Supporting Information

Catalytic, Asymmetric Synthesis and Diastereoselective Aldol Reactions of Dipropionate Equivalents

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[2S, 4R, 5S]-N-(5-hydroxy-2,4,6-trimethyl-3-oxo-heptanoyl)-4,N-dimethyl-benzenesulfonamide (6a). HPLC analysis (Chiralcel OD-H, 0.46 cm × 25 cm, hexane:isopropanol= 96:4, flow rate: 0.4 mL/min, λ =282 nm) of purified **6a** revealed a 96.5:3.5 ratio of enantiomers ($R_{t\ 2S,4R,5S}$ =36.2 min, $R_{t\ 2R,4S,5R}$ =42.1 min). Data for **6a**: $[\alpha]_D^{23}$ = +11.2° (c 0.50, CHCl₃); IR(neat film) 3545, 2961, 2876, 1713, 1690, 1596, 1455, 1357, 1164, 982; ¹H NMR (CDCl₃, 400 MHz) δ 7.76 (d, 2H, J=8.4 Hz), 7.38 (d, 2H, J=8.2 Hz), 4.66 (q, 1H, J=7.1 Hz), 3.47 (td, 1H J=8.8, 2.6 Hz) 3.20 (s 3H), 2.95 (qd, 1H, J=7.1, 2.3 Hz), 2.55 (d, 1H, J=2.9 Hz) 2.47 (s, 3H), 1.70-1.65 (m, 1H) 1.37 (d, 3H, J=7.1 Hz), 1.14 (d, 3H, J=7.1 Hz), 1.04 (d, 3H, J=6.5 Hz), 1.00 (d, 3H, J=6.7 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 211.5, 171.0, 145.4, 135.4, 130.1, 127.5, 76.1, 53.4, 45.5, 33.2, 30.7, 21.7, 19.4, 18.9, 14.2, 9.3; Anal Calcd for C₁₈H₂₇NO₅S: C, 58.51; H, 7.37; N, 3.79; Found: C, 58.65; H, 7.36; N, 3.55.

[2S, 4R, 5S]-N-(5-hydroxy-2,4-dimethyl-3-oxo-octanoyl)-4,N-dimethyl-benzenesulfonamide (6b). Isolated as 5.8:1 mixture of diastereomers, data for mixture: IR(neat film) 3498, 2953, 2929, 2857, 1716, 1690, 1461, 1359, 1163, 1090, 993; ¹H NMR (CDCl₃, 400 MHz) δ 7.77 (d, 2H, J=8.2 Hz), 7.38 (d, 2H, J=8.1 Hz), 4.63 (q, 1H, J=7.3 Hz), 3.86 (m 1H), 3.22 (s 3H), 2.74 (m, 1H), 2.47 (s, 3H), 2.42 (d, 1H, J=3.1 Hz), 1.47-1.44 (m, 2H), 1.34 (d, 3H, J=7.0 Hz), 1.34-1.30 (m, 2H), 1.14 (d, 3H, J=7.1 Hz) 0.94 (t, 3H, J=6.8 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 210.9, 171.1, 145.4, 135.4, 130.2, 127.5, 71.1, 53.6, 53.3, 48.4, 35.9, 33.3, 21.7, 19.3, 14.0, 10.4; Anal Calcd for C₁₈H₂₇NO₅S: C, 58.51; H, 7.37; N, 3.79; Found: C, 58.53; H, 7.45; N, 3.69.

[2S, 4R, 5R]-N-(5-hydroxy-2,4-dimethyl-3-oxo-5-phenyl-pentanoyl)-4,N-dimethyl-benzenesulfonamide (6c). $[\alpha]_D^{23}$ = -1.16° (c 0.35, CHCl₃); IR(neat film) 3527, 3030, 2983, 2938, 1715, 1690, 1596, 1492, 1453, 1356, 1163, 990; ¹H NMR (CDCl₃, 400 MHz) δ 7.76 (d, 2H, J=8.4 Hz), 7.38-7.28 (m 7H), 5.03 (m, 1H,), 4.43 (q, 1H J=7.0 Hz) 3.19 (s 3H), 2.97 (m, 1H,), 2.76 (d, 1H, J=2.3 Hz) 2.45 (s, 3H), 1.22 (d, 3H, J=7.1 Hz), 1.11 (d, 3H, J=7.0 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 210.3, 171.0, 145.4, 141.5, 135.4, 130.2, 130.1, 128.3, 127.6, 126.0, 73.3, 53.8, 51.3, 33.2, 21.7, 13.7, 10.8; Anal Calcd for C₂₁H₂₅NO₅S: C, 62.51; H, 6.24; N, 3.47; Found: C, 62.32; H, 6.23; N, 3.23.

[2S, 4R, 5R]-N-(6-Benzoyloxy-5-hydroxy-2,4-dimethyl-3-oxo-hexanoyl)-4,N-dimethyl-benzenesulfonamide (6d). $[\alpha]_D^{23}$ = +4.15° (c 0.97, CHCl₃); IR(neat film) 3518, 2980, 2924, 2873, 1720, 1690, 1597, 1454, 1358, 1164, 1105, 1090, 994; ¹H NMR (CDCl₃, 400 MHz) δ 7.79 (d, 2H, J=8.3 Hz), 7.37-7.31 (m 7H), 4.64 (q, 1H, J=7.1 Hz), 4.53 (d 2H, J=5.1 Hz), 4.03 (m, 1H), 3.50 (m 1H), 3.41 (m 1H), 3.20 (s 3H), 2.91 (m, 1H), 2.54 (d, 1H, J=3.7 Hz) 2.45 (s, 3H), 1.32 (d, 3H, J=7.0 Hz), 1.14 (d, 3H, J=7.1 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 209.1, 171.4, 145.2, 137.7, 135.4, 130.0, 129.7, 128.5, 127.8, 127.6, 73.5, 71.3, 71.1, 54.0, 46.7, 33.2, 21.7, 13.8, 12.2; Anal Calcd for C₂₃H₂₉NO₆S: C, 61.73; H, 6.53; N, 3.13; Found: C, 61.53; H, 6.53; N, 2.93.

[2S, 4R, 5S]-N-[7-(tert-Butyl-dimethyl-silanyloxy)-5-hydroxy-2,4-dimethyl-3-oxo-heptanoyl]-4,N-dimethyl-benzenesulfonamide (6e). $[\alpha]_D^{23}$ = -6.47° (c 0.85, CHCl₃); IR(neat film) 3498, 2980, 2953, 2929, 2857, 1716, 1690, 1461, 1359, 1163, 1090, 993; ¹H NMR (CDCl₃, 400 MHz) δ 7.82 (d, 2H, J=8.4 Hz), 7.36 (d, 2H, J=8.2 Hz), 4.64 (q, 1H, J=7.1 Hz), 4.00 (m, 1H), 3.86 (m, 1H), 3.78 (m, 1H), 3.64 (d, 1H), 3.24 (s, 3H), 2.8 (m, 1H), 2.46 (s, 3H), 1.56 (m, 2H), 1.34 (d, 3H, J=7.1 Hz), 1.10 (d, 3H, J=7.0 Hz), 0.9 (s, 9H), 0.08 (d, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 209.1, 171.7, 145.2, 135.6, 130.0, 127.7, 72.8, 62.7, 54.6, 49.6, 35.0, 33.2, 25.8, 21.7, 18.1, 13.7, 12.1, -5.5, -5.6; Anal Calcd for C₂₃H₃₉NO₆SSi: C, 56.88; H, 8.09; N, 2.88; Found: C, 56.70; H, 7.86; N, 2.98.

[2S, 4R, 5R]-N-(5-hydroxy-2,4,6-trimethyl-3-oxo-hept-6-enoyl)-4,N-dimethyl-benzenesulfonamide (6f). $[\alpha]_D^{23}$ = +15.0° (c 1.22, CHCl₃); IR(neat film) 3531, 2982, 2940, 2878,

1714, 1691, 1596, 1453, 1356, 1164, 991; ^1H NMR (CDCl_3 , 400 MHz) δ 7.77 (d, 2H, $J=8.4$ Hz), 7.38 (d, 2H, $J=8.0$ Hz), 5.10 (s, 1H), 4.96 (s, 1H), 4.67 (q, 1H, $J=7.0$ Hz), 4.49 (s, 1H), 3.19 (s, 3H), 2.91 (d, 1H), 2.82 (m, 1H), 2.47 (s, 3H), 1.65 (s, 3H), 1.39 (d, 3H, $J=7.0$ Hz), 1.01 (d, 3H, $J=7.1$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 210.4, 171.0, 145.4, 143.4, 135.4, 130.1, 127.6, 111.9, 73.5, 53.3, 46.2, 33.2, 21.7, 19.4, 14.1, 9.6; Anal Calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_5\text{S}$: C, 58.83; H, 6.86; N, 3.81; Found: C, 59.10; H, 6.81; N, 3.55.

[2R, 4R, 5R]-3,4-Dimethoxy-benzoic acid 7-benzyloxy-5-hydroxy-2,4-dimethyl-3-oxo-heptyl ester (9a). $[\alpha]_{\text{D}}^{23} = -17.7^\circ$ (c 1.05, CHCl_3); IR (neat) 3064, 2936, 1714, 1600, 1515, 1456, 1417, 1365, 1346, 1291, 1271, 1222, 1177, 1133, 1108, 1025, 984, 875 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (dd, $J = 1.9, 8.4$ Hz, 1H), 7.51 (d, $J = 1.9$ Hz, 1H), 7.36-7.30 (m, 5H), 6.89 (d, $J = 8.4$ Hz, 1H), 4.53 (s, 3H), 4.48 (dd, $J = 8.1, 10.9$ Hz, 1H), 4.41 (dd, $J = 5.1, 10.9$ Hz, 1H), 3.99-3.97 (m, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 3.75-3.73 (m, 1H), 3.71-3.66 (m, 1H), 3.21-3.17 (m, 1H), 2.86 (apparent quintet, $J = 7.2$ Hz, 1H), 1.86-1.82 (m, 1H), 1.78-1.73 (m, 1H), 1.18 (d, $J = 7.0$ Hz, 3H), 1.10 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 215.8, 166.0, 153.0, 148.6, 137.8, 128.4, 127.8, 127.7, 123.5, 122.3, 111.8, 110.2, 73.4, 72.8, 68.6, 65.6, 56.0, 55.9, 50.8, 45.5, 33.9, 13.2, 13.1. Anal. Calcd for $\text{C}_{25}\text{H}_{32}\text{O}_7$: C, 67.55; H, 7.26. Found: C, 67.82; H, 7.30.

[2R,4R,5R]-3,4-Dimethoxy-benzoic acid 5-hydroxy-2,4,6-trimethyl-3-oxo-heptyl ester (10a). $[\alpha]_{\text{D}}^{23} = -11.5^\circ$ (c 1.34, CHCl_3); IR (neat film) 3535, 2964, 2878, 1711, 1599, 1515, 1462, 1417, 1371, 1346, 1271, 1223, 1177, 1023 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.62 (dd, 1H, $J=1.9, 8.4$ Hz), 7.49 (d, 1H, $J=1.9$ Hz), 6.87 (d, 1H, $J=8.5$ Hz), 4.47 (dd, 1H, $J=8.3, 10.9$ Hz), 4.35 (dd, 1H, $J=5.1, 11.3$ Hz), 3.93 (s, 3H), 3.91 (s, 3H), 3.53 (m, 1H), 3.22-3.17 (m, 1H), 2.96-2.89 (m, 1H), 2.38 (d, 1H, $J=6.3$ Hz), 1.80-1.72 (m, 1H), 1.18 (d, 3H, $J=7.1$ Hz), 1.11 (d, 3H, $J=7.2$ Hz), 0.97 (d, 3H, $J=6.8$ Hz), 0.91 (d, 3H, $J=6.8$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 216.6, 166.0, 153.1, 148.6, 123.5, 122.3, 111.9, 110.2, 77.8, 65.5, 56.0, 55.9, 48.0, 45.3, 30.1, 20.0, 15.5, 13.7, 13.4; Anal Calcd for $\text{C}_{19}\text{H}_{28}\text{O}_6$: C, 64.75; H, 8.01; Found: C, 64.69; H, 8.29.

[2R,4R,5R]-3,4-Dimethoxy-benzoic acid 5-hydroxy-2,4-dimethyl-3-oxo-octyl ester (10b). White solid, m.p. 78-79°C; $[\alpha]_{\text{D}}^{23} = -5.00^\circ$ (c 1.80, CHCl_3); IR (neat film) 3408, 3343, 2953, 2894, 2872, 1708, 1596, 1515, 1463, 1414, 1375, 1345, 1275, 1222, 1180, 1017 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.60 (dd, 1H, $J=1.8, 8.0$ Hz), 7.47 (d, 1H, $J=1.8$ Hz), 6.86 (d, 1H, $J=8.4$ Hz), 4.46 (dd, 1H, $J=8.5, 10.8$ Hz), 4.33 (dd, 1H, $J=5.0, 10.9$ Hz), 3.92 (s, 3H), 3.89 (s, 3H), 3.72 (m, 1H), 3.21-3.12 (m, 1H), 2.81-2.74 (m, 1H), 2.60 (s, 1H), 1.55-1.44 (m, 4H), 1.16 (d, 3H, $J=7.1$ Hz), 1.13 (d, 3H, $J=7.2$ Hz), 0.91 (t, 3H, $J=7.0$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 216.6, 166.0, 153.0, 148.6, 123.5, 122.3, 111.8, 110.2, 73.1, 65.3, 56.0, 55.9, 50.7, 45.1, 36.7, 18.7, 13.9, 13.7, 13.3; Anal Calcd for $\text{C}_{19}\text{H}_{28}\text{O}_6$: C, 64.75; H, 8.01; Found: C, 64.54; H, 8.03.

[2R,4R,5S]-3,4-Dimethoxy-benzoic acid 5-hydroxy-2,4-dimethyl-3-oxo-5-phenyl-pentyl ester (10c). White solid, m.p. 39-40°C; $[\alpha]_{\text{D}}^{23} = -39.2^\circ$ (c 2.00, CHCl_3); IR (neat film) 3513, 2971, 2936, 1711, 1598, 1514, 1458, 1417, 1348, 1271, 1223, 1177, 1024 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 7.60 (dd, 1H, $J=1.9, 8.4$ Hz), 7.47 (d, 1H, $J=1.9$ Hz), 7.37-7.27 (m, 5H), 6.86 (d, 1H, $J=8.4$ Hz), 4.79 (dd, 1H, $J=3.8, 8.0$ Hz), 4.47 (dd, 1H, $J=8.1, 10.9$ Hz), 4.35 (dd, 1H, $J=5.1, 10.9$ Hz), 3.92 (s, 3H), 3.88 (s, 3H), 3.22-3.16 (m, 1H), 3.16-3.06 (m, 1H), 2.88 (d, 1H, $J=4.3$ Hz), 1.11 (d, 3H, $J=7.1$ Hz), 0.95 (d, 3H, $J=7.2$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 215.9, 166.0, 153.0, 148.6, 142.1, 128.5, 128.0, 126.5, 123.5, 122.3, 111.8, 110.2, 76.4, 65.4, 56.0, 55.9, 52.4, 45.7, 14.1, 12.9; Anal Calcd for $\text{C}_{22}\text{H}_{26}\text{O}_6$: C, 68.38; H, 6.78; Found: C, 67.09; H, 6.29.

[2R,4R,5R]-3,4-Dimethoxy-benzoic acid 5-hydroxy-2,4,6-trimethyl-3-oxo-hept-6-enyl ester (10d). White solid, m.p. 68-70°C; $[\alpha]_{\text{D}}^{23} = -28.1^\circ$ (c 1.62, CHCl_3); IR (KBr) 3517, 2972, 2936, 1711, 1599, 1514, 1459, 1417, 1371, 1348, 1271, 1223, 1177, 1024 cm^{-1} ; ^1H NMR (CDCl_3 , 400

MHz) δ 7.60 (dd, 1H, J=1.8, 8.6 Hz), 7.48 (d, 1H, J=1.4 Hz), 6.86 (d, 1H, J=8.4 Hz), 4.94 (s, 1H), 4.91 (s, 1H), 4.47 (dd, 1H, J=8.0, 10.8 Hz), 4.35 (dd, 1H, J=5.1, 10.9 Hz), 4.22 (d, 1H, J=8.2 Hz), 3.92 (s, 3H), 3.90 (s, 3H), 3.23-3.15 (m, 1H), 2.98-2.90 (m, 1H), 2.39 (s, 1H), 1.73 (s, 3H), 1.23 (d, 3H, J=8.4 Hz), 0.98 (d, 3H, J=7.1 Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 215.5, 166.0, 153.0, 148.5, 144.5, 123.5, 122.3, 114.2, 111.8, 110.2, 78.2, 65.5, 55.9, 55.9, 48.1, 45.7, 16.7, 13.8, 13.0; Anal Calcd for $\text{C}_{19}\text{H}_{26}\text{O}_6$: C, 65.13; H, 7.48; Found: C, 65.09; H, 7.53.