

Supporting Information

New protecting groups for 1,2-diols (Boc- and Moc-ethylidene). Cleavage of acetals with bases

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Typical procedure for protection

A 2.0 M solution of *tert*-butyl propynoate (0.6 mL, 1.2 mmol) in acetonitrile was added dropwise at room temperature to a solution of diol **1** (210 mg, 1.0 mmol) and DMAP (60 mg, 0.5 mmol) in acetonitrile (5 mL). The orange solution was stirred for 30 min. and quenched with methanol (1 mL). The solvent was removed and the residue was purified by column chromatography (CH₂Cl₂) through a short pad of silica gel to afford **1a** as a colorless solid (325 mg, 97%): mp 62–63 °C; ¹H (300 MHz, CDCl₃) δ 1.50 (s, 9 H, C(CH₃)₃), 2.86 (d, *J* = 5.1 Hz, 2 H, CH₂), 4.77 (s, 2 H, CHPh), 5.86 (t, *J* = 5.1 Hz, 2 H, CHCH₂), 7.21–7.34 (m, 10 H, Ph); ¹³C (75.4 MHz, CDCl₃) δ 28.1 (CH₃), 41.7 (CH₂), 81.1 (CCH₃), 84.2 (CHPh), 86.8 (CHPh), 102.3 (CHCH₂), 126.3 (C_o), 126.7 (C_o), 128.1 (C_p), 128.4 (C_p), 128.5 (2 C_m), 136.6 (C_{ipso}), 137.9 (C_{ipso}), 168.6 (C=O); HRMS (FAB) 341.1748 [M+1]⁺, calcd. for C₂₁H₂₅O₄ 341.1753.

Typical procedures for deprotection

Method A (pyrrolidine–butyllithium): A 1.5 M solution of butyllithium in hexanes (370 μL, 0.55 mmol) was added to solution of pyrrolidine (92 μL, 1.1 mmol) in anhydrous THF (1 mL) at –78 °C. The mixture was stirred for 30 min. at 0 °C and added via cannula to a solution of acetal **1a** (75 mg, 0.22 mmol) in anhydrous THF (1 mL). The orange solution was stirred overnight at room temperature. Afterwards, the reaction was acidified to pH 2 with aqueous HCl (2 M) and extracted with EtOAc. The organic layer was dried over Na₂SO₄ and purified by “flash” column chromatography (hexane–EtOAc) to give **1** (40 mg, 85%).

Method B (pyrrolidine): A solution of acetal **6a** (210 mg, 0.57 mmol) in pyrrolidine (8 mL) was heated to 90 °C for 48 hours. After removal of the solvent, the residue was purified by “flash” column chromatography (hexane–EtOAc) to obtain **6** (129 mg, 91%, 94% brsm).

Spectral data

2a: colorless solid; mp 95–97 °C; ¹H (200 MHz, CDCl₃) δ 1.48 (s, 9 H, C(CH₃)₃), 3.01 (d, *J* = 5.0 Hz, 2 H, CH₂), 5.35 (s, 2 H, CHPh), 5.63 (t, *J* = 5.0 Hz, 1 H, OCHO), 6.94–7.07 (m, 10 H, Ph); ¹³C (50.3 MHz, CDCl₃) δ 26.1 (C(CH₃)₃), 40.6 (CH₂COO), 81.3 (C(CH₃)₃), 82.4 (CHPh), 100.9

(CHCH₂), 126.8 (C_o), 127.2 (C_p), 127.4 (C_m), 136.8 (C_i), 168.5 (C=O); HRMS (FAB) 341.1745 [M + 1]⁺, calcd. for C₂₁H₂₅O₄ 341.1753.

3a: ¹H (200 MHz, CDCl₃) δ 1.48 (s, 9 H, C(CH₃)₃), 2.67–2.87 (ABX system, 2 H, CH₂COO), 3.77 (dd, *J* = 8.0 Hz, *J* = 6.7 Hz, 1 H, CHHO), 4.24 (dd, *J* = 8.0 Hz, *J* = 6.9 Hz, 1 H, CHHO), 5.05 (dd, *J* = 6.9 Hz, *J* = 6.7 Hz, 1 H, CHPh), 5.47 (t, *J* = 5.3 Hz, 1 H, OCHO), 7.26–7.37 (m, 5 H, Ph); ¹³C (50.3 MHz, CDCl₃) δ 28.0 (C(CH₃)₃), 41.0 (CH₂COO), 71.8 (OCH₂), 78.4 (CHPh), 81.0 (C(CH₃)₃), 102.0 (OCHO), 126.1–128.5 (C_o, C_m, C_p), 138.9 (C_i), 168.5 (C=O).

3b: ¹H (200 MHz, CDCl₃) δ 1.48 (s, 9 H, C(CH₃)₃), 2.60–2.80 (ABX system, 2 H, CH₂COO), 3.71 (dd, *J* = 8.4 Hz, *J* = 7.0 Hz, 1 H, CHHO), 4.40 (dd, *J* = 8.4 Hz, *J* = 6.2 Hz, 1 H, CHHO), 5.09 (dd, *J* = 7.0 Hz, *J* = 6.2 Hz, 1 H, CHPh), 5.62 (t, *J* = 5.1 Hz, 1 H, OCHO), 7.26–7.37 (m, 5 H, Ph); ¹³C (50.3 MHz, CDCl₃) δ 28.2 (C(CH₃)₃), 41.3 (CH₂COO), 72.6 (OCH₂), 77.5 (CHPh), 81.0 (C(CH₃)₃), 102.2 (OCHO), 125.7–128.8 (C_o, C_m, C_p), 139.1 (C_i), 168.5 (C=O).

4a: ¹H (200 MHz, CDCl₃) δ 1.35–1.95 (m, 6 H, (CH₂)₃), 1.45 (s, 9 H, C(CH₃)₃), 2.59 (d, *J* = 3.0 Hz, 2 H, CH₂COO), 4.51 (m, 2 H, CHO), 5.04 (t, *J* = 3.0 Hz, 1 H, OCHO); ¹³C (50.3 MHz, CDCl₃) δ 22.2 (CH₂), 28.0 (C(CH₃)₃), 33.0 (CHOCH₂), 40.1 (CH₂COO), 80.8 (C(CH₃)₃), 81.6 (CHO), 100.1 (OCHO), 168.7 (C=O).

4b: ¹H (200 MHz, CDCl₃) δ 1.35–1.95 (m, 6 H, (CH₂)₃), 1.45 (s, 9 H, C(CH₃)₃), 2.49 (d, *J* = 3.3 Hz, 2 H, CH₂COO), 4.63 (m, 2 H, CHO), 5.46 (t, *J* = 3.3 Hz, 1 H, OCHO); ¹³C (50.3 MHz, CDCl₃) δ 23.5 (CH₂), 28.0 (C(CH₃)₃), 33.1 (CHOCH₂), 41.1 (CH₂COO), 80.8 (C(CH₃)₃), 81.0 (CHO), 101.8 (OCHO), 168.7 (C=O).

5a: ¹H (200 MHz, CDCl₃) δ 1.47 (s, 9 H, C(CH₃)₃), 1.51 (s, 9 H, C(CH₃)₃), 2.67–2.89 (ABX system, 2 H, CH₂COO), 3.34–3.53 (m, 2 H, H5', H5''), 4.50 (m, 1 H, H4'), 4.83–4.94 (m, 2 H, H2', H3'), 5.43 (t, *J* = 4.6 Hz, 1 H, CHCH₂COO), 5.46 (d, *J* = 8.0 Hz, 1 H, H5), 5.86 (d, *J* = 2.2 Hz, 1 H, H1'), 6.84 (d, *J* = 15.0 Hz, 1 H, NCHCHCOO), 7.26–7.46 (m, 15 H, 3 Ph), 7.49 (d, *J* = 8.0 Hz, 1 H, H6), 8.04 (d, *J* = 15.0 Hz, 1 H, NCHCHCOO); ¹³C (50.3 MHz, CDCl₃) δ 28.1 (C(CH₃)₃), 40.6 (CH₂COO), 63.7 (C5'), 80.6 (C(CH₃)₃), 81.6 (C(CH₃)₃), 82.3 (C3'), 85.4 (C2'), 86.1 (C4'), 87.4 (Ph₃C), 94.0 (C1'), 101.4 (C5), 104.8 (CHCH₂COO), 116.3 (NCHCHCOO), 127.4–128.5 (C_o, C_m, C_p), 132.8 (NCHCHCOO), 139.3 (C6), 142.9 (C_i), 149.3 (C2), 160.7 (C4), 166.0 (CHCOO), 168.1 (CH₂COO).

5b: ¹H (200 MHz, CDCl₃) δ 1.47 (s, 9 H, C(CH₃)₃), 1.51 (s, 9 H, C(CH₃)₃), 2.65–2.68 (ABX system, 2 H, CH₂COO), 3.34–3.53 (m, 2 H, H5', H5''), 4.35 (m, 1 H, H4'), 4.83–4.94 (m, 2 H, H2', H3'), 5.53 (d, *J* = 8.0 Hz, 1 H, H5), 5.55 (t, *J* = 5.0 Hz, 1 H, CHCH₂COO), 5.79 (d, *J* = 1.8 Hz, 1 H, H1'), 6.81 (d, *J* = 14.6 Hz, 1 H, NCHCHCOO), 7.26–7.46 (m, 15 H, 3 Ph), 7.49 (d, *J* = 8.0 Hz, 1 H, H6), 8.00 (d, *J* = 14.6 Hz, 1 H, NCHCHCOO); ¹³C (50.3 MHz, CDCl₃) δ 28.2 (C(CH₃)₃), 40.3 (CH₂COO), 63.7 (C5'), 80.6 (C(CH₃)₃), 80.8 (C3'), 81.6 (C(CH₃)₃), 84.4 (C2'),

84.7 (C4'), 87.2 (Ph₃C), 94.0 (C1'), 101.6 (C5), 101.9 (CHCH₂COO), 116.3 (NCHCHCOO), 127.4–128.5 (C_o, C_m, C_p), 132.8 (NCHCHCOO), 139.7 (C6), 143.0 (C_i), 149.3 (C2), 160.7 (C4), 166.0 (CHCOO), 168.0 (CH₂COO).

6a: Oil; ¹H (200 MHz, CDCl₃) δ 1.34 (s, 6 H, 2 CH₃), 1.44 (s, 6 H, 2 CH₃), 1.45 (s, 9 H, C(CH₃)₃), 2.56 (dd, *J* = 5.2 Hz, 2 H, CH₂COO), 3.95–4.11 (m, 8 H, CHO), 5.41 (t, *J* = 5.2 Hz, 1 H, OCHO); ¹³C (50.3 MHz, CDCl₃) δ 25.0 (2 CH₃), 26.5 (2 CH₃), 28.0 (C(CH₃)₃), 40.2 (CH₂COO), 66.3 (CH₂O), 66.6 (CH₂O), 75.3 (CHO), 76.1 (CHO), 78.8 (CHO), 79.5 (CHO), 80.8 (C(CH₃)₃), 101.4 (CHCH₂COO), 109.7 (C(CH₃)₂), 109.8 (C(CH₃)₂), 169.4 (C=O); HRMS (FAB) 389.2092 [M+1]⁺, calcd. for C₁₉H₃₃O₈ 389.2097.

11a: Oil; ¹H (300 MHz, CDCl₃) δ 0.83 (d, *J* = 6.6 Hz, 3 H, CH₃CHCH₃), 1.00 (d, *J* = 6.3 Hz, 3 H, CH₃CHCH₃), 1.04 (d, *J* = 6.9 Hz, 3 H, CH₃CH), 1.42 (s, 9 H, C(CH₃)₃), 1.71 (m, 1 H CH(CH₃)₂), 1.98 (m, 1 H, CH₃CH), 2.36 (br s, 1 H, OH), 2.64 (dd, *J* = 15.2 Hz, *J* = 5.7 Hz, 1 H, CHHCOO), 2.70 (dd, *J* = 15.2 Hz, *J* = 5.1 Hz, 1 H, CHHCOO), 2.81 (dd, 1 H, *J* = 14.2 Hz, *J* = 4.4 Hz, CHHPh), 2.97 (dd, 1 H, *J* = 14.2 Hz, *J* = 9.3 Hz, CHHPh), 3.23 (dd, *J* = 9.0 Hz, *J* = 1.8 Hz, 1 H, CHOH), 4.17 (dd, *J* = 6.3 Hz, *J* = 4.5 Hz, 1 H, OCHCHO), 4.31 (ddd, *J* = 9.2 Hz, *J* = 6.2 Hz, *J* = 4.3 Hz, 1 H, OCHCH₂), 5.24 (t, *J* = 5.4 Hz, 1 H, CHCH₂COO), 7.19–7.33 (m, 5 H, Ph); ¹³C (75.4 MHz, CDCl₃) δ 8.0 (CH₃CH), 18.9 (CH₃CHCH₃), 19.6 (CH₃CHCH₃), 28.0 (C(CH₃)₃), 31.1, 34.4 (CH₃CH, (CH₃)₂CH), 35.8 (PhCH₂), 41.2 (CH₂COO), 79.7, 80.6, 82.6 (CHOH, CHCHO, OCHCH₂), 81.1 (C(CH₃)₃), 100.6 (OCHO), 126.5 (C_p), 128.4 (C_o), 129.0 (C_m), 138.0 (C_i), 168.6 (C=O); HRMS (FAB) 379.2480 [M+1]⁺, calcd. for C₂₂H₃₅O₅ 379.2484.