

Sample experimental write-up:

p-Tolyl 2,3,4-O-tris(acetyl)-6-O-(*tert*-butyldimethylsilyl)-1-thio- β -D-glucopyranoside

(6b)

To a round bottom flask equipped with a stirring bar under an atmosphere of nitrogen was added pyridine (13 ml), compound **18a** (2.17 g, 5.42 mmol), a solution of Ac₂O (2.21 g, 21.68 mmol) in 15 ml pyridine, and 5 mg of DMAP. The flask was then heated to 60 °C for 4 h and diluted with 2N HCl (60 ml), and 60 ml of a 50/50 Et₂O/hexanes solution. The resulting mixture was extracted three times with Et₂O and the combined ether extracts were washed three times with water, once with brine, and dried over Na₂SO₄. The solution was then filtered and the solvent removed under reduced pressure, and purified over silica gel column giving a white solid (m.p. 123-125 °C, 2.74 g, 96 %).

$[\alpha]_D$ -4.53 (MeOH $C = 2.56$), **¹H-NMR** (200 MHz, CDCl₃): δ 0.03 (3H, s), 0.05 (3H, s), 0.87 (9H, s), 1.93 (3H, s), 1.96 (3H, s), 2.03 (3H, s), 2.30 (3H, s), 3.50 (1H, ddd, $J = 2.7, 4.2, 9.7$ Hz), 3.68 (2H, m), 4.64 (1H, d, $J = 9.9$ Hz), 4.86 (1H, t, $J = 9.7$ Hz), 4.97 (1H, t, $J = 9.6$ Hz), 5.16 (1H, t, $J = 9.2$ Hz), 7.05 (2H, d, $J = 8.0$ Hz), 7.35 (2H, d, $J = 8.1$ Hz). **¹³C-NMR** (50 MHz, CDCl₃): δ -5.07 (CH₃), 18.70, 21.07 (CH₃), 21.21 (CH₃), 21.60 (CH₃), 26.24 (CH₃), 62.73 (CH₂), 68.85 (CH), 70.37 (CH), 74.89 (CH), 79.26 (CH), 86.04 (CH), 128.26, 130.83 (CH), 133.88 (CH), 138.83, 169.64, 169.66, 170.75. **IR**: ν cm⁻¹ 2930, 2857, 1757, 1374, 837, 810, 779, **HRMS**: calcd for C₂₅H₃₈O₈SSi + Na, 549.1954, Found M + Na: 549.1963.