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Block synthesis of blood group tetrasaccharides B (types 1, 3 and 4)

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Characteristics for compounds **4**, **9**, **10-α**, **10-β**, **12**, **15** *and* **16**.

4: ^{1}H NMR (selected data, 500 MHz, $CDCl_3$) δ: 5.97 (d, 1H, H-1aβ, $J_{1,2}$ 6.5 Hz), 6.60 (d, 3H, H-1aα, $J_{1,2}$ 3.2 Hz), 8.69 (s, 1H, NHβ), 8.80 (s, 3H, NHα).

9: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.12 (d, 3H, H-6c, $J_{1,2}$ 6.6 Hz), 1.37, 1.48 (2s, 2×9H, 2×(CH_3)$_3$C), 1.91, 1.98, 2.00, 2.04, 2.07, 2.08, 2.20 (7s, 5×3H, 2×6H, 9 Ac), 3.33 – 3.45 (m, 2H, OCH_2CH_2), 3.67 (dd, 1H, H-2a, $J_{1,2}$ 7.5 Hz, $J_{2,3}$ 9.9 Hz), 3.78 (dd, 1H, H-5a, $J_{5,6}$ 6.7 Hz, $J_{5,6'}$ 6.9 Hz), 3.91 (dd, 1H, H-3a, $J_{2,3}$ 10.1 Hz, $J_{3,4}$ 3.0 Hz), 3.97 (dd, 1H, H-6b, $J_{5,6}$ 6.4 Hz, $J_{6,6'}$ 11.3 Hz), 4.05 – 4.15 (m, 3H, OCHH, H-6a, H-6'a), 4.30 (dd, 1H, H-6'b, $J_{5,6}$ 6.7 Hz, $J_{6,6'}$ 11.1 Hz), 4.38 – 4.44 (m, 2H, H-5c, OCHH), 4.46 (d, 1H, H-1a, $J_{1,2}$ 8.6 Hz), 4.51 (dd, 1H, H-5b, $J_{5,6}$ 6.7 Hz, $J_{5,6'}$ 6.8 Hz), 5.13 (dd, 1H, H-3c, $J_{2,3}$ 11.1 Hz, $J_{3,4}$ 3.2), 5.18 (dd, 1H, H-2c, $J_{1,2}$ 3.6 Hz, $J_{2,3}$ 11.1 Hz), 5.23 (dd, 1H, H-4c, $J_{3,4}$ 3.2, $J_{4,5}$<1), 5.32 – 5.38 (m, 2H, H-1b, H-3b), 5.40 (dd, 1H, H-4a, $J_{3,4}$ 2.4 Hz, $J_{4,5}$<1), 5.45 (dd, 1H, H-2b, $J_{1,2}$ 3.2 Hz, $J_{2,3}$ 10.7 Hz), 5.52 (d, 1H, H-1c, $J_{1,2}$ 3.6 Hz), 5.62 (dd, 1H, H-4b, $J_{3,4}$ 2.4 Hz, $J_{4,5}$<1 Hz), 7.27 – 7.28 (m, 1H, ArH), 7.54 – 7.56 (m, 1H, ArH). MS, *m/z:* 1124 (M^++H), 1146 (M^++Na), 1163 (M^++K). $[\alpha]_D$ +17.2 (*c* 1, $CHCl_3$).

10-α: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.10 (d, 3H, H-6c, $J_{5,6}$ 6.5 Hz), 1.91, 2.00 (6H), 2.03, 2.07, 2.08, 2.10, 2.15, 2.17, 2.20 (9 s, 8×3H, 1×6H, 10Ac), 3.95 (dd, 1H, H-3a, $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 3.0 Hz,), 3.98 (dd, 1H, H-2a, $J_{1,2}$ 3.2 Hz, $J_{2,3}$ 10.5 Hz), 4.02 – 4.12 (m, 2H, H-6a, H-6b), 4.20 (dd, 1H, H-5a, $J_{5,6}$ 7.0 Hz, $J_{5,6'}$ 6,8 Hz), 4.31 – 4.43 (m, 3H, H-5c, H-6'a, H-6'b), 4.48 (dd, 1H, H-5b, $J_{5,6}$ 7.0 Hz, $J_{5,6'}$ 7.3 Hz), 5.12 (dd, 1H, H-3c, $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 3.2 Hz), 5.15 – 5.20 (m, 2H, H-2c, H-4c), 5.26 (d, 1H, H-1c, $J_{1,2}$ 3.0 Hz), 5.34 (dd, 1H, H-2b, $J_{1,2}$ 3.4 Hz, $J_{2,3}$ 10.9 Hz), 5.37 (d, 1H, H-1b, $J_{1,2}$ 3.4 Hz), 5.40 (dd, 1H, H-3b, $J_{2,3}$ 10.9 Hz, $J_{3,4}$ 3.2 Hz), 5.46 (dd ≈ br.s, 1H, H-4a,), 5.60 (dd, 1H, H-4b, $J_{3,4}$ 3.2 Hz, $J_{4,5}$<1 Hz), 6.38 (d, 1H, H-1a, $J_{1,2}$ 3.18 Hz).

10-β: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.07 (d, 3H, H-6c, $J_{5,6}$ 6.6 Hz), 1.90, 1.98, 2.01, 2.04, 2.08, 2.10 (6H), 2.15, 2.16, 2.17 (9s, 8×3H, 1×6H, 10Ac), 3.78 (dd, 1H, H-2a, $J_{1,2}$ 8.0 Hz, $J_{2,3}$ 10.1 Hz), 3.96 (dd, 1H, H-5a, $J_{5,6}$ 7.0 Hz, $J_{5,6'}$ 6,8), 4.02 (dd, 1H, H-3a, $J_{2,3}$ 10.1 Hz, $J_{3,4}$ 2.8 Hz), 4.08 (dd, 1H, H-6b, $J_{5,6}$ 6.4 Hz, $J_{6,6'}$ 11.1 Hz), 4.12 – 4.19 (m, 2H, H-6a, H-6'a), 4.23 – 4.30 (m, 2H, H-5c, H-6'b), 4.49 (dd, 1H, H-5b, $J_{5,6}$=$J_{5,6'}$ 6.4 Hz,), 5.09 (dd, 1H, H-3c, $J_{2,3}$ 11.3 Hz, $J_{3,4}$ 3.6 Hz), 5.16 (dd, 1H, H-2c, $J_{1,2}$ 3.4 Hz, $J_{2,3}$ 11.3 Hz), 5.21 (dd, 1H, H-4c, $J_{3,4}$ 3.4 Hz, $J_{4,5}$<1 Hz,), 5.35 – 5.39 (m, 3H, H-1c, H-1b, H-2b), 5.43 (dd, 1H, H-4a, $J_{3,4}$ 2.8 Hz, $J_{4,5}$<1 Hz,), 5.45 (dd, 1H, H-3b, $J_{2,3}$ 10.1 Hz, $J_{3,4}$ 3.2 Hz), 5.61 (dd, 1H, H-4b, $J_{3,4}$ 3.2 Hz, $J_{4,5}$<1 Hz), 5.67 (d, 1H, H-1a, $J_{1,2}$ 8.0 Hz).

12: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.24 (d, 3H, H-6d, $J_{5,6}$ 6.6 Hz), 1.85 – 1.91 (m, 2H, C$\underline{CH_2}$C), 1.92, 1.98, 1.99, 2.04, 2.05, 2.06, 2.08, 2.09, 2.10 (6H), 2.16, 2.17 (11s, 10×3H, 1×6H, 12Ac), 3.27 – 3.37 (m, 1H, H-2a), 3.40 – 3.54 (m, 2H, NHC$\underline{H_2}$), 3.62 – 3.76 (m, 4H, H-2b, OC$\underline{H}$H, H-5a, H-5b), 3.83 (dd, 1H, H-3b, $J_{2,3}$ 9.9 Hz, $J_{3,4}$ 2.5 Hz), 3.93 – 3.99 (m, 2H, OCH$\underline{H}$, H-6c), 4.03 – 4.06(m, 2H, H-6b, H-6'b), 4.19 – 4.23 (m, 2H, H-6a, H-6'a), 4.24 – 4.30 (m, 1H, H-6'c), 4.29 – 4.39 (m, 1H, H-3a), 4.40 (d, 1H, H-1b, $J_{1,2}$ 7.6 Hz), 4.39 – 4.45 (m, 1H, H-5c), 4.61 – 4.66 (m, 1H, H-5d), 4.95 (dd, 1H, H-4a, $J_{3,4}$=$J_{4,5}$ 8.8 Hz), 5.08 (d, 1H, H-1a, $J_{1,2}$ 7.8 Hz), 5.08 – 5.14 (m, 1H, H-3d), 5.25 (dd, 1H, H-4d, $J_{3,4}$ 2.7 Hz, $J_{4,5}$<1 Hz), 5.30 (dd, 1H, H-2d, $J_{1,2}$ 3.8 Hz, $J_{2,3}$ 11.1 Hz), 5.33 – 5.43 (m, 4H, H-1c, H-2c, H-3c, H-4b), 5.56 – 5.59 (m, 2H, H-1d, H-4c), 6.86 – 6.89 (m, 1H, N$\underline{H}$Ac), 7.37 – 7.43 (m, 1H, N$\underline{H}$C(O)CF_3). MS, *m/z*: 1329 (M^++Na), 1345 (M^++K). $[\alpha]_D$ +15.9 (*c* 1, $CHCl_3$).

15: ^{1}H NMR (selected data, 500 MHz, $CDCl_3$) δ: 1.26 (d, 3H, H-6d, $J_{6,5}$ 6.5 Hz), 1.80 – 1.87 (m, 2H, C$\underline{CH_2}$C), 1.90, 1.96, 2.00, 2.03, 2.06 (6H), 2.08, 2.10 (6H), 2.13, 2.16, 2.17 (10s, 8×3H, 2×6H, 12Ac), 3.36 – 3.53 (m, 3H, NHC$\underline{H_2}$, OC$\underline{H}$H), 3.64 – 3.70 (m, 1H, OCH$\underline{H}$), 3.73 (dd, 1H, H-2b, $J_{1,2}$ 7.6 Hz, $J_{2,3}$ 9.9 Hz), 3.79 – 3.83 (m, 1H, H-5b), 3.90 (dd, 1H, H-3b, $J_{2,3}$ 9.8 Hz, $J_{3,4}$ 2.8 Hz), 4.53 (d, 1H, H-1b, $J_{1,2}$ 7.6 Hz), 4.55 – 4.63 (m, 2H, H-5c, H-5d), 5.07 – 5.15 (m, 3H, H-1a, H-2d, H-3d), 5.27 (dd, 1H, H-4d, $J_{3,4}$ 2.2 Hz, $J_{4,5}$<1 Hz), 5.33 – 5.41 (m, 4H, H-2c, H-1c, H-1d, H-4b), 5.47 (dd, 1H, H-3c, $J_{2,3}$ 10.3 Hz, $J_{3,4}$ 3.2 Hz), 5.54 (dd, 1H, H-4a, $J_{3,4}$ 3.2 Hz, $J_{4,5}$<1 Hz), 5.60 (dd, 1H, H-4c, $J_{3,4}$ 2.2 Hz, $J_{4,5}$<1 Hz), 6.65 – 6.71 (m, 1H, N$\underline{H}$C(O)CF_3), 7.56 (d, 1H, N$\underline{H}$C(O)CH_3, $J_{NH,2}$ 7.2 Hz). MS, *m/z:* 1329 (M^++Na), 1345 (M^++K). $[\alpha]_D$ +58.5 (*c* 1, $CHCl_3$).

16: ^{1}H NMR (selected data, 500 MHz, $CDCl_3$) δ: 1.26 (d, 3H, H-6d, $J_{5,6}$ 6.5 Hz), 1.79 – 1.93 (m, 2H, CC$\underline{H_2}$C) 1.90, 1.97, 2.00, 2.03, 2.06, 2.07, 2.08, 2.09, 2.12, 2.13, 2.16, 2.17 (12c, 12×3H,

12Ac), 3.25 – 3.31 (m, 1H, H-2a), 3.61–3.67 (m, 2H, NHC$\underline{H}_2$), 3.69 (dd, 1H, H-2b, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 10.3 Hz), 3.74 – 3.77 (m, 1H, OC$\underline{H}$H), 3.78 – 3.81 (m, 1H, H-5b), 3.88 (dd, 1H, H-3b, $J_{2,3}$ 10.3 Hz, $J_{3,4}$ 2.4 Hz), 4.26 – 4.40 (m, 4H, H-1a, H-5a, H-6a, H-6c), 4.49 – 4.53(m, 1H, H-5c), 4.52 (d, 1H, H-1b, $J_{1,2}$ 7.8 Hz), 4.60 – 4.65 (m, 1H, H-5d), 5.08 (dd, 1H, H-3d, $J_{2,3}$ 11.2 Hz, $J_{3,4}$ 2.4 Hz), 5.10 (dd, 1H, H-2d, $J_{1,2}$ 3.0 Hz, $J_{2,3}$ 11.2 Hz), 5.27 (dd, 1H, H-4d, $J_{3,4}$ 2.4 Hz, $J_{4,5}$<1 Hz), 5.34 (dd . br.s, 1H, H-4b), 5.35 – 5.41 (m, 3H, H-4a, H-1c, H-3c), 5.45 (dd, 1H, H-3c, $J_{2,3}$ 10.7 Hz, $J_{3,4}$ 3.4 Hz), 5.54 (dd, 1H, H-4c, $J_{3,4}$ 3.0 Hz, $J_{4,5}$<1 Hz), 5.59 (d, 1H, H-1d, $J_{1,2}$ 3.0 Hz), 7.16 (d, 1H, N$\underline{H}$Ac, $J_{NH,2}$ 7.1 Hz), 7.81 – 7.84 (m, 1H, N$\underline{H}$C(O)CF_3). MS, *m/z*: 1329 (M^++Na), 1345 (M^++K). $[\alpha]_D$ +5.0 (c 1, $CHCl_3$).