MS: Calcd. for C$_{19}$H$_{33}$N$_3$O$_{10}$Na [M+Na]$^+$: m/z 486.20581 found: m/z 486.20602.
**tert-Butyl [N-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosylamino)malonyl]-N-2-[2-(aminoethyl)glycinate (8)**

In a similar manner as described in [14] building block 1c was deprotected according to following procedure.

The Fmoc-protected amine 1c (133 mg, 0.16 mmol) was stirred in 6 mL 20% piperidine/DMF at rt for 3 ½ h until TLC indicated complete consumption of the starting material. The solvent was removed under reduced pressure and the residue was co-evaporated with toluene (5 × 20 mL) to afford crude title compound 8 which was used without further purification.

**tert-Butyl 3-[N-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosylamino)malonyl]-11-(9H-fluoren-9-ylmethoxycarbonyl)-9-[N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)malonyl]-3,6,9,12-tetraazaazadodecanoate (4)**
Analogous as described in [14] dimeric glycoconjugate 4 was prepared according to following procedure.

In a 25 mL round bottom flask equipped with a gas inlet and a stirring bar 2a (124 mg, 0.16 mmol) was dissolved in 12 mL dry DMF under an atmosphere of nitrogen. The solution was cooled to 0 °C and HBTU (1.3 equiv), HOBt (1.3 equiv) and DIPEA (3.9 equiv) were added. The mixture was stirred at 0 °C for 10 min. Afterwards 8 (1 equiv) was added and the resulting solution was stirred at 0 °C for 2 h. Thereafter the solution was stirred at rt for 14 h. The solvent was removed under reduced pressure, the residue dissolved in ethyl acetate (70 mL) and successively washed with an aqueous solution of citric acid (10%) (2 × 20 mL), satd. aqueous NaHCO₃ solution (3 × 20 mL), satd. aqueous NaCl solution (20 mL), dried over Na₂SO₄, filtered and concentrated. Purification of the residue by column chromatography (CHCl₃/MeOH 100:1→25:1) afforded pure title compound 4 (126 mg, 58%) as amorphous solid.

Rf: 0.27 (CHCl₃/MeOH 25:1); [α]₀²⁰: -8.3 (c 1.0, CHCl₃); ¹H-NMR (CDCl₃) δ 8.77, 8.39, 8.32, 8.21, 8.11, 7.98, 7.71, 7.53, 7.12, 6.95, 6.75, 6.17, 5.75 (d, d, d, d, d, m, d, d, d, d, s, s, 4H, H-1NH, H-1’NH, CONHCH₂, H-2’NH trans-/trans-, trans-/cis-, cis-/trans-, cis-/cis-rotamer), 7.77-7.75 (m, 2H, H-aryl), 7.61-7.59 (m, 2H, H-aryl), 7.41-7.37 (m, 2H, H-aryl), 7.33-7.29 (m, 2H, H-aryl), 5.38-5.19 (m, 4 H, H-1, H-1’, H-3, H-3’ trans-/trans-, trans-/cis-, cis-/trans-, cis-/cis-rotamer), 5.13-4.99 (m, 3H, H-4’, H-4, H-2 trans-/trans-, trans-/cis-, cis-/trans-, cis-/cis-rotamer), 4.41-3.01 (m, 26H, Fmoc-CH₂, Fmoc-CH, H-6a, H-6b, H-6a’, H-6b’, H-5, H-5’, H-2’, NCH₂CO₂tBu, NHCH₂CH₂N, NCH₂CON, NHCH₂CH₂N, COCH₂CO, CHCH₂CO trans-/trans-, trans-/cis-, cis-/trans-, cis-/cis-rotamer), 2.05, 2.05, 2.05, 2.03, 2.02, 2.01, 2.00, 1.99, 1.95, 1.94, 1.93, 1.92 (12s, 24H, CH₃ trans-/trans-, trans-/cis-, cis-/trans-, cis-/cis-rotamer), 1.47, 1.46, 1.44, 1.42 (4s, 9H, CO₂C(CH₃)₃ trans-/trans-, trans-/cis-, cis-/trans-, cis-
/cis-rotamer); $^{13}$C-NMR (CDCl$_3$) δ 171.0, 170.8, 170.7, 170.3, 170.2, 169.7, 169.6, 169.3, 168.9, 168.7, 168.4, 168.2, 167.8, 167.5, 167.3, 156.9, 156.8 (15C, C=O rotamer a, b, c, d), 144.1, 144.1, 144.1, 144.0, 144.0, 141.4, 127.9, 127.2, 125.2, 120.1 (10C, C-aryl trans-/trans-, trans-/cis-, cis-/trans-, cis-/cis-rotamer), 84.0, 83.5, 83.3, 82.7 (1C, CO$_2$C(CH$_3$)$_3$ trans-/trans-, trans-/cis-, cis-/trans-, cis-/cis-rotamer), 79.6, 79.6, 79.0, 78.1, 78.1 (2C, C-1, C-1' trans-/trans-, trans-/cis-, cis-/trans-, cis-/cis-rotamer), 73.8, 73.7, 73.6, 73.5, 73.4, 73.2, 73.1, 73.0 (2C, C-5, C-5' rotamer a, b, c, d), 70.7, 70.5 (1C, C-4 trans-/trans-, trans-/cis-, cis-/trans-, cis-/cis-rotamer), 68.5, 68.5, 68.3, 68.2, 68.2 (2C, C-2, C-2' trans-/trans-, trans-/cis-, cis-/trans-, cis-/cis-rotamer), 66.9, 66.8 (1C, Fmoc-CH$_2$ trans-/trans-, trans-/cis-, cis-/trans-, cis-/cis-rotamer), 62.2, 62.1, 62.0, 61.9, 61.9, 61.7 (2C, C-6, C-6' trans-/trans-, trans-/cis-, cis-/trans-, cis-/cis-rotamer), 53.0, 52.7, 52.7, 52.6 (1C, C-2' trans-/trans-, trans-/cis-, cis-/trans-, cis-/cis-rotamer), 51.0, 50.8, 50.3, (2C, NCH$_2$CO$_2$Bu, NCH$_2$CONH trans-/trans-, trans-/cis-, cis-/trans-, cis-/cis-rotamer), 49.0, 48.4 (2C, COCH$_2$CO, COCH$_2$CO trans-/trans-, trans-/cis-, cis-/trans-, cis-/cis-rotamer), 47.3, 46.3 (1C, Fmoc-CH trans-/trans-, trans-/cis-, cis-/trans-, cis-/cis-rotamer), 41.7, 41.7, 41.3, 41.2, 39.8, 39.8, 39.7, 39.6, 39.5, 36.7, 36.7, 36.7, (4C, NHCH$_2$CH$_2$N, NHCH$_2$CH$_2$N trans-/trans-, trans-/cis-, cis-/trans-, cis-/cis-rotamer), 28.2, 28.1, 28.1 (12C, CO$_2$C(CH$_3$)$_3$ trans-/trans-, trans-/cis-, cis-/trans-, cis-/cis-rotamer), 23.2, 22.9, 20.9, 20.9, 20.8, 20.8, 20.7, 20.6 (8C, CH$_3$ trans-/trans-, trans-/cis-, cis-/trans-, cis-/cis-rotamer). Due to the rotameric structure the signals can be exchanged. ESI-TOF-MS: Calcd. for C$_{61}$H$_{79}$N$_7$O$_{26}$Na [M+Na]$^+$: m/z 1348.49670; found: m/z 1348.49739.

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References
