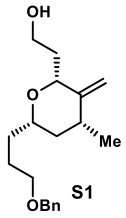
4 H), 1.06 (s, 9 H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ = 151.9, 138.8, 135.7, 135.6, 134.2, 129.6, 128.4, 127.8, 127.7, 127.6, 104.3, 77.4, 74.9, 72.9, 70.5, 60.8, 43.4, 36.0, 34.7, 32.8, 27.0, 26.2, 19.4, 18.2 ppm; HRMS (ESI-TOF) calcd for $C_{35}H_{46}O_3SiNa^+$ $[M+Na]^+$ 565.3108; Found 565.3111.

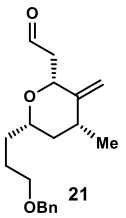
2-{(2*R*,4*R*,6*S*)-6-[3-(Benzyloxy)propyl]-4-methyl-3-methylidenetetrahydro-2*H*-pyran-2-yl}ethanol (S1): To a stirred solution of olefin derivative **19a** (500 mg, 0.921 mmol, 1.0 equiv) in THF (20 mL) at 0 °C



S1

was added dropwise tetra-*n*-butylammonium fluoride (1 M in THF, 0.920 mL, 0.920 mmol, 1.0 equiv), and the reaction mixture was allowed to warm to 23 °C. After 2.5 h, the reaction mixture was quenched by the addition of saturated aqueous NH_4Cl solution (15 mL). The aqueous layer was extracted with EtOAc (3 × 15 mL) and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The obtained residue was purified by flash column chromatography (SiO_2, 10 → 40% EtOAc in hexanes) to afford pure alcohol **S1** (264 mg, 0.866 mmol, 94% yield) as a colorless oil. **S1**: R_f = 0.40 (SiO_2, hexanes/EtOAc 3:2, *v*/*v*); $[\alpha]_D^{23}$ = +8.10 (*c* = 2.0, CH_2Cl_2); FT-IR (film) ν_{max} = 3431, 2954, 2850, 1650, 1454, 1364, 1312, 1091, 1058, 903, 736 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.36–7.32 (m, 4 H), 7.30–7.26 (m, 1 H), 4.87 (d, *J* = 1.6 Hz, 1 H), 4.82 (d, *J* = 1.6 Hz, 1 H), 4.49 (s, 2 H), 3.95–3.89 (m, 1 H), 3.84 (dd, *J* = 6.0, 4.9 Hz, 2 H), 3.66–3.57 (m, 1 H), 3.53–3.41 (m, 2 H), 2.31–2.23 (m, 1 H), 2.02–1.91 (m, 2 H), 1.81–1.61 (m, 3 H), 1.56 (td, *J* = 7.6, 6.1 Hz, 2 H), 1.13–1.06 (m, 4 H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ = 150.9, 138.7, 128.5, 127.8, 127.6, 105.0, 79.4, 77.7, 73.0, 70.3, 61.8, 42.6, 35.6, 33.5, 32.8, 26.1, 18.1 ppm; HRMS (ESI-TOF) calcd for $C_{19}H_{28}O_3Na^+$ $[M+Na]^+$ 327.1931; Found 327.1930.

{(2*R*,4*R*,6*S*)-6-[3-(Benzyloxy)propyl]-4-methyl-3-methylidenetetrahydro-2*H*-pyran-2-yl}acetaldehyde (21): To a stirred solution of alcohol **S1** (200 mg, 0.657 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) at

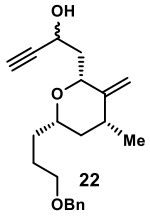


21

23 °C was added DMP (418 mg, 0.985 mmol, 1.5 equiv) portion wise. After 0.5 h, the reaction mixture was quenched by the addition of saturated aqueous $Na_2S_2O_3$ solution (20 mL) and the obtained suspension was further stirred for 2 h. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic layers were washed with saturated aqueous $NaHCO_3$

solution (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The obtained residue was purified by flash column chromatography (SiO_2, 10→30% EtOAc in hexanes) to afford pure aldehyde **21** (179 mg, 0.591 mmol, 90% yield) as a colorless foam. **21**: R_f = 0.80 (SiO_2, hexanes/EtOAc 3:2, *v*/*v*); $[\alpha]_D^{23}$ = +17.0 (*c* = 2.0, CH_2Cl_2); FT-IR (film) ν_{max} = 3004, 2848, 2725, 1725, 1650, 1454, 1363, 1087, 1028, 904, 735 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 9.81 (dd, *J* = 2.7, 2.0 Hz, 1 H), 7.36–7.32 (m, 4 H), 7.30–7.26 (m, 1 H), 4.84 (dd, *J* = 1.9, 0.6 Hz, 1 H), 4.75 (d, *J* = 1.9 Hz, 1 H), 4.49 (s, 2 H), 4.29–4.22 (m, 1 H), 3.62–3.54 (m, 1 H), 3.47 (ddt, *J* = 26.7, 9.3, 6.5 Hz, 2 H), 2.79–2.65 (m, 2 H), 2.36–2.28 (m, 1 H), 1.84–1.68 (m, 2 H), 1.67–1.59 (m, 1 H), 1.57–1.47 (m, 2 H), 1.14–1.07 (m, 4 H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ = 201.9, 150.2, 138.7, 128.4, 127.8, 127.6, 105.4, 77.7, 74.4, 72.9, 70.3, 45.7, 42.6, 35.6, 32.5, 26.0, 18.0 ppm; HRMS (ESI-TOF) calcd for $C_{19}H_{26}O_3Na^+$ $[M+Na]^+$ 325.1774; Found 325.1771.

1-{(2*R*,4*R*,6*S*)-6-[3-(Benzyloxy)propyl]-4-methyl-3-methylidenetetrahydro-2*H*-pyran-2-yl}but-3-yn-2-ol (22): To a stirred solution of aldehyde **21** (600 mg, 1.98 mmol, 1.0 equiv) in THF (15 mL) at −78 °C



was added ethynylmagnesium bromide (0.5 M in THF, 9.92 mL, 4.96 mmol, 2.5 equiv), and the reaction mixture was warmed to −10 °C. After 15 min, the reaction mixture was quenched by the addition of saturated aqueous NH_4Cl solution (30 mL). The aqueous layer was extracted with EtOAc (3 × 20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The obtained residue was purified by flash column chromatography (SiO_2, 5→20% EtOAc in hexanes) to afford alcohol **22** (mixture of diastereomers, 1.5:1 *dr*, 520 mg, 1.58 mmol, 80% yield) as a colorless foam. **22**: R_f = 0.35 (SiO_2, hexanes/EtOAc 5:1, *v*/*v*); $[\alpha]_D^{23}$ = +21.3 (*c* = 3.0, CH_2Cl_2); FT-IR (film) ν_{max} = 3415, 3297, 2956, 2850, 1650, 1454, 1365, 1312, 1206, 1089, 1062, 903, 697 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ = 7.36–7.31 (m, 4 H), 7.29–7.26 (m, 1 H), 4.87 (d, *J* = 1.5 Hz, 0.6 H), 4.84 (d, *J* = 1.6 Hz, 0.4 H), 4.83 (d, *J* = 1.6 Hz, 1 H), 4.67 (tdt, *J* = 7.3, 5.2, 2.4 Hz, 1 H), 4.51–4.47 (m, 2 H), 4.34–4.28 (m, 0.4 H), 3.98–3.93 (m, 0.6 H), 3.66 (dddd, *J* = 11.2, 7.3, 5.5, 2.1 Hz, 0.4 H), 3.62–3.57 (m, 0.6 H), 3.54–3.43 (m, 2 H), 2.46 (d, *J* = 2.1 Hz, 1 H), 2.45 (d, *J* = 2.1 Hz, 1 H), 2.35–2.23 (m, 1 H), 2.21–2.09 (m, 1.6 H), 2.05 (ddd, *J* = 14.4, 5.9, 2.7 Hz, 0.4 H), 1.83–1.61 (m, 3 H), 1.59–1.50 (m, 2 H), 1.15–1.08 (m, 4 H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ = 150.5, 150.3, 138.7, 138.6,