Supporting Information

A short route for the synthesis of “sweet” macrocycles via a click dimerization/ring-closing metathesis approach

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Content:

1   Experimental data and spectra for dimers 4–6 ................................................................. 2
2   Experimental data and spectra for bifunctional building blocks 9–13 ............................... 10
3   Experimental data and spectra for dimerized molecules 14–17 ........................................ 23
4   Experimental data and spectra for cyclic molecules 18–25 ............................................... 34
1 Experimental data and spectra for dimers 4–6

11,17-Butane-13,16-diylbis(8-{(2R,3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-[(benzyloxy)-methyl]tetrahydro-2H-pyran-2-yl}-1H-8,9,10-triazole) (4)

\[ \text{1H-NMR (400 MHz, CDCl}_3\text{): } \delta \text{ [ppm] = 1.75 (bs, 4H, 10-H), 2.75 (bs, 4H, 9-H), 3.70–3.74 (m, 4H), 3.76–3.86 (m, 4H), 4.00–4.07 (m, 4H), 4.43–4.62 (m, 8H), 4.82–4.96 (m, 6H), 5.52 (d, } J = 9.0 \text{ Hz, 2H, 2-H), 6.90–6.96 (m, 4H), 7.14–7.22 (m, 10H, CH arom.), 7.26–7.36 (m, 30H, CH arom.).} \]

\[ \text{13C-NMR (100 MHz, CDCl}_3\text{): } \delta \text{ [ppm] = 25.36, 28.86 (t, C-13, C-14), 68.34 (t, C-7), 73.47, 74.85, 75.18, 75.74 (t, CH}_2\text{arom.}, 77.23, 77.95, 80.79, 85.44 (d, C-3, C-4, C-5, C-6), 87.38 (d, C-2), 120.20 (d, C-12), 127.68–128.46 (d, CH arom.), 137.00, 137.68, 137.75, 138.14 (s, C arom), 148.05 (s, C-11).} \]

HRMS (ESI) \[ C_{76}H_{80}N_6O_{10}Na \text{ [M+Na}^+\text{]} \text{ calcld} \text{ 1259.5828 found} \text{ 1259.5798} \]
Butane-13,16-diylbis{1H-8,9,10-triazole-11,17-diyl(2R,3R,4R,5S,6R)-3-(acetylamino)-6-
[(acyloxy)methyl]tetrahydro-2H-pyran-2,4,5-triyl} tetraacetate (5)

\[\text{Butane-13,16-diylbis{1H-8,9,10-triazole-11,17-diyl(2R,3R,4R,5S,6R)-3-(acetylamino)-6-
[(acyloxy)methyl]tetrahydro-2H-pyran-2,4,5-triyl} tetraacetate (5)}\]

\[^{1}H\text{-NMR (400 MHz, DMSO-}d_6\text{): }\delta [\text{ppm}] = 1.54 \text{ (bs, 6H, } \text{CH}_3(\text{NHAc}), 1.56 \text{ (bs, 4H, 13-H), } 1.92, \]

\[^{13}C\text{-NMR (100 MHz, DMSO-}d_6\text{): }\delta [\text{ppm}] = 20.95, 21.11, 21.20 \text{ (q, } \text{CH}_3(\text{Ac}), 22.94 \text{ (q, } \text{CH}_3(\text{NHAc}),

\[^{13}C\text{-NMR (100 MHz, DMSO-}d_6\text{): }\delta [\text{ppm}] = 20.95, 21.11, 21.20 \text{ (q, } \text{CH}_3(\text{Ac}), 22.94 \text{ (q, } \text{CH}_3(\text{NHAc}),

\[\text{HRMS (ESI) } \text{C}_{36}H_{50}N_{8}O_{16}Na [M+Na^+] \text{ calcld 873.3237}

\[\text{found 873.3235}\]
Butane-13,16-diylbis(1H-8,9,10-triazole-11,8-diyl(2R,3R,4R,5R,6R)-3-{(trifluoroacetyl)amino}-6-{[(trifluoroacetyl)amino]methyl}tetrahydro-2H-pyran-2,4,5-triy) tetraacetate (6)

1H-NMR (500 MHz, DMSO-d6): δ [ppm] = 1.56 (bs, 4H, 16-H), 1.93, 2.03 (s, 6H, CH3(Ac)), 2.61 (bs, 4H, 13-H), 3.40–3.44 (m, 4H, 7-H), 4.13 (ddd, J = 10.0, 6.2, 3.3 Hz, 2H, 6-H), 4.84 (ddd, J = 10.4, 9.8, 8.8 Hz, 2H, 3-H), 5.11 (dd, J = 10.0, 9.5 Hz, 2H, 5-H), 5.38 (dd, J = 10.4, 9.5 Hz, 2H, 4-H), 6.07 (d, J = 9.8 Hz, 2H, 2-H), 8.11 (s, 2H, 12-H), 9.47 (bt, J = 5.5 Hz, 2H, 7-NH) 9.70 (bd J = 8.8 Hz, 2H, 3-NH).

13C-NMR (125 MHz, DMSO-d6): δ [ppm] = 20.05, 20.45 (q, CH3(Ac)), 24.47 (t, C-13), 27.93 (t, C-14), 40.21 (t, C-7), 52.77 (d, C-3), 68.92 (d, C-5), 71.99 (d, C-4), 73.58 (d, C-6), 84.06 (d, C-2), 115.77 (q, 1J(13C,19F) = 287.7 Hz, CF3), 115.36 (q, 1J(13C,19F) = 288.2 Hz, CF3), 120.68 (d, C-12), 147.26 (s, C-11), 156.33 (q, 1J(13C,19F) = 37.2 Hz, C(O)CF3), 156.70 (q, 2J(13C,19F) = 36.4 Hz, C(O)CF3), 169.41, 169.61 (s, CO).–

found 1087.2440
2 Experimental data and spectra for bifunctional building blocks 9–13

Methyl 6-azido-2,3-di-O-benzyl-6-deoxy-α-D-glucopyranoside (9)\[1\]

![Chemical Structure]

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta [\text{ppm}] = 2.15 \text{ (bs, 1H, OH)}, 3.37–3.45 \text{ (m, 5H)}, 3.46–3.51 \text{ (m, 1H)}, 3.53 \text{ (dd, } J = 9.4, 3.5 \text{ Hz, 1H)}, 3.70–3.78 \text{ (m, 2H)}, 4.64 \text{ (d, } J = 3.5 \text{ Hz, 1H)}, 4.67 \text{ (d, } J = 11.3 \text{ Hz, 1H)}, 4.67 \text{ (d, } J = 12.1 \text{ Hz, 1H)}, 5.04 \text{ 4.67 (d, } J = 11.3 \text{ Hz, 1H)}, 4.77 4.67 \text{ (d, } J = 12.1 \text{ Hz, 1H}), 7.28–7.41 \text{ (m, 10H, CH arom.).–}

\(^{13}\text{C-NMR (100 MHz, CDCl}_3\)): \(\delta [\text{ppm}] = 51.48 \text{ (t, C-6)}, 55.38, 70.17, 70.55 \text{ (d, CH)}, 73.06, 75.31 \text{ (t, CH\(_2\) benzyl)}, 79.66, 80.97 \text{ (d, CH)}, 97.94 \text{ (d, C-1)}, 127.82, 127.85, 127.89, 127.92, 128.37, 128.53 \text{ (d, CH arom.), 137.66, 138.38 (s, C arom.).–}

HRMS (ESI) \(\text{C}_{21}\text{H}_{25}\text{N}_3\text{O}_5\text{Na} \quad [\text{M+Na}^+] \quad \text{calcd} \quad 422.1686 \quad \text{found} \quad 422.1683\)
Allyl 2,3,4-tri-O-acetyl-6-azido-6-deoxy-β-D-glucopyranoside (10)

Allyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (1.0 g, 2.57 mmol) was dissolved in methanol (20 ml) and treated with a catalytic amount of NaOMe (1 M). The reaction was stirred for 30 min neutralized with Lewatit S1080 resin and filtered. The residue was dried, dissolved in dry pyridine (10 ml) and cooled in an ice bath. Then TsCl (736 mg, 2.57 mmol) was slowly added and the mixture was allowed to stir overnight. Acetic anhydride (1.1 ml, 11.6 mmol) was added and the mixture was stirred for 60 min. The solution was diluted with ethyl acetate and extracted with diluted HCl to remove the pyridine. The organic phase was dried and concentrated. The residue was diluted with dry DMF (15 ml) and treated with sodium azide (0.5 g, 7.72 mmol). After heating the reaction mixture for 4 h at 90°C DMF was evaporated and the residue was diluted with ethyl acetate, extracted with water and brine, concentrated and dried. The product was purified by flash chromatography (silica, eluent: hexanes/ethyl acetate = 1/1, Rf=0.59) to yield 666 mg (1.79 mmol, 70%) of a colourless solid.

$^1$H-NMR (400 MHz, CDCl₃): δ [ppm] = 2.01, 2.04, 2.06 (s, 3H, CH₃(Ac)), 3.18 (dd, J = 13.3, 2.3 Hz, 1H, 6⁻H), 3.43 (dd, J = 13.3, 7.6 Hz, 1H, 6⁺-H), 3.69 (ddd, J = 10.0, 7.6, 2.3 Hz, 1H, 5-H), 4.13 (dddd, J = 13.3, 6.3, 1.4, 1.4 Hz, 1H, 7⁻H), 4.37 (dddd, J = 13.3, 4.9, 1.6, 1.6 Hz, 1H, 7⁺-H), 4.60 (d, J = 7.8 Hz, 1H, 1-H), 4.97 (dd, J = 9.8, 9.4 Hz, 1H, 3-H), 5.03 (dd, J = 9.8, 7.8 Hz, 1H, 2-H), 5.21 (dd, J = 9.4, 9.4 Hz, 1H, 4-H), 5.22 (dddd, J = 10.5, 2.9, 1.4, 1.4 Hz, 1H, 9⁻-H), 5.30 (dddd, J = 17.2, 3.3, 1.6, 1.6 Hz, 1H, 9⁺-H), 5.86 (dddd, J = 17.2, 10.5, 6.3, 4.9 Hz, 1H, 8-H).

$^{13}$C-NMR (100 MHz, CDCl₃): δ [ppm] = 20.58, 20.64 (s, 3H, CH₃(Ac)), 51.13 (t, C-6), 69.70 (d, CH), 69.85 (t, C-7), 71.22, 72.53, 73.64 (d, CH), 99.25 (d, C-1), 117.82 (t, C-9), 133.10 (d, C-8), 169.30, 169.53, 170.24 (s, CO).

HRMS (ESI) C₁₅H₂₁N₃O₈Na [M+Na⁺] calcd 394.1221 found 394.1221

C₁₅H₂₁N₃O₈ (371.34) Calcd C 48.52 H 5.70
Found C 48.70 H 5.89
3,4-Di-O-acetyl-5-(acetylamino)-2,6-anhydro-1-azido-1,5,7,8,9-pentadeoxy-D-glycero-L-gulo-non-8-enitol (11)

The product was prepared in analogy to (10).

**^1H-NMR** (400 MHz, CDCl₃): δ [ppm] = 1.96 (s, 3H, CH₃(NHAc)), 2.08, 2.09 (s, 3H, CH₃(Ac)), 2.29–2.37 (m, 1H, 7¹-H), 2.43–2.52 (m, 1H, 7⁷-H), 3.22 (dd, J = 13.4, 3.5 Hz, 1H, 1³-H), 3.44 (dd, J = 13.4, 7.6 Hz, 1H, 1⁷-H), 3.84 (ddd, J = 7.6, 7.6, 3.5 Hz, 1H, 2-H), 4.23–4.33 (m, 2H, 5-H, 6-H), 4.92 (ddd, J = 7.6, 7.6 Hz, 1H, 3-H), 5.08 (dd, J = 8.6, 7.6 Hz, 1H, 3-H), 5.13–5.21 (m, 2H, 9-H), 5.75–5.86 (m, 1H, 8-H), 5.90 (bd, J = 8.2 Hz, 1H, NH).–

**^13C-NMR** (100 MHz, CDCl₃): δ [ppm] = 20.73, 20.83 (q, CH₃(Ac)), 23.17 (q, CH₃(NHAc)), 31.62 (t, C-7), 50.59 (t, C-1), 50.91 (d, C-3), 69.00, 70.14, 71.22, 71.39 (d, C-2, C-3, C-4, C-6), 117.92 (t, C-9), 132.97 (d, C-8), 169.16, 169.81, 171.30 (s, CO).–

**HRMS (ESI)** \(^{15}C_{15}H_{22}N_4O_6Na\) [M+Na⁺] calcd 377.1432 found 377.1433
Methyl 6-azido-2,3-di-\(O\)-benzyl-6-deoxy-\(\alpha\)-D-glucopyranoside (12)

Methyl 6-azido-2,3-di-\(O\)-benzyl-6-deoxy-\(\alpha\)-D-glucopyranoside (1.0 g, 2.50 mmol) was dissolved in dry THF and treated with NaH (150 mg, 3.76 mmol). 6-Bromo-1-hexene (0.39 ml, 2.88 mmol) was added dropwise and the mixture was refluxed for 3 h. Excess NaH was quenched by adding methanol and the solution was diluted with water, extracted with ethyl acetate, dried and concentrated. The product was purified by flash chromatography (silica, eluent: hexanes/ethyl acetate = 4/1, \(R_f=0.43\)) to yield 521 mg (1.10 mmol, 43%) of (12).

\[ \text{\(^1H\)-NMR (400 MHz, CDCl}_3\): \(\delta [ppm] = 1.34–1.43\ (m, 2H), 1.48–1.58\ (m, 2H), 2.03\ (q, J = 7.0 Hz, 2H), 3.22\ (dd, J = 9.8, 9.4 Hz, 1H), 3.40\ (s, 3H, OCH}_3\), 3.45–3.51\ (m, 3H), 3.72\ (ddd, J = 9.9, 5.6, 2.5 Hz, 1H, 5-H), 3.80–3.90\ (m, 2H), 4.59\ (d, J = 3.5 Hz, 1H), 4.64\ (d, J = 12.1 Hz, 1H), 4.77\ (d, J = 10.9 Hz, 1H), 4.78\ (d, J = 12.1 Hz, 1H), 4.94\ (d, J = 10.9 Hz, 1H), 5.72–5.82\ (m, 1H, 11-H), 7.26–7.37\ (m, 10H, CH arom.).–}

\[ \text{\(^13C\)-NMR (100 MHz, CDCl}_3\): \(\delta [ppm] = 25.46, 29.83, 33.56\ (t, C-8, C-9, C-10), 51.41\ (t, C-6), 55.31, 70.04\ (d, CH), 73.17, 73.38, 75.63\ (t, C-7, CH}_2\ benzyl), 78.68, 79.72, 81.62\ (d, CH), 97.97\ (d, C-1), 114.55\ (t, C-12), 127.49–128.33\ (d, CH arom.), 137.88, 138.36\ (s, C arom.), 138.49\ (d, C-11).–}

\[ \text{HRMS (ESI)}\quad \text{C}_{27}\text{H}_{35}\text{N}_3\text{O}_5\text{Na}^{+}\quad \text{[M+Na\(^+\)] calcd 504.2469 found 504.2464} \]

\[ \text{C}_{27}\text{H}_{35}\text{N}_3\text{O}_5\ (481.58)\quad \text{Calcd C 67.34 H 7.33 N 8.73} \quad \text{Found C 67.53 H 7.40 N 8.34} \]
Allyl 3,4-di-\(O\)-acetyl-6-azido-2,6-dideoxy-2-[(trifluoroacetyl)amino]-\(\beta\)-D-glucopyranoside (13)

\[
\begin{align*}
\text{AcO} & \quad 3 \quad \text{NHCOCF}_3 \\
\text{O} & \quad 5 \\
\text{O} & \quad 7 \\
\text{H} & \quad 9 \\
\end{align*}
\]

\(^{1}H\)-NMR (500 MHz, CDCl\(_3\)): \(\delta\) [ppm] = 2.04, 2.05 (s, 3H, CH\(_3\)(Ac)), 3.22 (dd, \(J = 13.4, 2.4\) Hz, 1H, 6\(^{b}\)-H), 3.46 (dd, \(J = 13.4, 7.6\) Hz, 1H, 6\(^{a}\)-H), 3.75 (ddd, \(J = 10.0, 7.6, 2.4\) Hz, 1H, 5-H), 4.05–4.09 (m, 1H, 2-H), 4.12 (dddd, \(J = 13.2, 6.4, 1.3, 1.3\) Hz, 1H, 7\(^{a}\)-H), 4.37 (ddddd, \(J = 13.2, 4.9, 1.5, 1.5\) Hz, 1H, 7\(^{b}\)-H), 4.73 (d, \(J = 8.3\) Hz, 1H, 1-H), 5.00 (ddd, \(J = 10.0, 9.3\) Hz, 1H, 4-H), 5.22 (dd, \(J = 10.4, 2.6, 1.3\) Hz, 1H, 9\(^{a}\)-H), 5.28 (dd, \(J = 17.2, 3.2, 1.6\) Hz, 1H, 9\(^{b}\)-H), 5.34 (dd, \(J = 10.7, 9.3\) Hz, 1H, 3-H), 5.84 (dddd, \(J = 17.2, 10.4, 6.4, 4.9\) Hz, 1H, 8-H), 6.91 (bd, \(J = 9.0\) Hz, 1H, NH)

\(^{13}C\)-NMR (125 MHz, CDCl\(_3\)): \(\delta\) [ppm] = 20.49, 20.68 (q, CH\(_3\)(Ac)), 51.14 (t, C-6), 54.80 (d, C-2), 69.67 (d, C-4), 69.97 (t, C-7), 77.52 (d, C-3), 73.70 (d, C-5), 98.71 (d, C-1), 115.45 (q, \(^{1}J\text{(C,}^{19}\text{F)} = 287.3\) Hz, CF\(_3\)), 118.21 (t, C-9), 120.01 (d, C-8), 157.23 (q, \(^{2}J\text{(C,}^{19}\text{F)} = 37.4\) Hz, C(O)CF\(_3\)), 169.30, 171.04 (s, CO).

HRMS (ESI) \(C_{15}H_{19}F_{3}N_{4}O_{7}Na\) [M+Na\(^{+}\)] calcd 447.1098
found 447.1095


3 Experimental data and spectra for dimerized molecules 14–17

Butane-1,4-diylbis[1H-7,8,9-triazole-5,7-diylmethylene(12S,13S,14R,15S,16S)-16-(allyloxy)tetrahydro-2H-pyran-12,13,14,15-tetrayl] hexaacetate (14)

\[ \alpha^\text{D} = -21.5 \text{ (c = 0.265, CHCl}_3) \]

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 1.75 (bs, 4H), 2.01, 2.04, 2.10 (s, 3H, CH$_3$(Ac)), 2.75 (bs, 4H), 3.85–3.98 (m, 4H), 4.16 (dd, J = 13.3, 4.7 Hz, 2H), 4.33 (dd, J = 14.4, 8.6 Hz, 2H), 4.46 (d, J = 8.2 Hz, 2H), 4.58 (dd, J = 14.4, 1.2 Hz, 2H), 4.88 (t, J = 9.8 Hz, 2H), 5.00 (dd, J = 9.6, 8.0 Hz, 2H), 5.10–5.18 (m, 4H), 5.22 (t, J = 9.6 Hz, 2H), 5.69–5.80 (m, 2H), 7.42 (bs, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ [ppm] = 20.65, 20.71, 20.75 (q, CH$_3$(Ac)), 25.38, 29.08, (t, C-4, C-3), 50.80 (t, C-10), 69.93 (t, C-17), 70.13, 71.08, 72.39 (d, C-12, C-13, C-14, C-15), 99.29 (d, C-16), 117.86 (t, C-18), 122.50 (d, C-6), 132.63 (d, C-18), 147.65 (s, C-5), 169.14, 169.54, 169.90 (s, CO).–

HRMS (ESI) C$_{38}$H$_{52}$N$_6$O$_{16}$Na [M+Na$^+$] calcd 871.3332 found 871.3318

C$_{38}$H$_{52}$N$_6$O$_{16}$ (848.85) Calcd C 53.77 H 6.17
Found C 53.99 H 6.46
Butane-1,4-diylbis[1H-5,6,7-triazol-9,7-diylmethylene(11S,12S,13S,14R,15S)-14-(acetyl-amino)-15-allyltetrahydro-2H-pyran-11,12,13-triyl] tetraacetate (15)

\[
\text{\begin{tikzpicture}
\node (n1) at (0,0) {O};
\node (n2) at (1,0) {\text{\(\text{OAc}\)}};
\node (n3) at (2,0) {\text{\(\text{AcO}\)}};
\node (n4) at (3,0) {\text{\(\text{NHAc}\)}};
\node (n5) at (4,0) {N};
\node (n6) at (5,0) {N};
\node (n7) at (6,0) {N};
\node (n8) at (7,0) {N};
\node (n9) at (8,0) {O};
\node (n10) at (9,0) {\text{\(\text{OAc}\)}};
\node (n11) at (10,0) {\text{\(\text{OAc}\)}};
\node (n12) at (11,0) {\text{\(\text{NHAc}\)}};
\end{tikzpicture}}
\]

\[^1\text{H-NMR}\ (400\text{ MHz, CDCl}_3):\ \delta [\text{ppm}] = 1.69–1.83 (\text{bs}, 4\text{H}, 3-\text{H}), 1.96 (\text{s}, 6\text{H}, \text{CH}_3(\text{NHAc})), 2.10, 2.12 (\text{s}, 6\text{H}, \text{CH}_3(\text{Ac})), 2.18–2.40 (\text{m}, 4\text{H}, 16-\text{H}), 2.70–2.80 (\text{bs}, 4\text{H}, 4-\text{H}), 3.97 (\text{dt}, J = 8.6, 2.7\text{ Hz}, 1\text{H}, 11-\text{H}), 4.25–4.38 (\text{m}, 6\text{H}), 4.54 (\text{dd}, J = 14.2, 2.5\text{ Hz}, 2\text{H}), 4.84–4.95 (\text{m}, 6\text{H}), 5.10 (\text{t}, J = 8.4\text{ Hz}, 2\text{H}), 5.36–5.48 (\text{m}, 2\text{H}, 17-\text{H}), 5.94 (\text{d}, J = 7.8\text{ Hz}, 2\text{H}, \text{NH}), 7.38 (\text{s}, 2\text{H}, 8-\text{H}).\]

\[^{13}\text{C-NMR}\ (100\text{ MHz, CDCl}_3):\ \delta [\text{ppm}] = 20.75, 20.80 (\text{q}, \text{CH}_3(\text{Ac})), 23.10 (\text{q}, \text{CH}_3(\text{NHAc})), 25.17, 28.90, 30.93 (\text{t}, \text{C}-3, \text{C}-4, \text{C}-16), 50.42 (\text{t}, \text{C}-10), 51.30 (\text{d}, \text{C}-14), 69.39, 70.15, 70.57, 71.79 (\text{d}, \text{C}-11, \text{C}-12, \text{C}-13, \text{C}-15), 117.85 (\text{t}, \text{C}-18), 122.36 (\text{d}, \text{C}-8), 132.81 (\text{d}, \text{C}-17), 147.81 (\text{s}, \text{C}-9), 169.42, 169.93, 171.44 (\text{s}, \text{CO}).\]

\text{HRMS (ESI)} \quad \text{C}_{38}\text{H}_{54}\text{N}_8\text{O}_{12}\text{Na} \quad [\text{M+Na}^+] \quad \text{calcld} \quad 837.3753

\text{found} \quad 837.3745
18,23-Butane-19,22-diylbis(14-\{[(2R,3R,4S,5R,6S)-4,5-bis(benzyloxy)-3-(hex-11-ene-7-yloxy)-6-methoxytetrahydro-2H-pyran-2-yl]methyl\}-1H-14,15,16-triazole) (16)

\[
\text{\textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3})}: \delta [\text{ppm}] = 1.41–1.65 (m, 12H), 1.73 (bs, 4H, 16-H), 2.03–2.10 (m, 4H), 2.73 (bs, 4H, 15-H), 2.95 (t, \( J = 9.0 \) Hz, 2H), 3.18 (s, 6H, 17-H), 3.38 (dd, \( J = 9.8, 3.5 \) Hz, 2H), 3.60–3.67 (m, 2H), 3.82–3.93 (m, 6H), 4.48–4.57 (m, 4H), 4.62 (d, \( J = 12.5 \) Hz, 2H), 4.76 (d, \( J = 11.7 \) Hz, 4H), 4.92–5.01 (m, 6H), 5.74–5.85 (m, 2H, 11-H), 7.29–7.36 (m, 20H, CH arom.).–
\]

\[
\text{\textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3})}: \delta [\text{ppm}] = 25.31, 25.40, 28.90, 29.86, 33.57, 50.59 (t, CH\textsubscript{2}), 55.20 (d, CH), 69.39 (d, CH), 73.18, 73.39, 75.70 (t, CH\textsubscript{2} benzyl., C-7), 78.61, 79.68, 81.66 (d, CH), 97.97 (d, C-1), 114.61 (t, C-12), 122.14 (d, C-13), 127.68–128.45 (d, CH arom.), 137.96, 138.43 (s, C arom.), 138.56 (d, C-11), 147.83 (s, C-14).–
\]

\[
\text{HRMS (ESI)} \quad C_{62}H_{80}N_{6}O_{10}Na \quad [\text{M+Na}^+] \quad \text{calc} \quad 1091.5828 \quad \text{found} \quad 1091.5816
\]
Butane-1,4-diylbis{1H-7,8,9-triazole-5,7-diylmethylene(12S,13S,14S,15S,16S)-16-(allyloxy)-15-[(trifluoroacetyl)amino]tetrahydro-2H-pyran-12,13,14-triyl} tetraacetate (17)

\[ \text{F}_3\text{COCHN} \]

\[ \text{OAc} \]

\[ \text{AcO} \]

\[ \text{NHCOCF}_3 \]

\[ \text{OAc} \]

\[ \text{O} \]

\[ \text{N} \]

\[ \text{N} \]

\[ \text{N} \]

\[ \text{N} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

\[ \text{O} \]

1H-NMR (400 MHz, DMSO-\(d_6\)): \(\delta [\text{ppm}] = 1.60 \text{ (bs, 4H)}, 1.90, 2.01 \text{ (s, 3H, CH}_3\text{(Ac)}), 2.61 \text{ (bs, 4H)}, 3.79–3.90 \text{ (m, 4H)}, 3.93–4.06 \text{ (m, 4H)}, 4.43 \text{ (dd, } J = 14.6, 8.4 \text{ Hz, 2H)}, 4.58 \text{ (dd, } J = 14.4, 2.7 \text{ Hz, 2H)}, 4.62 \text{ (d, } J = 8.6 \text{ Hz, 2H)}, 4.80 \text{ (t, } J = 9.6 \text{ Hz, 2H)}, 5.00–5.07 \text{ (m, 4H)}, 5.17 \text{ (dd, } J = 10.3, 9.6 \text{ Hz, 2H)}, 5.63–5.74 \text{ (m, 2H)}, 7.80 \text{ (s, 2H)}, 9.63 \text{ (d, } J = 9.0 \text{ Hz, 2H)}.

13C-NMR (100 MHz, DMSO-\(d_6\)): \(\delta [\text{ppm}] = 20.16, 20.60 \text{ (q, CH}_3\text{(Ac)}), 24.71, 28.57 \text{ (t, C-4, C-3)}, 49.83 \text{ (t, C-10)}, 53.69 \text{ (d, C-15)}, 69.09 \text{ (t, C-17)}, 69.88, 71.39, 71.78 \text{ (d, C-14, C-13, C-12)}, 98.42 \text{ (d, C-16)}, 115.70 \text{ (m, CF}_3\text{)}, 116.76 \text{ (t, C-19)}, 122.83 \text{ (d, C-6)}, 133.59 \text{ (d, C-18)}, 146.36 \text{ (s, C-5)}, 156.47 \text{ (m, C(O)CF}_3\text{)}, 169.20, 169.39 \text{ (s, CO)}.

HRMS (ESI) \( C_{38}H_{62}N_{6}O_{16}Na \) [M+Na\(^+\)] calcld 871.3332 found 871.3318
4 Experimental data and spectra for cyclic molecules 18–25

\[(1R,16R,17R,18S,19R,20R,23(E;Z),27R,28R,29S,30R)-21,26,31,32-tetraoxa-3,4,5,12,13,14-hexaazapentacyclo[25.3.1.1^{3,6}.1^{11,14}.1^{16,20}]tetratriaconta-4,6(34),11(33),12,23-pentaene-17,18,19,28,29,30-hexayl hexaacetate (18)\]

\[\text{\[^{1}H\text{-NMR}\ (400\text{ MHz}, \text{CDCl}_3): isomer mixture: } \delta [\text{ppm}] = 1.66–1.82 (m, 4H, 8-H), 2.02, 2.02, 2.03, 2.12, 2.13 (s, 6H, CH_3(Ac)), 2.70–2.88 (m, 4H, 7-H), 3.77–4.03 (m, 6H), 4.22–4.44 (m, 4H), 4.55–4.66 (m, 2H), 4.90–5.04 (m, 4H), 5.20–5.54 (m, 4H), 7.39, 7.59 (s, 2H, 33-H).–\]

\[\text{\[^{13}C\text{-NMR}\ (100\text{ MHz}, \text{CDCl}_3) major isomer: } \delta [\text{ppm}] = 20.56, 20.59, 20.61 (q, \text{CH}_3(Ac)), 25.32, 28.29 (t, C-7, C-8), 50.67 (t, C-2), 68.32 (t, C-22), 70.09, 71.22, 72.39, 72.56 (d, C-16–C-19), 99.67 (d, C-20), 122.61 (d, C-33), 128.34 (d, C-23), 147.53 (s, C-6), 169.87, 169.96, 170.04 (s, CO).–\]

\[\text{HRMS (ESI)} \quad \text{C}_{36}\text{H}_{46}\text{N}_6\text{O}_{18}\text{Na} \quad [\text{M+Na}^+] \quad \text{calcld} \quad 843.3019 \quad \text{found} \quad 843.3017\]

\[ \text{HRMS (ESI)} \quad C_{36}H_{44}F_{6}N_{8}O_{14}\text{Na} \quad [\text{M+Na}^+] \quad \text{calcd} \quad 949.2773 \]
\[ \text{found} \quad 949.2773 \]

**1H-NMR** (400 MHz, CDCl₃) isomer mixture: δ [ppm] = 1.56–1.68 (m, 4H), 1.88–1.95 (m, 6H), 1.98–2.09 (m, 6H), 2.57–2.69 (m, 4H), 3.70–4.06 (m, 8H), 4.34–4.66 (m, 6H), 4.76–4.90 (m, 2H), 5.00–5.40 (m, 4H), 7.78–7.87 (m, 2H), 9.55–9.69 (m, 2H).

\[ \begin{array}{c}
\text{N} \\
\text{OAc} \\
\text{AcHN} \\
\text{OAc} \\
\text{N=N} \\
\text{N=N} \\
\text{O} \\
\text{OAc} \\
\end{array} \]

\[ \text{HRMS (ESI)} \quad C_{36}H_{50}N_{8}O_{12}Na \quad [\text{M+Na}^+] \quad \text{calcd} \quad 809.3440 \]
\[ \text{found} \quad 809.3452 \]

\[^1H\text{-NMR}\ (400\text{MHz, CDCl}_3): \delta [\text{ppm}] = 1.66–1.79 \ (m, \ 4H), \ 1.85–1.98 \ (m, \ 4H), \ 1.98–2.18 \ (m, \ 18H), \ 2.67–2.90 \ (m, \ 4H), \ 3.62–3.89 \ (m, \ 2H), \ 4.07–4.35 \ (m, \ 6H), \ 4.45–4.67 \ (m, \ 4H), \ 4.86–4.96 \ (m, \ 2H), \ 5.03–5.13 \ (m, \ 2H), \ 5.80–5.99 \ (m, \ 2H), \ 7.40 \ (s, \ 2H). \]

\[^1\text{H}-\text{NMR}\ (400\text{MHz, CDCl}_3): \delta [\text{ppm}] = 1.66–1.79 \ (m, \ 4H), \ 1.85–1.98 \ (m, \ 4H), \ 1.98–2.18 \ (m, \ 18H), \ 2.67–2.90 \ (m, \ 4H), \ 3.62–3.89 \ (m, \ 2H), \ 4.07–4.35 \ (m, \ 6H), \ 4.45–4.67 \ (m, \ 4H), \ 4.86–4.96 \ (m, \ 2H), \ 5.03–5.13 \ (m, \ 2H), \ 5.80–5.99 \ (m, \ 2H), \ 7.40 \ (s, \ 2H). \]

\[\text{\textsuperscript{1}H-NMR (400 MHz, CD}_3\text{OD)} isomer mixture: } \delta [\text{ppm}] = 1.33–1.74 (m, 16H), 1.96–2.03 (bs, 4H), 2.67–2.76 (m, 4H), 2.95–3.02 (m, 2H), 3.16 (s, 6H, CH\textsubscript{3}), 3.37–3.43 (m, 2H), 3.50–3.61 (m, 2H), 3.85–3.94 (m, 6H), 4.48–4.55 (m, 4H), 4.60 (d, \( J = 12.1 \) Hz, 2H), 4.75 (d, \( J = 10.2 \) Hz, 2H), 4.94 (d, \( J = 10.9 \) Hz, 2H), 5.39 (bt, \( J = 3.5 \) Hz, 2H, 14-H), 7.28–7.36 (m, 20H, CH arom.).–

\[\text{\textsuperscript{13}C-NMR (100 MHz, CD}_3\text{OD)} major isomer: } \delta [\text{ppm}] = 25.12, 26.14, 28.43, 29.96, 32.46 (t, C-11–C-13, C-32, C-33), 50.78 (t, C-2), 55.12 (q, CH\textsubscript{3}), 69.36 (d, CH), 73.44 (t, C-10), 75.69, 75.71 (t, CH\textsubscript{2}(Bn)), 78.85, 79.64, 81.79, 97.88 (d, CH), 121.61 (d, C-39), 127.59, 127.85, 127.93, 128.31, 128.35 (d, CH arom.), 130.10 (d, C-14), 137.81, 138.31 (s, C arom.), 147.53 (s, C-31).–

\[\text{HRMS (ESI)} \quad C_{60}H_{76}N_{6}O_{10}\text{Na} \quad [\text{M+Na\textsuperscript{+}}] \quad \text{calc} \quad 1063.5515 \quad \text{found} \quad 1063.5509\]

1H-NMR (400 MHz, CDCl3): δ [ppm] = 1.47 (bs, 4H, 23-H) 1.64–1.80 (m, 4H, 8-H) 2.01 (s, 3H, 18-CH3(Ac)), 2.03 (s, 3H, 19-CH3(Ac)), 2.12 (s, 3H, 17-CH3(Ac)), 2.71–2.78 (m, 2H, 7-H), 2.78–2.86 (m, 2H, 7-H), 3.42–3.48 (m, 2H, 22-H), 3.52–3.58 (m, 2H, 22-H), 3.93 (ddd, J = 9.6, 8.8, 2.8 Hz, 2H, 1-H), 4.32 (dd, J = 14.5, 8.2 Hz, 2H, 2-H), 4.40 (d, J = 8.2 Hz, 2H, 20-H), 4.60 (dd, J = 14.5, 2.8 Hz, 2H, 2-H), 4.87 (dd, J = 9.6, 9.2 Hz, 2H, 17-H), 4.94 (dd, J = 9.8, 8.2 Hz, 2H, 19-H), 5.24 (dd, J = 9.8, 9.2 Hz, 2H, 18-H), 7.37 (s, 2H, 33-H).

13C-NMR (100 MHz, CDCl3): δ [ppm] = 20.58 (q, CH3(Ac)-18), 20.63 (q, CH3(Ac)-19), 20.69 (q, CH3(Ac)-17), 25.21 (t, C-7), 26.03 (t, C-23), 28.16 (t, C-8), 50.51 (t, C-2), 69.65 (t, C-22), 69.86 (d, C-17), 71.13 (d, C-19), 72.12 (d, C-16), 72.38 (d, 18), 100.59 (d, C-20), 122.32 (d, C-33), 147.77 (s, C-6), 169.34 (s, CO-19), 169.74 (s, CO-17), 170.10 (s, CO-18).

HRMS (ESI) C36H50N6O16Na [M+Na+] calcd 845.3176
found 845.3175
(1R,16R,17S,18S,19R,20R,27R,28R,29S,30S)-21,26,31,32-Tetraoxa-3,4,5,12,13,14-hexaazapentacyclo[25.3.1.1^{3,6} \cdot 1^{11,14} \cdot 1^{16,20}] tetratriaconta-4,6(34),11(33),12-tetraene-17,18,19,28,29,30-hexol (22)

\[
\begin{align*}
\text{HO} & \\
\text{O} & \\
\text{OH} & \\
\text{HO} & \\
\text{N} & \\
\text{NN} & \\
\text{NN} & \\
\text{N} & \\
\text{O} & \\
\text{OH} & \\
\text{HO} & \\
\text{HO} & \\
\end{align*}
\]

\[\begin{align*}
1^H\text{-NMR} \ (400 \text{ MHz, CD}_3\text{OD}): \delta \ [\text{ppm}] = 1.47–1.59 \ (\text{bs, } 4\text{H}), 1.65–1.74 \ (\text{bs, } 4\text{H}), 2.69–2.79 \ (\text{bs, } 4\text{H}), 3.13 \ (\text{q, } J = 9.2 \text{ Hz, } 4\text{H}) \ 3.35–3.39 \ (\text{m, } 2\text{H}), 3.46–3.53 \ (\text{m, } 2\text{H}), 3.55–3.65 \ (\text{m, } 4\text{H}), 4.19 \ (\text{d, } J = 7.8 \text{ Hz, } 2\text{H}), 4.46 \ (\text{dd, } J = 14.1, 8.6 \text{ Hz, } 2\text{H}), 4.81 \ (\text{dd, } J = 14.1, 2.3 \text{ Hz, } 2\text{H}), 7.73 \ (\text{s, } 2\text{H}).–
\end{align*}\]

\[\begin{align*}
13^C\text{-NMR} \ (100 \text{ MHz, CD}_3\text{OD}): \delta \ [\text{ppm}] = 25.85, 27.62, 29.47 \ (t, \text{C-7, C-8, C-24}), 52.41 \ (t, \text{C-2}), 70.79 \ (t, \text{C-25}), 72.95, 74.95, 75.39, 77.74 \ (d, \text{C-1, C-28–C-30}), 104.39 \ (d, \text{C-27}), 124.20 \ (d, \text{C-33}), 148.28 \ (s, \text{C-6}).–
\end{align*}\]

**HRMS (ESI)**  \(\text{C}_{24}\text{H}_{38}\text{N}_6\text{O}_{10}\text{Na} \ [\text{M+Na}^+] \)  
\[
\begin{align*}
\text{calcd} \ & 593.2542 \\
\text{found} \ & 593.2546
\end{align*}
\]
49
**1H-NMR** (400 MHz, D$_2$O): δ [ppm] = 1.20 (bs, 4H), 1.56 (bs, 4H), 2.53–2.70 (m, 6H), 3.26–3.39 (m, 8H), 3.61–3.78 (m, 4H), 4.19 (d, $J = 7.8$ Hz, 2H), 4.41 (dd, $J = 14.1$, 10.9 Hz, 2H), 7.75 (s, 2H).

**13C-NMR** (100 MHz, D$_2$O): δ [ppm] = 24.18, 25.68, 28.52 (t, C-7, C-8, C-23), 51.29 (t, C-2), 56.34 (d, C-19), 61.61 (t, C-22), 71.87, 73.97, 74.55 (d, C-16, C-17, C-18), 102.21 (d, C-20), 123.42 (d, C-33), 148.41 (s, C-6).

**HRMS (ESI)** \( \text{C}_{24}\text{H}_{41}\text{N}_8\text{O}_6\text{Na} \) [M+Na$^+$] berechnet: 591.2861
gefunden: 591.2866

$\delta^\text{[a]}^{[\text{c}]} = +41.8$ (c = 0.225, CHCl$_3$)

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ [ppm] = 0.80–0.91 (m, 4H), 1.22–1.34 (m, 4H), 1.68–1.76 (m, 4H), 1.99 (s, 6H, CH$_3$(NHAc)), 2.11, 2.15 (s, 6H, CH$_3$(OAc)), 1.66–1.88 (m, 4H), 3.89 (ddd, $J$ = 10.5, 8.4, 2.5 Hz, 2H), 4.00–4.07 (m, 2H), 4.24–4.34 (m, 4H), 4.53 (dd, $J$ = 14.2, 2.2 Hz, 2H), 4.92 (t, $J$ = 8.2 Hz, 2H), 5.05 (dd, $J$ = 9.6, 8.0 Hz, 2H), 5.84 (d, $J$ = 7.8 Hz, 2H), 7.40 (s, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ [ppm] = 20.80, 20.85, 23.08, 23.32, 25.12, 28.26, 29.67, 50.58, 51.72, 69.50, 70.31, 70.62, 72.35 (d, C-1, C-25, 122.32 (d, C-32), 147.66 (s, C-6), 169.62, 169.87, 171.72 (s, CO).

HRMS (ESI) $\text{C}_{36}\text{H}_{52}\text{N}_8\text{O}_{12}\text{Na}$ [M+Na$^+$] calcd 811.3597
found 811.3613

![Chemical structure image]

$^1$H-NMR (400 MHz, D$_2$O): $\delta$ [ppm] = 0.50 (bs, 4H), 1.22 (bs, 4H), 1.56 (bs, 4H), 1.93 (s, 6H, CH$_3$(NHAc)), 2.60–2.75 (m, 4H), 3.34 (t, $J = 8.9$ Hz, 2H), 3.56–3.69 (m, 4H), 3.70–3.78 (m, 2H), 3.93 (dd, $J = 10.7, 5.7$ Hz, 2H), 4.32 (dd, $J = 14.1, 10.5$ Hz, 2H), 4.75–4.79 (m, 2H), 7.70 (s, 2H).

$^{13}$C-NMR (100 MHz, D$_2$O): $\delta$ [ppm] = 21.97, 22.20, 24.03, 27.86 (t, C-7, C-8, C-21, C-22), 51.57 (t, C-2), 53.39 (d, C-19), 70.66, 71.70, 72.63, 73.81 (d, C-16, C-17, C-18, C-20), 123.82 (d, C-31), 148.35 (s, C-6), 174.27 (s, CO).

HRMS (ESI) $C_{28}H_{44}N_8O_8Na$ [M+Na$^+$] calcd 643.3174
found 643.3159

\[
\begin{align*}
\text{\textsuperscript{1}H-NMR} & (400 \text{ MHz, CD}\text{\textsubscript{3}OD}): \delta [\text{ppm}] = 1.27–1.69 \text{ (m, 24H)}, 2.72 \text{ (bs, 4H)}, 2.87 \text{ (dd, } J = 10.0, 8.8 \text{ Hz, 2H)}, 3.19 \text{ (s, 6H)}, 3.33–3.35 \text{ (m, 2H)}, 3.51–3.58 \text{ (m, 2H)}, 3.70 \text{ (dd, } J = 9.8, 9.0 \text{ Hz, 2H)}, 3.68–3.92 \text{ (m, 2H)}, 3.97 \text{ (ddd, } J = 9.0, 6.1, 6.1 \text{ Hz, 2H)}, 4.59–4.62 \text{ (m, 6H)}, 7.74 \text{ (s, 2H)}.–
\end{align*}
\]

\[
\text{\textsuperscript{13}C-NMR} (100 \text{ MHz, CD}\text{\textsubscript{3}OD}): \delta [\text{ppm}] = 25.64, 27.08, 29.45, 30.36, 30.43, 31.28 \text{ (t, C-11–C-14, C-37, C-38)}, 52.22 \text{ (t, C-2)}, 55.54 \text{ (q, CH\textsubscript{3})}, 70.64, 73.49 \text{ (d, CH)}, 73.96 \text{ (t, C-10)}, 75.47, 80.76, 101.14 \text{ (d, CH)}, 124.52 \text{ (d, C-39)}, 148.52 \text{ (s, C-36)}.–
\]

\[
\text{HRMS (ESI)} \quad \text{C}_{32}\text{H}_{54}\text{N}_{6}\text{O}_{10}\text{Na} \quad [\text{M+Na}^+] \quad \text{calc}d \quad 705.3794
\]

\[
\text{found} \quad 705.3788
\]
Reference List
