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Synthesis of blood group pentasaccharides ALe^y, BLe^y and related tri- and tetrasaccharides

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Spectral characteristics for oligosaccharides.

^{1}H NMR spectra were registered on a Bruker BioSpin GmbH spectrometer (700 MHz) at 303K. Chemical shifts δ for characteristic protons are given in ppm with the use of HOD (4.750), $CHCl_3$ (δ 7.270) as the reference and coupling constants *J*, in Hz. The signals in ^{1}H NMR spectra were assigned using a technique of spin–spin decoupling (double resonance) and 2D-^{1}H,^{1}H-COSY experiments. The values of optical rotation were measured on a digital polarimeter Perkin Elmer 341 at 25°C. Mass spectra were registered on a MALDI-TOF Vision-2000 spectrometer using dihydroxybenzoic acid as a matrix.

1: ^{1}H-NMR (700 MHz, D_2O): 1.924–2.002 (m, 2H, CH_2 sp); 2.060, 2.064 (2s, 2×3H, NCOCH_3); 3.102 (m ≈ t, 2H, NCH_2 sp, *J* 6.8); 3.592–3.644 (m, 1H, H-5a); 3.655 (dd, 1H, H-2b, $J_{1,2}$ 7.9, $J_{2,3}$ 9.9); 3.702 (br. dd, 1H, H-5b, $J_{5,6'}$ 3.8, $J_{5,6''}$ 8.2, $J_{4,5} \leq 1$); 3.713–3.815 (m, 9H); 3.846 (dd, 1H, H-6'a, $J_{6',6''}$ 12.3, $J_{5,6'}$ 5.3); 3.984–4.062 (m, 4H, OC*H* sp, H-6''a, H-4b, H-3c); 4.123 (dd ≈ d, 1H, H-4c, *J* 2.9); 4.206 (br. t, 1H, H-5c, *J* 6.3); 4.248 (dd, 1H, H-2c, $J_{1,2}$ 3.6, $J_{2,3}$ 11.0); 4.542 (2d ≈ t, 2H, H-1a, H-1b, *J* 7.4); 5.100 (d, 1H, H-1c, $J_{1,2}$ 3.5). R_f 0.55 (MeOH–1M aq. Py·AcOH, 5:1). MS, *m/z* calculated for $[C_{25}H_{45}N_3O_{16}]H^+$: 644.28; found 644. $[\alpha]_{546\ nm}$ +128 (c 0.3; MeCN-H_2O, 1:1).

1β: ^{1}H-NMR (700 MHz, D_2O): 1.938–1.991 (m, 2H, CH_2 sp); 2.055, 2.062 (2s, 2×3H, NCOCH_3); 3.100 (m ≈ t, 2H, NCH_2 sp, *J* 6.9); 3.610 (dd, 1H, H-2b, $J_{1,2}$ 7.9, $J_{2,3}$ 9.9); 3.603–3.636 (m, 1H, H-5a); 3.682 (br. dd, 1H, H-5b, $J_{5,6'}$ 4.9, $J_{5,6''}$ 7.8, $J_{4,5} \leq 1$); 3.693–3.826 (m, 11H); 3.842 (dd, 1H, H-6'a, $J_{6',6''}$ 12.1, $J_{5,6'}$ 5.2); 3.934–3.972 (m, 2H, H-4b, H-2c); 4.012 (dd, 1H, H-6''a, $J_{6',6''}$ 12.2, $J_{5,6''}$ 2.0); 4.023–4.057 (m, 1H, OC*H* sp); 4.175 (dd ≈ d, 1H, H-4c, *J* 2.9); 4.478 (d, 1H, H-1b, $J_{1,2}$ 7.9); 4.531 (d, 1H, H-1a, $J_{1,2}$ 8.1); 4.638 (d, 1H, H-1c, $J_{1,2}$ 8.4). R_f 0.48

(MeOH–1M aq. Py·AcOH, 5:1). MS, *m/z* calculated for $[C_{25}H_{45}N_3O_{16}]H^+$: 644.28; found 644. $[\alpha]_{546\ nm}$ +6 (c 0.3; MeCN-H_2O, 1:1).

2: ^{1}H-NMR (700 MHz, D_2O): 1.926–2.006 (m, 2H, CH_2 sp); 2.066, 2.082 (2s, 2×3H, NCOCH_3); 3.104 (m ≈ t, 2H, NCH_2 sp, *J* 6.8); 3.607 (dd, 1H, H-2b, $J_{1,2}$ 8.0, $J_{2,3}$ 10.1); 3.601–3.636 (m, 1H, H-5a); 3.688–3.806 (m, 10H); 3.875 (dd, 1H, H-6'a, $J_{6',6''}$ 12.3, $J_{5,6'}$ 5.2); 3.981 (dd, 1H, H-3c, $J_{3,4}$ 2.8, $J_{2,3}$ 11.2); 3.997–4.076 (m, 4H, OC*H* sp, H-6"a, H-4b, H-4c); 4.210 (dd, 1H, H-2c, $J_{1,2}$ 3.5, $J_{2,3}$ 11.2); 4.405 (br. t, 1H, H-5c, *J* 6.3); 4.542 (d, 1H, H-1b, $J_{1,2}$ 8.1); 4.546 (d, 1H, H-1a, $J_{1,2}$ 7.6); 4.915 (d, 1H, H-1c, $J_{1,2}$ 3.4). R_f 0.54 (MeOH–1M aq. Py·AcOH, 4:1). MS, *m/z* calculated for $[C_{25}H_{45}N_3O_{16}]H^+$: 644.28; found 644. $[\alpha]_{546\ nm}$ +98 (c 0.3; MeCN-H_2O, 1:1).

3: ^{1}H-NMR (700 MHz, D_2O): 1.215 (d, 3H, H-6d, $J_{5,6}$ 6.6); 1.911–2.005 (m, 2H, CH_2 sp); 2.053 (s, 2×3H, NCOCH_3); 3.092 (m ≈ t, 2H, NCH_2 sp, *J* 6.9); 3.550–3.603 (m, 2H, H-2b, H-5b); 3.623 (ddd, 1H, H-5a, $J_{5,6'}$ 4.7, $J_{5,6''}$ 2.2, $J_{4,5}$ 9.7); 3.688–3.807 (m, 8H); 3.850–3.982 (m, 5H); 3.986–4.061 (m, 4H, OC*H* sp, H-6"a, H-4b, H-3c); 4.084 (dd ≈ d, 1H, H-4c, *J* 3.1); 4.229 (br. t, 1H, H-5c, *J* 6.4); 4.255 (dd, 1H, H-2c, $J_{1,2}$ 3.7, $J_{2,3}$ 11.1); 4.516 (d, 1H, H-1b, $J_{1,2}$ 7.8); 4.539 (d, 1H, H-1a, $J_{1,2}$ 8.4); 4.823 (br. q, 1H, H-5d, *J* 6.7); 5.079 (d, 1H, H-1c, $J_{1,2}$ 3.7); 5.147 (d, 1H, H-1d, $J_{1,2}$ 4.0). R_f 0.46 (MeOH–1M aq. Py·AcOH, 5:1). MS, *m/z* calculated for $[C_{31}H_{55}N_3O_{20}]H^+$: 790.34; found 790. $[\alpha]_{546\ nm}$ +42 (c 0.2; MeCN-H_2O, 1:1).

4: ^{1}H-NMR (700 MHz, D_2O): 1.198 (d, 3H, H-6d, $J_{5,6}$ 6.6); 1.919–2.004 (m, 2H, CH_2 sp); 2.057 (s, 3H, $NCOCH_3$); 3.097 (m ≈ t, 2H, NCH_2 sp, *J* 6.9); 3.581–3.647 (m, 3H); 3.694–3.810 (m, 8H); 3.844–3.994 (m, 7H); 4.001–4.057 (m, 3H, H-4b, OC*H* sp, H-6"a); 4.172 (dd ≈ d, 1H, H-4c, *J* 2.8); 4.208 (br. t, 1H, H-5c, *J* 6.3); 4.538 (d, 1H, H-1b, $J_{1,2}$ 7.8); 4.543 (d, 1H, H-1a, $J_{1,2}$ 8.4); 4.830 (br. q, 1H, H-5d, *J* 6.6); 5.144, 5.160 (2d, 2×1H, H-1c, H-1d, *J* 3.9). R_f 0.42 (MeOH–1M aq. Py·AcOH, 5:1). MS, *m/z* calculated for $[C_{29}H_{52}N_2O_{20}]H^+$: 749.31; found 749. $[\alpha]_{546\ nm}$ +11 (c 0.3; MeCN-H_2O, 1:1).

5: ^{1}H-NMR (700 MHz, D_2O): 1.292 (d, 3H, H-6d, $J_{5,6}$ 6.6); 1.316 (d, 3H, H-6e, $J_{5,6}$ 6.7); 1.918–2.009 (m, 2H, CH_2 sp); 2.053, 2.061 (2s, 2×3H, NCOCH_3); 3.097 (m ≈ t, 2H, NCH_2 sp, *J* 7.0); 3.471 (ddd, 1H, H-5a, $J_{5,6'}$ 5.8, $J_{5,6''}$ 2.1, $J_{4,5}$ 10.0); 3.581 (br. dd, 1H, H-5b, $J_{5,6'}$ 4.5, $J_{5,6''}$ 7.8, $J_{4,5} \leq 1$); 3.681–3.977 (m, 18H); 4.013 (dd ≈ d, 1H, H-4b, *J* 2.3); 4.017–4.047 (m, 1H, OC*H* sp); 4.063 (dd, 1H, H-6"a, $J_{6',6''}$ 11.9, $J_{5,6''}$ 2.0); 4.214 (dd ≈ d, 1H, H-4c, *J* 3.0); 4.258 (dd, 1H, H-2c, $J_{1,2}$ 3.6, $J_{2,3}$ 11.1); 4.266 (br. t, 1H, H-5c, *J* 6.2); 4.350 (br. q, 1H, H-5e, *J* 6.7); 4.522 (d,

1H, H-1a, $J_{1,2}$ 8.4); 4.576 (d, 1H, H-1b, $J_{1,2}$ 7.7); 4.877 (br. q, 1H, H-5d, *J* 6.6); 5.143 (d, 1H, H-1d, $J_{1,2}$ 4.0); 5.219 (d, 1H, H-1c, $J_{1,2}$ 3.7); 5.322 (d, 1H, H-1e, $J_{1,2}$ 4.2). R_f 0.44 (MeOH–1M aq. Py·AcOH, 5:1). MS, *m/z* calculated for $[C_{37}H_{65}N_3O_{24}]H^+$: 936.40; found 936. $[\alpha]_{546\ nm}$ -44 (c 0.3; MeCN-H_2O, 1:1).

5β: ^{1}H-NMR (700 MHz, D_2O): 1.231 (d, 3H, H-6d, $J_{5,6}$ 6.7); 1.282 (d, 3H, H-6e, $J_{5,6}$ 6.7); 1.911–2.004 (m, 2H, C*H*$_2$ sp); 2.052, 2.094 (2s, 2×3H, NCOC*H*$_3$); 3.088 (m ≈ t, 2H, NC*H*$_2$ sp, *J* 7.0); 3.445 (ddd, 1H, H-5a, $J_{5,6'}$ 5.7, $J_{5,6''}$ 2.1, $J_{4,5}$ 10.0); 3.640 (br. dd, 1H, H-5b, $J_{5,6'}$ 4.4, $J_{5,6''}$ 7.9, $J_{4,5}$ ≤1); 3.658 (br. dd, 1H, H-5c, $J_{5,6'}$ 4.5, $J_{5,6''}$ 8.3, $J_{4,5}$ ≤ 1); 3.675–3.856 (m, 14H); 3.887–4.051 (m, 8H); 4.146 (dd ≈ d, 1H, H-4c, *J* 3.3); 4.291 (br. q, 1H, H-5e, *J* 6.7); 4.510 (d, 1H, H-1a, $J_{1,2}$ 8.5); 4.527 (d, 1H, H-1b, $J_{1,2}$ 7.8); 4.706 (d, 1H, H-1c, $J_{1,2}$ 8.3); 4.836 (br. q, 1H, H-5d, *J* 6.6); 5.058 (d, 1H, H-1e, $J_{1,2}$ 3.8); 5.106 (d, 1H, H-1d, $J_{1,2}$ 4.0). R_f 0.38 (MeOH–1M aq. Py·AcOH, 5:1). MS, *m/z* calculated for $[C_{37}H_{65}N_3O_{24}]H^+$: 936.40; found 936. $[\alpha]_{546\ nm}$ -104 (c 0.4; MeCN-H_2O, 1:1).

6: ^{1}H-NMR (500 MHz, D_2O): 1.245 (d, 3H, H-6d, $J_{5,6}$ 6.6); 1.285 (d, 3H, H-6e, $J_{5,6}$ 6.6); 1.903-1.979 (m, 2H, C*H*$_2$ sp); 2.038 (s, 3H, NCOC*H*$_3$); 3.073 (m ≈ t, 2H, NC*H*$_2$ sp, *J* 6.9); 3.420 – 3.476 (m, 1H, H-5a); 3.602 (br. dd, 1H, H-5b, $J_{5,6'}$ 5.0, $J_{5,6''}$ 6.8); 3.655–4.064 (m, 22H); 4.214 (br. t, 1H, H-5c, *J* 6.0); 4.255 (dd ≈ d, 1H, H-4c, *J* 2.2); 4.323 (br. q, 1H, H-5e, *J* 6.6); 4.495 (d, 1H, H-1a, $J_{1,2}$ 8.4); 4.572 (d, 1H, H-1b, $J_{1,2}$ 7.7); 4.871 (br. q, 1H, H-5d, *J* 6.7); 5.115 (d, 1H, H-1c, $J_{1,2}$ 3.8); 5.241 (d, 1H, H-1e, $J_{1,2}$ 3.0); 5.282 (d, 1H, H-1d, $J_{1,2}$ 4.1). R_f 0.39 (MeOH–1M aq. Py·AcOH, 5:1). MS, *m/z* calculated for $[C_{35}H_{62}N_2O_{24}]H^+$: 895.37; found 895. $[\alpha]_D$ -46 (c 0.25; MeCN-H_2O, 1:1).

11: ^{1}H-NMR (700 MHz, D_2O): 1.769–1.835 (m, 1H, C*H* sp); 1.848–1.914 (m, 1H, C*H* sp); 1.953, 1.959, 1.986, 2.079 (4s, 4×3H, COC*H*$_3$); 3.227–3.291 (m, 1H, NC*H* sp); 3.455–3.512 (m, 2H, H-5a, H-5b); 3.553–3.602 (m, 1H, OC*H* sp); 3.603–3.662 (m, 1H, NC*H* sp); 3.667–3.708 (m, 2H, H-6'a, H-6'b); 3.725 (dd, 1H, H-6"a, $J_{6',6''}$ 10.8, $J_{5,6''}$ 3.8); 3.768 (dd, 1H, H-6"b, $J_{6',6''}$ 9.8, $J_{5,6''}$ 5.8); 3.909–3.948 (m, 1H, OC*H* sp); 3.938 (dd ≈ t, 1H, H-4a, *J* 8.7); 4.055 (ddd, 1H, H-2a, $J_{1,2}$ 8.0, $J_{2,3}$ 9.7, $J_{2,NH}$ 9.0); 4.109 (dd ≈ d, 1H, H-4b, *J* 2.9); 4.366 (d, 1H, H-1a, $J_{1,2}$ 8.0); 4.426 (d, 1H, H-1b, $J_{1,2}$ 7.9); 4.492, 4.529, 4.558, 4.687 (4d, 4×1H, C*H*Ph, J_{gem}~12.0); 4.801 (dd, 1H, H-3b, $J_{3,4}$ 3.1, $J_{2,3}$ 10.2); 4.974 (dd, 1H, H-3a, $J_{3,4}$ 8.6, $J_{2,3}$ 9.7); 5.132 (dd, 1H, H-2b, $J_{1,2}$ 7.9, $J_{2,3}$ 10.2); 5.854 (d, 1H, N*H*Ac a, $J_{2,NH}$ 9.0); 7.289–7.395 (m, 2×5H, Ph); 7.459–7.514 (m, 1H,

N*H*COCF$_3$ sp). R_f 0.40 (EtOAc). MS, *m/z* calculated for [$C_{64}H_{75}N_2F_3O_{18}$]H^+: 1217.45; found 1217.

13: ^{1}H-NMR (700 MHz, D_2O): 1.094 (d, 3H, H-6d, $J_{5,6}$ 6.4); 1.690–1.744 (m, 2H, CH_2 sp); 1.734, 1.952, 2.069 (s, 3H, COCH_3); 3.273–3.373 (m, 2H, NCH_2 sp); 3.391–3.442 (m, 1H, H-5b); 3.446–3.493 (m, 1H, OC*H* sp); 3.501–3.582 (m, 4H, H-5a, H-4d, H-6'b, H-6"b); 3.607 (q, 1H, H-2a, *J* 7.0); 3.644 (dd, 1H, H-3b, $J_{3,4}$ 3.6, $J_{2,3}$ 10.0); 3.740 (dd, 1H, H-6'a, $J_{6',6''}$ 10.3, $J_{5,6'}$ 4.4); 3.793 (dd, 1H, H-6"a, $J_{6',6''}$ 10.3, $J_{5,6''}$ 4.0); 3.833–3.881 (m, 2H, OC*H* sp, H-3d); 3.929 (dd ≈ t, 1H, H-4a, *J* 6.8); 3.992 (dd ≈ t, 1H, H-3a, *J* 7.1); 4.114 (dd, 1H, H-2d, $J_{1,2}$ 3.7, $J_{2,3}$ 10.1); 4.234 (br. q, 1H, H-5d, $J_{5,6'}$ 6.3); 4.361, 4.442, 4.463, 4.582, 4.642, 4.6574.688 (2), 4.847, 4.950 (10d, 10×1H, C*H*Ph, J_{gem}~12.0); 4.489 (d, 1H, H-1b, $J_{1,2}$ 8.1); 4.768 (d, 1H, H-1a, $J_{1,2}$ 6.6); 4.821 (dd, 1H, H-2b, $J_{1,2}$ 8.0, $J_{2,3}$ 10.0); 5.084 (d, 1H, H-1d, $J_{1,2}$ 3.6); 5.324 (dd ≈ d, 1H, H-4b, *J* 3.6); 6.139 (d, 1H, N*H*Ac a, $J_{2,NH}$ 7.5); 7.212–7.365 (m, 5×5H, Ph); 7.390–7.444 (m, 1H, N*H*COCF$_3$ sp). R_f 0.30 (EtOAc–toluene, 3:1). MS, *m/z* calculated for [$C_{89}H_{101}N_2F_3O_{21}$]$H^+$: 1591.69; found 1592.

16: ^{1}H-NMR (700 MHz, $CDCl_3$): 1.759–1.834 (m, 1H, C*H* sp); 1.853–1.927 (m, 1H, C*H* sp); 1.972, 1.986, 1.996, 2.046, 2.053, 2.087, 2.106, 2.115, 2.130, 2.224 (10s, 10×3H, COCH_3); 3.222–3.276 (m, 1H, NC*H* sp); 3.544–3.583 (m, 1H, OC*H* sp); 3.591–3.661 (m, 2H, NC*H* sp, H-5a); 3.764 (dd ≈ t, 1H, H-4a, *J* 8.8); 3.787 (dd, 1H, H-3b, $J_{3,4}$ 3.7, $J_{2,3}$ 9.9); 3.836 (br. t, 1H, H-5b, *J* 7.3); 3.882–3.920 (m, 1H, OC*H* sp); 3.950 (dd, 1H, H-6'c, $J_{6',6''}$ 10.6, $J_{5,6'}$ 5.2); 4.009 (ddd, 1H, H-2a, $J_{1,2}$ 7.9, $J_{2,3}$ 10.0, $J_{2,NH}$ 9.0); 4.076–4.188 (m, 5H, H-6'a, H-6'b, H-6"b, H-5c, H-6"c); 4.415 (d, 1H, H-1a, $J_{1,2}$ 7.9); 4.443 (d, 1H, H-1b, $J_{1,2}$ 7.9); 4.529 (dd, 1H, H-6"a, $J_{6',6''}$ 12.0, $J_{5,6''}$ 2.5); 4.548 (ddd, 1H, H-2c, $J_{1,2}$ 3.4, $J_{2,3}$ 11.6, $J_{2,NH}$ 9.4); 4.893 (dd, 1H, H-3c, $J_{3,4}$ 3.1, $J_{2,3}$ 11.6); 5.021 (d, 1H, H-1c, $J_{1,2}$ 3.4); 5.039–5.075 (m, 2H, H-3a, H-2b); 5.339 (dd ≈ d, 1H, H-4b, *J* 2.9); 5.359 (dd, 1H, H-4c, $J_{3,4}$ 2.7, $J_{4,5}$ 0.9); 5.810 (d, 1H, N*H*Ac a, $J_{2,NH}$ 9.0); 6.184 (d, 1H, N*H*Ac c, $J_{2,NH}$ 9.4); 7.310–7.413 (m, 1H, N*H*COCF$_3$ sp). R_f 0.31 (EtOAc–iPrOH, 10:1). MS, *m/z* calculated for [$C_{43}H_{60}N_3F_3O_{25}$]H^+: 1076.35, found 1076.

16β: ^{1}H-NMR (700 MHz, $CDCl_3$): 1.766–1.832 (m, 1H, C*H* sp); 1.850–1.908 (m, 1H, C*H* sp); 1.923, 1.969, 1.982, 2.059, 2.071, 2.099 (2), 2.120, 2.136, 2.148 (10s, 10×3H, COCH_3); 3.230–3.289 (m, 1H, NC*H* sp); 3.521 (ddd, 1H, H-2c, $J_{1,2}$ 8.2, $J_{2,3}$ 11.2, $J_{2,NH}$ 7.8); 3.548–3.591 (m, 1H, OC*H* sp); 3.591–3.648 (m, 2H, NC*H* sp, H-5a); 3.743 (dd ≈ t, 1H, H-4a, *J* 8.6); 3.795 (br. t, 1H, H-5b, *J* 6.5); 3.852 (dd, 1H, H-3b, $J_{3,4}$ 3.6, $J_{2,3}$ 9.9); 3.873–3.923 (m, 2H, H-5c, OC*H*

sp); 4.002 (ddd, 1H, H-2a, $J_{1,2}$ 8.0, $J_{2,3}$ 9.5, $J_{2,NH}$ 8.9); 4.039 (dd, 1H, H-6'b, $J_{6',6''}$ 11.6, $J_{5,6'}$ 6.9); 4.087–4.144 (m, 3H, H-6'a, H-6"b, H-6'c); 4.160 (dd, 1H, H-6"c, $J_{6',6''}$ 11.2, $J_{5,6"}$ 6.0); 4.409, 4.417 (2d ≈ t, 2×1H, H-1a, H-1b, *J* 7.6); 4.519 (dd, 1H, H-6"a, $J_{6',6''}$ 11.8, $J_{5,6"}$ 2.5); 4.992 (d, 1H, H-1c, $J_{1,2}$ 8.2); 5.043 (dd, 1H, H-3a, $J_{3,4}$ 8.6, $J_{2,3}$ 9.5); 5.066 (dd, 1H, H-2b, $J_{1,2}$ 8.0, $J_{2,3}$ 9.8); 5.350 (dd ≈ d, 1H, H-4c, *J* 3.2); 5.372 (dd ≈ d, 1H, H-4b, *J* 3.4); 5.399 (d, 1H, N*H*Ac c, $J_{2,NH}$ 7.8); 5.449 (dd, 1H, H-3c, $J_{3,4}$ 3.4, $J_{2,3}$ 11.3); 5.856 (d, 1H, N*H*Ac a, $J_{2,NH}$ 8.9); 7.361–7.466 (m, 1H, N*H*COCF$_3$ sp). R_f 0.24 (EtOAc–iPrOH, 10:1). MS, *m/z* calculated for $[C_{43}H_{60}N_3F_3O_{25}]H^+$: 1076.35, found 1076.

17: ^{1}H-NMR (700 MHz, D_2O): 1.092 (d, 2×3H, H-6d, H-6e, $J_{5,6}$ 6.5); 1.723–1.780 (m, 2H, C*H*$_2$ sp); 1.769 (s, 3H, COC*H*$_3$); 3.312–3.434 (m, 5H, NC*H*$_2$ sp, H-2a, H-5b, H-2b); 3.465–3.532 (m, 4H, OC*H* sp, H-5a, H-6'b, H-6"b); 3.566 (dd, 1H, H-3b, $J_{3,4}$ 3.7, $J_{2,3}$ 9.7); 3.593 (dd ≈ d, 1H, H-4e, *J* 2.2); 3.608 (dd, 1H, H-6'a, $J_{6',6''}$ 11.3, $J_{5,6'}$ 3.0); 3.624 (dd ≈ d, 1H, H-4d, *J* 1.7); 3.805–3.859 (m, 2H, H-5e, H-6"a); 3.880 (dd, 1H, H-3d, $J_{3,4}$ 2.6, $J_{2,3}$ 10.1); 3.891–3.936 (m, 3H, OC*H* sp, H-4a, H-3e); 3.956 (dd ≈ t, 1H, H-3a, *J* 8.3); 4.076 (dd, 1H, H-2e, $J_{1,2}$ 3.6, $J_{2,3}$ 10.1); 4.126 (dd, 1H, H-2d, $J_{1,2}$ 3.7, $J_{2,3}$ 10.1); 4.352–4.388 (m, 3H, H-1b, 2 C*H*Ph); 4.427 (br. q, 1H, H-5d, $J_{5,6'}$ 6.4); 4.617–4.657 (m, 5×1H, C*H*Ph); 4.451, 4.672, 4.702, 4.742, 4.776, 4.871, 4.899, 4.965, 4.976 (9d, 9×1H, C*H*Ph, J_{gem}~12.0); 4.862 (d, 1H, H-1a, $J_{1,2}$ 7.2); 4.946 (d, 1H, H-1e, $J_{1,2}$ 3.5); 5.019 (d, 1H, H-1d, $J_{1,2}$ 3.5); 5.342 (dd ≈ d, 1H, H-4b, *J* 3.8); 6.119 (d, 1H, N*H*Ac a, $J_{2,NH}$ 6.7); 7.229–7.456 (m, 8×5H, Ph); 7.526–7.589 (m, 1H, N*H*COCF$_3$ sp). R_f 0.45 (EtOAc–toluene, 1:1). MS, *m/z* calculated for $[C_{39}H_{49}N_2F_3O_{15}]H^+$: 843.31; found 843.

19: ^{1}H-NMR (700 MHz, $CDCl_3$): 1.757–1.829 (m, 1H, C*H* sp); 1.852–1.933 (m, 1H, C*H* sp); 1.974, 2.008, 2.022, 2.041, 2.061, 2.074, 2.106, 2.110, 2.111, 2.149 (10s, 10×3H, COC*H*$_3$); 3.233–3.288 (m, 1H, NC*H* sp); 3.540–3.591 (m, 1H, OC*H* sp); 3.599–3.672 (m, 2H, NC*H* sp, H-5a); 3.763–3.814 (m, 2H, H-4a, H-5b); 3.882–3.926 (m, 1H, OC*H* sp); 3.942–4.005 (m, 2H, H-6'b, H-2a); 4.059 (dd, 1H, H-6'c, $J_{6',6''}$ 11.0, $J_{5,6'}$ 5.7); 4.095 (dd ≈ d, 1H, H-4b, *J* 2.3); 4.120 (dd, 1H, H-6'a, $J_{6',6''}$ 11.9, $J_{5,6'}$ 5.2); 4.143 (dd, 1H, H-6"c, $J_{6',6''}$ 11.0, $J_{5,6"}$ 8.4); 4.420 (dd, 1H, H-6"b, $J_{6',6''}$ 11.2, $J_{5,6"}$ 6.4); 4.445 (d, 1H, H-1a, $J_{1,2}$ 8.0); 4.469 (br. t, 1H, H-5c, *J* 7.3); 4.549 (dd, 1H, H-6"a, $J_{6',6''}$ 11.9, $J_{5,6"}$ 2.4); 4.574–4.622 (m, 2H, H-2c, H-1b, $J_{1,2}$ 7.7); 4.923 (dd, 1H, H-3b, $J_{3,4}$ 2.8, $J_{2,3}$ 10.6); 5.020 (d, 1H, H-1c, $J_{1,2}$ 3.5); 5.119 (dd ≈ t, 1H, H-3a, *J* 8.8); 5.134 (dd, 1H, H-2b, $J_{1,2}$ 7.7, $J_{2,3}$ 10.5); 5.237 (dd, 1H, H-3c, $J_{3,4}$ 3.2, $J_{2,3}$ 11.7); 5.491 (dd ≈ d, 1H, H-4c, *J* 2.0); 5.829 (d, 1H, N*H*Ac a, $J_{2,NH}$ 9.0); 6.018 (d, 1H, N*H*Ac c, $J_{2,NH}$ 8.7); 7.288–7.364 (m, 1H, N*H*COCF$_3$

sp). R_f 0.30 ($CHCl_3$–MeOH, 8:1). MS, *m/z* calculated for $[C_{43}H_{60}N_3F_3O_{25}]H^+$: 1076.35, found 1076.

21: ^{1}H-NMR (700 MHz, $CDCl_3$): 1.216 (d, 3H, H-6d, $J_{5,6}$ 6.5); 1.730–1.799 (m, 1H, C*H* sp); 1.824–1.895 (m, 1H, C*H* sp); 1.985 (2), 1.996, 2.014, 2.032, 2.073, 2.099, 2.119, 2.128, 2.132, 2.160, 2.273 (12s, 12×3H, COC*H*$_3$); 3.210–3.271 (m, 1H, NC*H* sp); 3.486–3.525 (m, 1H, OC*H* sp); 3.528–3.558 (m, 1H, H-5a); 3.570–3.631 (m, 1H, NC*H* sp); 3.788 (dd, 1H, H-3b, $J_{3,4}$ 3.6, $J_{2,3}$ 9.9); 3.807–3.899 (m, 4H, H-2a, H-4a, H-5b, OC*H* sp); 3.918 (dd, 1H, H-6'c, $J_{6',6''}$ 10.8, $J_{5,6'}$ 5.3); 3.975 (dd ≈ t, 1H, H-3a, *J* 8.5); 4.082 (br. t, 1H, H-5c, *J* 6.6); 4.131–4.183 (m, 2H, H-6'a, H-6"c); 4.317 (dd, 1H, H-6'b, $J_{6',6''}$ 11.5, $J_{5,6'}$ 7.8); 4.434 (d, 1H, H-1b, $J_{1,2}$ 8.2); 4.501 (dd, 1H, H-6"b, $J_{6',6''}$ 11.5, $J_{5,6''}$ 6.3); 4.522–4.581 (m, 2H, H-1a, H-2c); 4.635 (dd, 1H, H-6"a, $J_{6',6''}$ 12.0, $J_{5,6''}$ 2.2); 4.834 (br. q, 1H, H-5d, *J* 6.4); 4.896 (dd, 1H, H-3c, $J_{3,4}$ 3.0, $J_{2,3}$ 11.6); 4.993–5.052 (m, 3H, H-1c, H-2b, H-2d);5.230 (dd, 1H, H-3d, $J_{3,4}$ 3.3, $J_{2,3}$ 10.9); 5.357 (dd ≈ d, 1H, H-4c, *J* 1.2); 5.371 (dd ≈ d, 1H, H-4d, *J* 3.0); 5.391 (dd ≈ d, 1H, H-4b, *J* 3.5); 5.449 (d, 1H, H-1d, $J_{1,2}$ 3.9); 5.814 (d, 1H, N*H*Ac a, $J_{2,NH}$ 8.9); 6.297 (d, 1H, N*H*Ac c, $J_{2,NH}$ 9.4); 7.302–7.374 (m, 1H, N*H*COCF_3 sp). R_f 0.40 ($CHCl_3$–MeOH, 8:1). MS, *m/z* calculated for $[C_{53}H_{74}N_3F_3O_{31}]H^+$: 1306.42; found 1307.

23: ^{1}H-NMR (700 MHz, $CDCl_3$): 1.231 (d, 3H, H-6d, $J_{5,6}$ 6.6); 1.747–1.901 (m, 2H, CH_2 sp); 1.949, 1.982, 2.008, 2.045, 2.064, 2.092, 2.117 (2), 2.140, 2.144, 2.157, 2.192 (12s, 12×3H, COC*H*$_3$); 3.225–3.290 (m, 1H, NC*H* sp); 3.492–3.546 (m, 1H, OC*H* sp); 3.561–3.627 (m, 2H, H-5a, NC*H* sp); 3.808–3.839 (m, 2H, H-4a, H-5b); 3.843–3.882 (m, 1H, OC*H* sp); 3.888 (dd, 1H, H-3b, $J_{3,4}$ 3.3, $J_{2,3}$ 10.4); 3.903–3.947 (m, 1H, H-2 a); 3.969 (dd ≈ t, 1H, H-3a, *J* 8.1); 4.063 (dd, 1H, H-6'c, $J_{6',6''}$ 11.2, $J_{5,6'}$ 6.1); 4.177 (dd, 1H, H-6"c, $J_{6',6''}$ 11.2, $J_{5,6}$ 7.0); 4.214 (dd, 1H, H-6'a, $J_{6',6''}$ 12.0, $J_{5,6'}$ 4.8); 4.233–4.294 (m, 2H, H-6'b, H-5c); 4.432 (d, 1H, H-1b, $J_{1,2}$ 8.3); 4.452 (dd, 1H, H-6"b, $J_{6',6''}$ 12.0, $J_{5,6''}$ 6.9); 4.545 (d, 1H, H-1a, $J_{1,2}$ 6.7); 4.616 (dd, 1H, H-6"a, $J_{6',6''}$ 11.9, $J_{5,6''}$ 2.9); 4.783 (br. q, 1H, H-5d, *J* 6.4); 5.026 (dd, 1H, H-2d, $J_{1,2}$ 3.9, $J_{2,3}$ 10.9); 5.107–5.165 (m, 2H, H-2b, H-3c); 5.238 (dd, 1H, H-3d, $J_{3,4}$ 3.3, $J_{2,3}$ 10.9); 5.262 (d, 1H, H-1c, $J_{1,2}$ 3.4); 5.294 (dd, 1H, H-2c, $J_{1,2}$ 3.4, $J_{2,3}$ 11.1); 5.357 (dd ≈ d, 1H, H-4d, *J* 3.0); 5.405 (dd ≈ d, 1H, H-4b, *J* 2.9); 5.426–5.473 (m, 2H, H-1d, H-4c); 5.841 (d, 1H, N*H*Ac a, $J_{2,NH}$ 8.8); 7.376–7.402 (m, 1H, N*H*COCF_3 sp). R_f 0.38 (EtOAc). MS, *m/z* calculated for $[C_{53}H_{73}N_2F_3O_{32}]H^+$: 1307.41; found 1307.

25: ^{1}H-NMR (700 MHz, $CDCl_3$): 1.136 (d, 3H, H-6d, $J_{5,6}$ 6.5); 1.175 (d, 3H, H-6e, $J_{5,6}$ 6.5); 1.745–1.814 (m, 1H, C*H* sp); 1.856–1.919 (m, 1H, C*H* sp); 1.932, 1.964, 1.980, 1.984 (2), 2.070, 2.082, 2.106, 2.132, 2.143, 2.147, 2.153, 2.159, 2.210 (14s, 14×3H, COCH_3); 3.250–3.312 (m, 1H, NC*H* sp); 3.560–3.696 (m, 5H, NC*H* and OC*H* sp, H-2a, H-5a, H-2b); 3.793 (br. t, 1H, H-5b, *J* 7.1); 3.882 (dd, 1H, H-3b, $J_{3,4}$ 3.6, $J_{2,3}$ 9.7); 3.892–3.923 (m, 1H, OC*H* sp); 3.945 (dd ≈ t, 1H, H-4a, *J* 9.2); 4.033–4.092 (m, 2H, H-3a, H-6'c); 4.124 (dd, 1H, H-6"c, $J_{6',6''}$ 10.6, $J_{5,6"}$ 4.6); 4.242–4.281 (m, 2H, H-5c, H-6'b, $J_{6',6''}$ 11.5, $J_{5,6'}$ 7.7); 4.329 (dd, 1H, H-6'a, $J_{6',6''}$ 11.25, $J_{5,6}$ 3.4); 4.445–4.518 (m, 4H, H-5e, H-2c, H-6"b, H-1b, $J_{1,2}$ 7.9); 4.611–4.681 (m, 2H, H-6"a, H-1a, $J_{1,2}$ 8.1); 4.890 (br. q, 1H, H-5d, *J* 6.5); 4.967–5.032 (m, 2H, H-3c, H-2d); 5.075 (dd, 1H, H-3e, $J_{3,4}$ 3.3, $J_{2,3}$ 11.1); 5.210 (dd, 1H, H-3d, $J_{3,4}$ 3.3, $J_{2,3}$ 11.0); 5.268 (d, 1H, H-1c, $J_{1,2}$ 3.5); 5.300 (dd ≈ d, 1H, H-4e, *J* 2.6); 5.353 (dd ≈ d, 1H, H-4d, *J* 2.9); 5.392 (dd, 1H, H-2e, $J_{1,2}$ 3.7, $J_{2,3}$ 11.0); 5.452 (2d, 2×1H, H-1e, H-4b, *J* 3.8); 5.493 (2d, 2×1H, H-1d, H-4c, *J* 3.7); 5.673 (d, 1H, N*H*Ac a, $J_{2,NH}$ 8.6); 5.938–6.258 (m, 1H, N*H*Ac c); 7.234–7.266 (m, 1H, N*H*COCF_3 sp). R_f 0.51 (EtOAc–iPrOH, 10:1). MS, *m/z* calculated for $[C_{63}H_{88}N_3F_3O_{37}]H^+$: 1536.50; found 1536.

25β: ^{1}H-NMR (700 MHz, $CDCl_3$): 1.150 (d, 3H, H-6d, $J_{5,6}$ 6.7); 1.166 (d, 3H, H-6e, $J_{5,6}$ 6.5); 1.753–1.822 (m, 1H, C*H* sp); 1.848–1.914 (m, 1H, C*H* sp); 1.954, 1.971, 1.990, 2.002, 2.007, 2.070, 2.092, 2.104, 2.138 (3), 2.154, 2.162, 2.184 (14s, 14×3H, COCH_3); 3.255–3.323 (m, 1H, NC*H* sp); 3.543–3.630 (m, 3H, NC*H* and OC*H* sp, H-5a); 3.639–3.689 (m, 1H, H-2a); 3.688 (dd, 1H, H-3b, $J_{3,4}$ 3.8, $J_{2,3}$ 9.1); 3.732 (dd, 1H, H-2b, $J_{1,2}$ 7.9, $J_{2,3}$ 9.0); 3.773 (br. t, 1H, H-5b, *J* 6.9); 3.793 (br. t, 1H, H-5c, *J* 6.7); 3.868 (dd, 1H, H-4a, $J_{3,4}$ 8.9, $J_{4,5}$ 9.4); 3.897–3.936 (m, 1H, OC*H* sp); 4.013 (dd ≈ t, 1H, H-3a, *J* 9.2); 4.119 (dd, 1H, H-6'c, $J_{6',6''}$ 11.3, $J_{5,6'}$ 6.7); 4.170 (dd, 1H, H-6"c, $J_{6',6''}$ 11.3, $J_{5,6"}$ 6.2); 4.203 (ddd, 1H, H-2c, $J_{1,2}$ 8.4, $J_{2,3}$ 10.9, $J_{2,NH}$ 9.8); 4.236 (dd, 1H, H-6'b, $J_{6',6''}$ 11.9, $J_{5,6'}$ 6.0); 4.323 (dd, 1H, H-6"b, $J_{6',6''}$ 11.9, $J_{5,6"}$ 7.4); 4.331 (d, 1H, H-1b, $J_{1,2}$ 7.8); 4.354 (br. q, 1H, H-5e, *J* 6.6); 4.396 (d, 1H, H-1c, $J_{1,2}$ 8.4); 4.392 (dd, 1H, H-6'a, $J_{6',6''}$ 12.3, $J_{5,6'}$ 4.1); 4.537 (dd, 1H, H-6"a, $J_{6',6''}$ 12.3, $J_{5,6"}$ 1.8); 4.656 (d, 1H, H-1a, $J_{1,2}$ 8.1); 4.850–4.930 (m, 3H, H-5d, H-3c, H-2e); 4.998 (dd, 1H, H-2d, $J_{1,2}$ 4.0, $J_{2,3}$ 11.0); 5.191 (dd, 1H, H-3e, $J_{3,4}$ 3.2, $J_{2,3}$ 10.9); 5.221 (dd, 1H, H-3d, $J_{3,4}$ 3.3, $J_{2,3}$ 11.0); 5.276 (dd ≈ d, 1H, H-4d, *J* 2.5); 5.303 (br. s, 2H, H-4c, H-4e); 5.431 (d, 1H, H-1d, $J_{1,2}$ 4.0); 5.461 (dd ≈ d, 1H, H-4b, *J* 3.8); 5.665 (d, 1H, H-1e, $J_{1,2}$ 3.8); 5.684 (d, 1H, N*H*Ac a, $J_{2,NH}$ 8.6); 6.213 (d, 1H, N*H*Ac c, $J_{2,NH}$ 9.8); 7.303–7.366 (m, 1H, N*H*COCF_3 sp). R_f 0.55 (EtOAc–iPrOH, 10:1). MS, *m/z* calculated for $[C_{63}H_{88}N_3F_3O_{37}]H^+$: 1536.50; found 1536.

27: ^{1}H-NMR (500 MHz, $CDCl_3$): 1.083 (d, 3H, H-6e, $J_{5,6}$ 6.6); 1.159 (d, 3H, H-6d, $J_{5,6}$, 6.4); 1.716–1.915 (m, 2H, CH_2 sp); 1.900, 1.958, 1.967, 1.978, 2.001, 2.071 (2), 2.090, 2.133, 2.138 (2), 2.155, 2.161, 2.179 (14s, 14×3H, COCH_3); 3.198–3.295 (m, 1H, NC*H* sp); 3.502–3.655 (m, 3H, H-2b, OC*H* and NC*H* sp); 3.723–3.788 (m, 2H, H-5a, H-5b); 3.830 (ddd ≈ q, 1H, H-2a, *J* 8.5); 3.848–3.905 (m, 1H, NC*H* sp); 3.912 (dd, 1H, H-3b, $J_{3,4}$ 3.1, $J_{2,3}$ 10.1); 3.981 (dd ≈ t, 1H, H-4a, *J* 8.8); 4.039 (dd ≈ t, 1H, H-3a, *J* 8.5); 4.148 (dd, 1H, H-6'c, $J_{6',6''}$ 11.1, $J_{5,6'}$ 6.9); 4.231 (dd, 1H, H-6'e, $J_{6',6''}$ 11.6, $J_{5,6'}$ 7.5); 4.272 (dd, 1H, H-6"c, $J_{6',6"}$ 11.1, $J_{5,6"}$ 6,9); 4.385–4.594 (m, 7H, H-1a, H-6'a, H-6"a, H-1b, H- 6"b, H-5e, H-5c); 4.841 (br. q, 1H, H-5d, *J* 6.4); 5.010–5.056 (m, 2H, H-2d, H-3e); 5.211 (dd, 1H, H-3d, $J_{3,4}$ 3.2, $J_{2,3}$ 11.0); 5.277 (dd ≈ d, 1H, H-4e, *J* 2.8); 5.314 (dd, 1H, H-2e, $J_{1,2}$ 3.8, $J_{2,3}$ 11.0); 5.321–5.423 (m, 4H, H-1c, H-2c, H-1e, H-4d); 5.430–5.507 (m, 3H, H-1d, H-4b, H-3c); 5.614 (dd ≈ d, 1H, H-4c, *J* 2.4); 5.690 (d, 1H, N*H*Ac a, $J_{2,NH}$ 9.0); 7.289–7.355 (m, 1H, N*H*COCF_3 sp). R_f 0.35 (EtOAc). MS, *m/z* calculated for $[C_{63}H_{87}N_2F_3O_{38}]H^+$: 1537.49; found 1537.