Supplementary Material (ESI) for Chemical Communications

Spectral Data of **11**: ^{1}H NMR (CD_3OD, 400 MHz) δ 5.81 (m, 1H), 5.1 (m, 2H), 4.45 (d, 1H, *J* = 8.0 Hz), 4.37 (d, 1H, *J* = 8.0 Hz), 3.88 (m, 3H), 3.68 (m, 3H), 3.52 (m, 2H), 3.40 (m, 2H), 3.29 (br s, 2H), 2.04 (m, 2H), 1.95 (s, 3H), 1.52 (m, 2H); ^{13}C NMR (CD_3OD) δ 173.0, 171.0, 138.20, 114.1, 103.8, 101.1, 84.3, 76.2, 75.9, 74.8, 73.0, 71.7, 69.2, 68.7, 61.4, 55.0, 30.0, 28.7, 22.0; HRMS (FAB) calcd. for $C_{19}H_{30}O_{12}N$ (M^+ + 2Li – H) 478.2088, found 478.2068.

Spectral Data of **14**: ^{1}H NMR (D_2O, 400 MHz) δ 5.99 (m, 4H), 4.37 (m, 2H), 3.98–3.89 (m, 4H), 3.66–3.53 (m, 14H), 3.40–3.32 (m, 9H), 3.17 (m, 3H), 2.88 (m, 2H), 2.75–2.70 (m, 4H), 2.56–2.54 (m, 2H), 2.22 (br m, 2H), 1.84 (s, 6H), 1.82 (m, 1H), 1.52 (br m, 8H), 1.24–1.14 (m, 6H), 0.52 (m, 1H); ^{13}C NMR (CD_3OD, 400 MHz) δ 176.4, 174.2, 139.8, 138.4, 137.2, 132.5, 106.1, 104.8, 103.6, 98.6, 82.4, 77.7, 77.3, 75.8, 74.7, 73.6, 71.0, 68.7, 64.4, 62.8, 54.5, 53.2, 46.1, 45.3, 44.8, 43.8, 43.1, 38.8, 38.6, 32.0, 31.3, 30.6, 25.7 22.9; Maldi-Tof calcd. for $C_{26}H_{42}O_{12}N_2$ (M^+ + H) 575.2752, found 575.2810.

Representative experimental procedure: The glycomonomer **14** (0.122 mmol, 70 mg) and DTAB (0.122 mmol, 37 mg) were dissolved in water (1.5 ml) and degassed (argon). The Ru initiator**15** (5 mol%, 0.006 mmol, 5.06 mg) dissolved in dichloroethane (1.0 ml) was degassed and added to the solution of **14**. The reaction mixture was stirred at room temperature for 30 min and then heated at 60 °C for 5 h. On completion of the reaction, confirmed by disappearance of monomer **14** on TLC, an excess of ethyl vinyl ether was added in order to quench the active alkylidene. The crude mixture was then concentrated, purified using gel filtration chromatography (Sephadex G-75, deionised water as eluant) and lyophilized to give a pale brown spongy solid (60 mg). Yield: 85%; ^{1}H NMR (D_2O, 400 MHz) δ 7.25 (br m, ArH protons), 5.34 (br s, olefinic protons), 5.24 (br s, olefinic protons), 4.8 (br s), 4.00–3.00 (m, sugar ring protons), 1.9–1.75 (br m), 1.72 (s, NHAc), 1.6–1.4 (br m), 1.18–0.9 (br m); *cis*:*trans* ratio (^{1}H NMR) 60:40.