

Spectral Data:

β -Keto- δ -lactone 4a: $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 7.37-7.26 (m, 5H), 4.76 (AB system, $J_{\text{AB}} = 11.3$ Hz, 2H), 4.74-4.68 (m, 1H, H_5), 4.36 (AB part of an ABX system, $J_{\text{AB}} = 24.6$ Hz, $J_{\text{AX}} = 2.5$ Hz, $J_{\text{BX}} = 3.6$ Hz, 2H), 3.97 (d, $J = 7.3$ Hz, 1H, H_4), 3.62 (AB system, $J_{\text{AB}} = 20.2$ Hz, 2H), 1.16 (s, 9H); $^{13}\text{C-NMR}$ (50 MHz, CDCl_3) δ 199.1 (C_3); 178.1, 165.9 (C_1), 136.4, 129.5, 129.3, 129.2, 128.9, 76.5, 76.1, 74.2, 62.8, 45.2 (C_2), 39.4, 27.5. Anal Calcd for $\text{C}_{18}\text{H}_{28}\text{O}_6$: C, 63.49; H, 8.30. Found C, 63.71; H, 8.15.

Cycloadduct 11: $[\alpha]_{\text{D}}^{25} = +119.1$ (c 2.89, CHCl_3); $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 7.38-7.26 (m, 20H), 5.54 (d, $J = 2.6$ Hz, 1H), 4.91-4.54 (m, 8H), 4.45-4.32 (m, 3H), 4.14-3.96 (m, 1H), 3.88-3.76 (m, 4H), 3.59 (dd, $J = 10.7$ Hz, $J = 8.8$ Hz); 3.28 (dd, $J = 10.7$ Hz, $J = 2.6$ Hz), 1.12 (s, 9H); $^{13}\text{C-NMR}$ (50 MHz, CDCl_3) δ 178.0, 162.3, 157.3, 137.5, 137.4, 137.0, 136.6, 128.8, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 99.0, 96.0 (C_1), 78.4, 76.4, 75.9, 73.4, 69.4, 75.8, 75.3, 73.6, 72.7, 67.7, 61.7, 42.5 (C_2); 38.7 (C_q Piv.), 27.0.

2-Deoxydisaccharide 12: $[\alpha]_{\text{D}}^{25} = +50.6$ (c 0.47, CHCl_3); $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 7.35-7.15 (m, 20H), 5.65-5.64 (m, 2H), 4.93-4.39 (m, 11H), 4.02-3.56 (m, 6H), 2.43-2.34 (m, 1H, H_{2eq}); 1.89 (ddd, $J = 14.3$ Hz, $J = 11.0$ Hz, $J = 3.3$ Hz, 1H, H_{2ax}); 1.20 (s, 9H); $^{13}\text{C-NMR}$ (50 MHz, CDCl_3) δ 178.1, 167.0, 164.6 ($\text{C}_1 + \text{C}_3'$), 138.3, 138.1, 137.7, 136.5, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 97.1, 96.5 ($\text{C}_1 + \text{C}_2'$); 76.3, 76.0, 75.0, 73.5, 73.4, 73.1, 72.1, 70.0, 67.9, 61.8, 34.5 (C_2); 38.8, 27.1. Anal Calcd for $\text{C}_{45}\text{H}_{50}\text{O}_{10}$: C, 71.97; H, 6.72. Found C, 71.93; H, 6.71.

Spiro Derivative 4a: $[\alpha]_{\text{D}}^{25} = +35.0$ (c 0.33, CHCl_3); $^1\text{H-NMR}$ (200 MHz, CDCl_3) δ 7.38-7.06 (m, 25H), 5.30-4.34 (m, 13H), 4.24-4.23 (d, $J = 3.0$ Hz, 1H), 4.18-4.13 (m, 1H), 3.91 (t, $J = 10.3$ Hz, 1H), 3.76-3.71 (m, 1H), 3.56 (d, $J = 9.5$ Hz, 1H, H_2), 3.50 (bs, 1H), 3.07-3.00 (A part of an AB system, $J_{\text{AB}} = 13.2$ Hz, 1H), 2.50-2.43 (B part of an AB system, $J_{\text{AB}} = 13.2$ Hz); 1.24 (s, 9H); $^{13}\text{C-NMR}$ (50 MHz, CDCl_3) δ 178.0, 162.5, 154.7 ($\text{C}_1 + \text{C}_3'$), 138.1, 136.8, 136.3, 129.0, 128.8, 128.6, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7, 127.0, 104.0 (C_2'), 95.8 (C_1), 83.0, 81.2, 77.8, 76.1, 75.8, 75.0, 74.7, 73.4, 73.2, 71.0, 67.5, 61.3, 53.4, 30.2, 27.2; Anal Calcd for $\text{C}_{53}\text{H}_{56}\text{O}_{11}\text{S}$: C, 70.64; H, 6.27. Found C, 69.96; H, 6.30.

Spiro Derivative 4b: $[\alpha]_{\text{D}}^{25} = -6.82$ (c 0.66, CHCl_3); $^1\text{H-NMR}$ (800 MHz, CDCl_3) δ 7.38-7.07 (m, 25H), 4.87-4.81 (m, 4H), 4.78-4.76 (m, 1H), 4.70-4.68 (A part of an AB system, $J_{\text{AB}} = 12.3$ Hz, 1H), 4.67-4.66 (A part of an AB system, $J_{\text{AB}} = 11.4$ Hz, 1H), 4.59 (td, $J = 6.5$ Hz, $J = 2.5$ Hz, 1H), 4.58-4.56 (B part of an AB system, $J_{\text{AB}} = 10.6$ Hz, 1H), 4.52-4.50 (m, 2H), 4.41-4.39 (A part of an ABX system, $J_{\text{AB}} = 11.6$ Hz, $J_{\text{AX}} = 6.9$ Hz, 1H), 4.33-4.31 (B part of an ABX system, $J_{\text{AB}} = 11.6$ Hz, $J_{\text{BX}} = 5.6$ Hz, 1H), 4.04 (t, $J = 9.4$ Hz, 1H), 4.04 (d, $J = 2.5$ Hz, 1H); 4.00 (d, $J = 8.0$ Hz, 1H),

3.85 (t, $J = 8.4$ Hz, 1H); 3.82-3.80 (A part of an ABX system, $J_{AB} = 10.9$ Hz, $J_{AX} = 2.6$ Hz), 3.74-3.71 (m, 2H, 1H), 3.24-3.22 (A part of an AB system, $J_{AB} = 14.4$ Hz, 1H), 3.20-3.18 (B part of an AB system, $J_{AB} = 14.4$ Hz, 1H), 1.28 (s, 9H). ^{13}C -NMR (50 MHz, CDCl_3) δ 178.1, 162.0, 157.2 ($\text{C}_{1'}$ + $\text{C}_{3'}$), 137.9, 137.8, 137.1, 136.7, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 127.3, 103.1 ($\text{C}_{2'}$), 97.4 (C_1), 83.3, 82.3, 77.1, 76.1, 75.2, 74.9, 74.8, 73.3, 73.1, 72.6, 70.5, 68.0, 61.9, 53.4, 38.7, 27.1. Anal Calcd for $\text{C}_{53}\text{H}_{56}\text{O}_{11}\text{S}$: C, 70.64; H, 6.27. Found C, 70.09; H, 6.24.