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Supporting Information

Hydroxyalkylation of α -C-H Bonds of Tetrahydrofuran with Aldehydes in the Presence of Triethylborane and *t*-Butyl Hydroperoxide

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General procedures and characterization data are provided. In addition, ^1H and ^{13}C NMR spectra of *threo* alcohols **1a**–**f** and *erythro* alcohols **2a**–**f** as well as ^1H NMR spectra of *threo/erythro* alcohols **1a/2a**–**1d/2d** and *threo/erythro* acetates derived from **1e/2e** and **1f/2f** are attached.

General Procedures. All reactions were conducted under argon unless otherwise indicated. All solvents and reagents were purified by standard procedures as necessary. Trialkylboranes (THF solution and neat materials) from Aldrich were used as received. *t*-Butyl hydroperoxide (5.78 M in nonane) was from Aldrich; molarity was determined by iodometric titration before use. ¹H NMR spectra (400 or 300 MHz) and ¹³C NMR spectra (100 or 75 MHz) were recorded in CDCl₃ solutions, respectively. Chemical shifts are reported in ppm relative to the internal solvent signal; CHCl₃ (7.26 ppm) and CDCl₃ (77.0 ppm). FT-IR spectra were recorded as films on NaCl plates. Low- and high-resolution mass spectra were obtained according to the specified technique and performed by the Meiji Pharmaceutical University. Melting points are uncorrected. Column chromatography was carried out on silica gel 60 (Merck, 70-230 mesh ASTM), and flash chromatography, on silica gel 60 (Merck, 230-400 mesh ASTM).

***threo*-α-(4-Methoxyphenyl)tetrahydro-2-furanmethanol (1a):** colorless solid, mp 50-52 °C; IR (neat) $\nu_{\max}$ 3437 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, 2H, *J*=8.8 Hz), 6.88 (d, 2H, *J*=8.8 Hz), 4.39 (d, 1H, *J*=6.84 Hz), 3.98 (dd, 1H, *J*=14.4, 7.08 Hz), 3.94-3.82 (m, 2H), 3.80 (s, 3H), 2.95 (s, 1H), 1.98-1.80 (m, 2H), 1.75-1.65 (m, 1H), 1.64-

1.53 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.2, 132.7, 128.1, 113.7, 83.5, 76.6, 68.4, 55.3, 27.9, 26.1; MS (EI) m/z : 208 (M^+), 190, 137 (100%); HRMS calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3$ (M^+) 208.1100, found 208.1100.

***erythro*- α -(4-Methoxyphenyl)tetrahydro-2-furanmethanol (2a):** colorless solid, mp 72-74 °C; IR (neat) ν_{max} 3427 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.28 (d, 2H, $J=8.8$ Hz), 6.87 (d, 2H, $J=8.8$ Hz), 4.84 (m, 1H), 4.06-4.01 (m, 1H), 3.93-3.87 (m, 1H), 3.81-3.75 (m, 1H), 3.79 (s, 3H), 2.56 (s, 1H), 1.88-1.76 (m, 3H), 1.67-1.62 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.8, 132.7, 127.1, 113.6, 83.1, 73.8, 68.9, 55.2, 26.0, 25.1; MS (EI) m/z : 208 (M^+), 190, 137 (100%); HRMS calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3$ (M^+) 208.1100, found 208.1102.

***threo*- α -Phenyltetrahydro-2-furanmethanol (1b):** colorless oil; IR (neat) ν_{max} 3437 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.18 (m, 5H), 4.37 (dd, 1H, $J=7.6, 2.0$ Hz), 3.93 (dd, 1H, $J=14.4, 7.3$ Hz), 3.88-3.76 (m, 2H), 2.92 (s, 1H), 1.91-1.74 (m, 2H), 1.69-1.52 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.6, 128.3, 127.9, 126.9, 83.4, 77.0, 68.4, 27.9, 26.1; MS (EI) m/z : 178 (M^+), 160, 71 (100%); HRMS calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2$ (M^+) 178.0994, found 178.0992.

***erythro*- α -Phenyltetrahydro-2-furanmethanol (2b):** colorless oil; IR (neat) ν_{max} 3427

cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.20 (m, 5H), 4.88 (dd, 1H, *J*=3.2, 3.2 Hz), 4.08-4.03 (m, 1H), 3.91-3.86 (m, 1H), 3.80-3.74 (m, 1H), 2.98 (d, 1H, *J*=2.7 Hz), 1.90-1.76 (m, 1H), 1.61-1.54 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 140.5, 128.0, 127.2, 125.9, 83.1, 73.9, 68.9, 25.9, 24.8; MS (EI) *m/z*: 178 (M⁺), 160, 71 (100%); HRMS calcd for C₁₁H₁₄O₂ (M⁺) 178.0994, found 178.0986.

***threo*-α-(Tetrahydro-2-furanyl)-1,3-benzodioxole-5-methanol (1c):** colorless oil; IR (neat) ν_{max} 3437 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.89 (d, 1H, *J*=1.22 Hz), 6.81 (dd, 1H, *J*=7.8, 1.7 Hz), 6.75 (d, 1H, *J*=8.06 Hz), 5.93 (s, 2H), 4.34 (d, 1H, *J*=7.57 Hz), 3.94 (dd, 1H, *J*=14.4, 7.08 Hz), 3.93-3.81 (m, 2H), 3.03 (brs, 1H), 1.95-1.54 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 147.6, 147.1, 134.6, 120.4, 108.0, 107.3, 100.9, 83.4, 76.8, 68.4, 27.9, 26.0; MS (EI) *m/z*: 222 (M⁺), 204, 151 (100%); HRMS calcd for C₁₂H₁₄O₄ (M⁺) 222.0892, found 222.0897.

***erythro*-α-(Tetrahydro-2-furanyl)-1,3-benzodioxole-5-methanol (2c):** colorless oil; IR (neat) ν_{max} 3416 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.89 (m, 1H, *J*=1.22 Hz), 6.83-6.79 (m, 1H), 6.76 (d, 1H, *J*=7.89 Hz), 5.93 (s, 2H), 4.79 (m, 1H), 4.04-3.98 (m, 1H), 3.94-3.87 (m, 1H), 3.82-3.75 (m, 1H), 2.56 (brs, 1H), 1.90-1.61 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 147.5, 146.7, 134.6, 119.3, 108.0, 106.6, 100.8, 83.1, 74.0, 68.9, 26.0,

25.2; MS (EI) m/z : 222 (M^+), 204, 151 (100%); HRMS calcd for $C_{12}H_{14}O_4$ (M^+)

222.0892, found 222.0888.

***threo*- α -(2-Bromophenyl)tetrahydro-2-furanmethanol (1d):** colorless oil; IR (neat)

$\nu_{\max}$ 3437 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.54-7.52 (m, 2H), 7.35-7.32 (m, 1H),

7.15-7.12 (m, 1H), 5.00 (dd, 1H, $J=5.6, 4.6$ Hz), 4.07 (dd, 1H, $J=12.9, 6.6$ Hz), 3.97 (dt,

1H, $J=7.6, 6.8$ Hz), 3.84 (dt, 1H, $J=7.6, 7.3$ Hz), 3.10 (d, 1H, $J=4.2$ Hz), 2.02-1.75 (m,

4H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.3, 132.5, 129.0, 128.5, 127.6, 122.8, 82.9, 73.9,

68.6, 27.7, 26.1; HRFAB MS calcd for $C_{11}H_{14}O_2\text{Br}$ (MH^+) 257.0177, found 257.0166.

***erythro*- α -(2-Bromophenyl)tetrahydro-2-furanmethanol (2d):** colorless solid, mp

81-83 $^{\circ}\text{C}$; IR (neat) $\nu_{\max}$ 3408 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.61-7.59 (m, 1H),

7.52-7.50 (m, 1H), 7.35-7.31 (m, 1H), 7.15-7.11 (m, 1H), 5.30 (m, 1H), 4.30-4.23 (m,

1H), 3.97-3.92 (m, 1H), 3.86-3.78 (m, 1H), 2.71 (d, 1H, $J=2.2$ Hz), 1.94-1.78 (m, 3H),

1.55-1.44 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.4, 132.4, 128.9, 128.0, 127.4,

122.1, 80.3, 72.6, 69.0, 26.2, 24.5; HRFAB MS calcd for $C_{11}H_{14}O_2\text{Br}$ (MH^+) 257.0177,

found 257.0137.

***threo*- α -Dodecyltetrahydro-2-furanmethanol (1e):** colorless waxy solid; IR (neat)

$\nu_{\max}$ 3470 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.80-3.63 (m, 3H), 3.38-3.30 (m, 1H),

2.59 (brs, 1H), 1.85-1.82 (m, 3H), 1.60-1.15 (m, 23H), 0.83 (t, 3H, $J=6.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 82.4, 73.8, 67.9, 33.7, 31.9, 29.7, 29.63, 29.62, 29.60, 29.58, 29.56, 29.3, 27.9, 26.2, 25.7, 22.6, 14.0; MS (EI) m/z : 270 (M^+), 252, 71 (100%); HRMS calcd for $\text{C}_{17}\text{H}_{34}\text{O}_2$ (M^+) 270.2550, found 270.2554.

erythro- α -Dodecyltetrahydro-2-furanmethanol (2e): colorless waxy solid; IR (neat) ν_{max} 3449 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.90-3.84 (m, 1H), 3.80-3.72 (m, 3H), 2.09 (brs, 1H), 1.92-1.74 (m, 4H), 1.55-1.20 (m, 23H), 0.87 (t, 3H, $J=6.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 82.2, 71.9, 68.5, 32.9, 32.0, 29.8, 29.7, 29.69, 29.65, 29.61, 29.4, 26.2, 26.0, 24.5, 22.7, 14.2; MS (EI) m/z : 270 (M^+), 252, 71 (100%); HRMS calcd for $\text{C}_{17}\text{H}_{34}\text{O}_2$ (M^+) 270.2550, found 270.2559.

threo- α -Cyclohexyltetrahydro-2-furanmethanol (1f): colorless oil; IR (neat) ν_{max} 3460 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.95-3.73 (m, 3H), 3.16 (dd, 1H, $J=5.1$, 5.1 Hz), 2.19 (brs, 1H), 1.95-1.60 (m, 9H), 1.45-1.05 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 79.5, 77.6, 68.2, 41.4, 30.0, 28.4, 27.8, 26.51, 26.48, 26.3, 26.27; MS (EI) m/z : 184 (M^+), 166, 112, 95, 71 (100%); HRMS calcd for $\text{C}_{11}\text{H}_{20}\text{O}_2$ (M^+) 184.1464, found 184.1460.

erythro- α -Cyclohexyltetrahydro-2-furanmethanol (2f): colorless oil; IR (neat) ν_{max}

3460 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 3.93-3.82 (m, 2H), 3.75-3.68 (m, 1H), 3.53-3.48 (m, 1H), 2.15 (s, 1H), 2.02-1.98 (m, 1H), 1.90-1.54 (m, 8H), 1.42-1.30 (m, 1H), 1.28-0.95 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 80.1, 75.8, 68.3, 40.4, 29.2, 29.0, 26.5, 26.3, 26.1, 25.9, 24.5; MS (EI) m/z : 184 (M^+), 166, 112, 95, 71 (100%); HRMS calcd for $\text{C}_{11}\text{H}_{20}\text{O}_2$ (M^+) 184.1464, found 184.1459.

anisaldehyde, threo, CDCl₃, 100MHz

anisaldehyde, erythro, CDCl₃, 400MHz

S10

anisaldehyde, erythro, CDCl₃, 100MHz

S11

S12

benzaldehyde, threo, CDCl₃, 100MHz

S13

benzaldehyde erythro.

S14

benzaldehyde erythro 13C

S15

piperonal threo, CDCl₃, 100MHz.

S17

ERYTHRO ALCOHOL PIPERONAL

S18

bromobenzaldehyde, threo, CDCl₃, 400MHz

S20

bromobenzaldehyde, CDCl₃, 13C, 100MHz

S21

S23

tridecanal threo

S24

tridecanal threo 13C, CDCl₃, 100MHz

S25

tridecanal erythro, CDCl₃, 400MHz.

S26

threo
cyclohexanecarboxaldehyde, *erythro*, CDCl₃, 100MHz

S29

cyclohexanecarboxaldehyde, erythro, CDCl₃, 400MHz

S30

cyclohexanecarboxaldehyde, erythro, CDCl₃, 100MHz

TABLE4-2 BENZALDEHYDE

TABLE4-2 BENZALDEHYDE

TABLE4-3 PIPERONAL

TABLE4-3 PIPERONAL

2-bromobenzaldehyde, table4-4, CDCl₃, 300MHz

S38

2-bromobenzaldehyde, table 4-4, CDCl₃, 300MHz

TABLE4-5 TRIDECANAL ACETATE