

A Convergent Strategy for the Synthesis of β -Carba-galacto-Disaccharides

Xuhong Cheng, Noshena Khan, Govindaraj Kumaran and David R. Mootoo*

Department of Chemistry, Hunter College/CUNY, 695 Park Avenue, New York, New York 10021

SUPPLEMENTARY MATERIAL

TIA-acid **22**

Clear oil; $R_f = 0.1$ (20% ethyl acetate:petroleum ether). ^1H NMR (300 MHz, C_6D_6) δ 1.41, 1.50 (both s, 3H ea), 2.6 (m, 3H), 3.45 (m, 2H), 4.30 (m, 3H), 5.53, 5.60 (both d, $J = 6.0$ Hz, 1H), 7.0-7.6 (m, 10H). ^{13}C NMR (75MHz, C_6D_6), major isomer 26.5, 28.0, 33.5, 39.9, 70.5, 73.8, 81.8, 81.9, 88.3, 111.6, 127.0 –140.0 (several lines), 179.5. FABHRMS: calcd for $\text{C}_{22}\text{H}_{26}\text{O}_5\text{SK}$ (M+K) 441.1139, found 441.1139

Carbasugar **27a**

Colorless oil, $R_f = 0.45$ (40% ethyl acetate:petroleum ether); ^1H NMR (500 MHz, CDCl_3) δ 1.35 (s, 3H), 1.35 (m buried under s at 1.35, 1H), 1.49 (s, 3H), 1.97 (m, 1H), 2.07 (m, 1H), 2.33 (br s, 1H, D_2O ex), 3.33 (m, 2H), 3.50 (m, 2H), 3.71 (m, 3H), 3.85 (m, 4H), 4.27 (t, $J = 4.0$ Hz, 1H), 4.40 - 4.70 (m, 9H), 4.86 (apparent d, $J = 11.0$ Hz, 1H), 5.08 (br s, 1H), 7.30 (m, 25H). ^{13}C NMR (75 MHz, CDCl_3) δ 26.6, 29.8 (2xC), 36.1, 69.7, 71.2, 72.5, 72.6, 72.7, 73.4, 73.6, 74.1, 75.2, 75.3, 77.4, 80.0, 80.5, 99.5, 109.4, 128.0-130.0 (several lines), 138.3, 138.5, 138.6. FABHRMS: calcd for $\text{C}_{51}\text{H}_{58}\text{O}_{10}$ Na (M+Na) 853.3931, found 853.3927.

27a - acetate

^1H NMR (500 MHz, CDCl_3) δ 1.25 (s, 3H), 1.33 (s, 3H), 1.51 (m, 1H), 1.84 (s, 3H), 2.06 (m, 2H), 3.32 (m, 1H), 3.48 (dt, $J = 3.0, 10.0$ Hz, 1H), 3.56 (t, $J = 8.5$ Hz, 1H), 3.63 (t, $J = 2.0$ Hz, 1H), 3.72 (m, 2H), 3.89 (m, 4H), 4.29 (t, $J = 4.0$ Hz, 1H), 4.46 (m, 3H), 4.65 (m, 6H), 4.84 (apparent d, $J = 11.0$ Hz, 1H), 4.94 (br s, 1H), 5.02 (dd, $J = 8.0, 10.0$ Hz, 1H), 7.20 (m, 25H).

^1H NMR (500 MHz, C_6D_6) δ 1.21 (s, 3H), 1.58 (s, 3H), 1.61 (m, buried under s at δ 1.58 and 1.65, 1H), 1.65 (s, 3H), 1.82 (m, 1H), 2.14 (dt, $J = 4.4, 12.7$ Hz, 1H), 3.21 (m, 1H), 3.44 (dt, $J = 4.0, 10.5$ Hz, 1H), 3.50 (t, $J = 8.5$ Hz, 1H), 3.80 (m, 4H), 4.10 (br t, $J = 3.0$ Hz, 1H), 4.14 (m, 3H), 4.28 (ABq, $\Delta\delta = 0.04$ ppm, $J = 12.0$ Hz, 2H), 4.38 (apparent d, $J = 11.5$ Hz, 1H), 4.48 (m, 4H), 4.65 (ABq, $\Delta\delta = 0.09$ ppm, $J = 12.0$ Hz, 2H), 4.93 (apparent d, $J = 11.5$ Hz, 1H), 5.14 (br s, 1H), 5.44 (t, $J = 10.0$ Hz, 1H), 7.20 (m, 25H). nOe between δ 2.14 (H5) and 3.44 (H1) and 3.80 (H3 buried in multiplet).

Carbasugar **27b**

Colorless oil, $R_f = 0.25$ (40% ethyl acetate:petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 1.18 (m, 1H), 1.33 (s, 3H), 1.48 (s, 3H), 1.72 (m, 1H), 1.82 (dt, $J = 2.0, 12.8$ Hz, 1H), 3.15 (dd, $J = 6.2, 8.4$ Hz, 1H), 3.30 - 3.48 (m, 4H), 3.35 (s, 3H), 3.50 (dd, $J = 3.0, 11.0$ Hz, 1H), 3.68 - 3.82 (m, 5H), 3.94 (dd, $J = 2.2, 10.8$ Hz, 1H), 4.16 (t, $J = 4.0$ Hz, 1H), 4.36 - 4.80 (m, 8H), 5.0 (apparent d, $J = 11.4$ Hz, 1H), 7.3 (m, 20H). ^{13}C NMR (75 MHz, CDCl_3) δ 26.6, 28.5, 28.7, 35.7, 55.4, 68.7, 70.6, 71.2, 73.3, 73.6, 73.9, 74.1, 75.9, 76.2, 77.0, 77.4, 78.1, 80.4, 80.5, 80.9, 81.8, 98.3, 109.2, 127.4 - 128.8 (several lines), 137.7, 138.3. FABHRMS: calcd for $\text{C}_{45}\text{H}_{55}\text{O}_{10}$ (M+H) 755.3795, found 755.3795.

27b – acetate

^1H NMR (500 MHz, CDCl_3) δ 1.20 (m, 1H), 1.32 (s, 3H), 1.54 (s, 3H), 1.77 (m, 1H), 2.00 (s, 3H), 2.02 (m, buried under s at δ 2.00, 1H), 3.11 (dd, $J = 6.0, 9.0$ Hz, 1H), 3.16 (dd, $J = 3.0, 11.0$, 1H), 3.36 (s, 3H), 3.36 (m, buried under s at δ 3.36, 1H), 3.44 (m, 2H), 3.52 (br d, $J = 9.0$ Hz, 1H), 3.59 (br d, $J = 10.5$ Hz, 1H), 3.65 (dd, $J = 5.0, 8.0$ Hz, 1H), 3.72 (t, $J = 9.5$ Hz, 1H), 3.81 (dd, $J = 3.0, 10.5$ Hz, 1H), 4.17 (br t, $J = 3.5$ Hz, 1H), 4.42 (m, 3H), 4.57 (d, $J = 3.5$ Hz, 1H), 4.62 (apparent d, $J = 12.0$ Hz, 1H), 4.72 (m, 3H), 4.91 (apparent d, $J = 11.0$ Hz, 1H), 4.95 (dd, $J = 8.5, 10.5$ Hz, 1H), 7.30 (m, 20H).

Carbadisaccharide **1**

White, foamy solid; mp 130-135 °C; $R_f = 0.50$ (50% methanol: ethyl acetate); ^1H NMR (400 MHz, D_2O) δ 1.40 (dt, $J = 11.3, 12.7$ Hz, 1H), 1.75 (m, 1H), 1.88 (br d, $J = 13.2$ Hz, 1H), 3.42 (dd, $J = 2.9, 9.5$ Hz, 1H), 3.47 (dd, $J = 8.6, 11.0$ Hz, 1H), 3.54 - 3.65 (m, 4H), 3.70 (m, 2H), 3.78 (dd, $J = 3.3, 9.5$ Hz, 1H), 3.85 (br d, $J = 9.5$ Hz, 1H), 3.99 (m, 2H), 5.04 (br s, 1H). ^{13}C NMR (75 MHz, D_2O) δ 28.1, 38.6, 61.3, 62.5, 67.2, 69.4, 70.4, 70.7, 73.3, 74.2 (2C), 80.6, 102.0. ESMS: m/z 363.2 (M+Na).

Carbadisaccharide **4**

White, amorphous solid, mp 159-168 °C;; $R_f = 0.40$ (30% methanol: ethyl acetate); ^1H NMR (400 MHz, D_2O) δ 1.31 (q, $J = 12.4$ Hz, 1H), 1.72 (m, 1H), 1.98 (br d, $J = 13.2$ Hz, 1H), 3.39 (s, 3H), 3.40 - 3.74 (m, 9H), 3.90 (m, 2H), 4.00 (br s, 1H), 4.78 (br s, 1H). ^{13}C NMR (75 MHz, D_2O) δ 27.3, 38.3, 55.2, 60.5, 60.9, 69.3, 71.2, 71.4, 72.9, 74.4, 74.5, 77.0, 81.4, 99.3. ESMS: m/z 377.2 (M+Na).