Supporting Information

A versatile strategy for the synthesis of 2,6-disubstituted dihydropyranones

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Materials and Methods: Reactions were carried out in oven or flame-dried glassware under an argon atmosphere, unless otherwise noted. All solvents were reagent grade. Diethyl ether (Et₂O) and tetrahydrofuran (THF) were freshly distilled from sodium / benzophenone under argon. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) with 0.25 mm pre-coated silica gel plates. Flash chromatography was performed with silica gel 60 (particle size 0.040 – 0.062 mm). Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise stated. Proton and carbon-13 NMR spectra were recorded on a 300 MHz spectrometer. Chemical shifts are reported relative to chloroform (δ 7.26) for ¹H NMR and chloroform (δ 77.0) ¹³C NMR. Optical rotations were measured on a polarimeter (Hg, λ_{546}).

Experimental Procedures and Compound Characterization Data

3a: To a well stirred solution of TBS-dithiane **1** (120 mg, 0.51 mmol) in THF (1 mL) was added *n*-BuLi (1.6 M in hexane, 0.35 mL) via syringe at r.t. and the reaction mixture was stirred for 10 min. A solution of (*R*)-(+)-propylene oxide (120 mg, 0.51 mmol) in THF/HMPA (35.8 mg HMPA in 0.5 mL THF) was then added to the reaction mixture at -78 °C. The mixture was warm to room temperature over 1.5 h and then quenched with saturated aqueous NH₄Cl (1 mL). The layers were separated. The aqueous phase was extracted with Et₂O (3 × 10 mL), and the combined organic layers were dried over Na₂SO₄, filtered and concentrated *in vacuo*. Flash chromatography (hexanes/ethyl acetate 30:1) provided (-)-**3a** (171.5 mg, 96%). [α]_D²³ -40.8 (*c* 1.1, CDCl₃); ¹H NMR (300 MHz, CDCl₃) δ 4.36-4.26 (m, 1H), 4.21-4.13 (m, 1H), 3.92 (d, *J*=3.6 Hz, 1H), 2.87-2.73 (m, 4H), 2.44-2.22 (m, 2H), 2.14-1.94 (m, 4H), 1.25 (d, *J*=6.0 Hz, 3H), 1.19 (d, *J*=6.6 Hz, 3H), 0.92 (s, 9H), 0.16 (s, 3H), 0.14 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 66.9, 64.1, 51.4, 47.1, 46.9, 26.2, 25.7, 25.1, 24.7, 18.0, -3.6, -4.2; mass spectrum (ESI) *m/z* 389.5, [M+K]⁺, HRMS (ES⁺) *m/z* 373.1676 [(M+Na)⁺; calcd for C₁₆H₃₄O₂S₂SiNa: 373.1667].

3b was prepared using the same procedure for **3a**. Yield: 91%; $[\alpha]_D^{23}$ -55.0 (*c* 0.5, MeOH); ^1H NMR (300 MHz, CDCl_3) δ 7.54 (m, 10H), 5.36 (d, $J=8.7$ Hz, 2H), 5.03 (br, s, 1H), 3.03 (m, 5H), 2.78 (dd, $J=9.3, 13.1$ Hz, 1H), 2.65 (d, $J=15.3$ Hz, 1H), 2.48 (d, $J=15.3$ Hz, 1H), 2.16 (m, 2H), 1.01 (s, 9H), 0.24 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 145.7, 144.9, 128.5, 128.2, 127.7, 126.8, 126.3, 125.5, 74.3, 69.9, 51.7, 49.3, 47.1, 29.7, 26.2, 25.9, 25.1, 18.1, -4.0, -4.4; mass spectrum (ESI) m/z 497.5, $[\text{M}+\text{Na}]^+$.

3c was prepared using the same procedure for **3a**. Yield: 96%; $[\alpha]_D^{23}$ -30.6 (*c* 1.0, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.25 (m, 10H), 4.49 (s, 2H), 4.45 (s, 2H), 4.19 (m, 2H), 3.56 (d, $J=3.3$ Hz, 1H), 3.40-3.22 (m, 4H), 2.73 (m, 4H), 2.43 (dd, $J=3.0, 15.3$ Hz, 1H), 2.20 (m, 3H), 1.84 (m, 2H), 0.79 (s, 9H), 0.05 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 138.2, 138.1, 128.3, 128.2, 127.7, 127.6, 127.5, 74.55, 74.53, 73.14, 73.11, 69.5, 67.0, 51.4, 43.0, 42.8, 26.2, 26.0, 25.9, 24.9, 18.0, -3.6, -4.3; mass spectrum (ESI) m/z 585.6, $[\text{M}+\text{Na}]^+$.

Compounds 3d-3g were prepared following the procedure developed by Smith et al¹ Yield: 65%; $[\alpha]_D^{23}$ -45.7 (*c* 1.1, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.38-7.23 (m, 10H), 5.12 (dd, $J=9.6, 2.7$ Hz, 1H), 4.58 (s, 2H), 4.24-4.17 (m, 2H), 3.49-3.31 (m, 2H), 2.91-2.64 (m, 5H), 2.40-2.19 (m, 3H), 2.01-1.90 (m, 2H), 0.81 (s, 9H), 0.06 (s, 3H), -0.24 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 142.5, 138.3, 128.4, 128.3, 127.7, 127.6, 127.5, 125.3, 74.6, 73.9, 73.1, 70.0, 51.5, 47.6, 42.5, 26.1, 26.0, 25.2, 18.1, -4.1, -4.4; mass spectrum (ESI) m/z 557.3, $[\text{M}+\text{K}]^+$.

Yield: 60%; $[\alpha]_D^{23}$ -36.8 (*c* 0.5, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.38-7.20 (m, 10H), 5.14-5.10 (m, 1H), 4.52 (s, 2H), 4.28-4.26 (m, 1H), 4.23 (d, $J=2.7$ Hz, 1H), 3.46 (dd, $J=4.2, 9.3$ Hz, 1H), 3.34

(1) Smith III, A. B.; Boldi, A. M. *J. Am. Chem. Soc.* **1997**, *119*, 6925.

(dd, $J=6.9, 9.3$ Hz, 1H), 2.86-2.76 (m, 4H), 2.60-2.30 (m, 4H), 1.98-1.92 (m, 2H), 0.84 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 145.4, 138.0, 128.4, 128.3, 127.65, 127.60, 126.9, 125.6, 74.4, 73.2, 70.2, 69.8, 51.6, 49.5, 42.3, 26.4, 26.0, 25.9, 25.0, 18.1, -3.4, -4.4; mass spectrum (ESI) m/z 557.7, $[\text{M}+\text{K}]^+$.

Yield: 64%; $[\alpha]_{\text{D}}^{23}$ -35.4 (c 1.43, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.35-7.33 (m, 5H), 4.53 (s, 2H), 4.28-4.22 (m, 1H), 3.97-3.92 (m, 1H), 3.66 (d, $J=2.7$ Hz, 1H), 3.46 (dd, $J=9.6, 4.5$ Hz, 1H), 3.34 (dd, $J=9.6, 7.2$ Hz, 1H), 2.91-2.75 (m, 4H), 2.52 (dd, $J=15.6, 2.7$ Hz, 1H), 2.29-2.13 (m, 2H), 2.07-1.96 (m, 3H), 1.51-1.41 (m, 2H), 0.94 (t, $J=7.5$ Hz, 3H), 0.87 (s, 9H), 0.14 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 138.3, 128.6, 127.9, 127.8, 74.4, 73.4, 70.1, 69.1, 51.8, 46.5, 42.7, 31.4, 26.6, 26.2, 25.3, 18.3, 10.1, -3.3, -4.0; mass spectrum (ESI) m/z 493.7, $[\text{M}+\text{Na}]^+$.

Yield: 84%; $[\alpha]_{\text{D}}^{23}$ -25.1 (c 0.3, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.35-7.28 (m, 5H), 4.57 (d, $J=1.5$ Hz, 2H), 4.21-4.13 (m, 2H), 3.99 (d, $J=3.9$ Hz, 1H), 3.43 (ddd, $J=30.3, 10.2, 4.2$ Hz, 2H), 2.91-2.70 (m, 4H), 2.41-2.21 (m, 4H), 2.12-1.93 (m, 4H), 0.93 (t, $J=7.2$ Hz, 3H), 0.89 (s, 9H), 0.14 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 138.7, 128.6, 128.0, 127.8, 74.9, 73.5, 71.4, 67.5, 51.8, 43.8, 42.4, 30.7, 29.1, 24.5, 17.5, -4.0, -5.0; mass spectrum (ESI) m/z 493.7, $[\text{M}+\text{Na}]^+$.

(Sa): To a well stirred solution of (-)-**3a** (31 mg, 0.09 mmol) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (4 mL/1 mL) was added $\text{HgCl}_2/\text{CaCO}_3$ (72 mg, 0.26 mmol; 36 mg, 0.35 mmol) in one portion. The reaction mixture was warmed to 65 $^\circ\text{C}$ and stirred for 2h. After starting material disappeared (monitored by TLC), Et_2O (20 mL) was added to the mixture and filtered through celite. The aqueous phase was extracted with Et_2O (3×5 mL), and the combined organic phase were dried over Na_2SO_4 , filtered and concentrated *in vacuo*. Flash chromatograph (hexanes/ethyl acetate 15:1) gave **Sa** as colorless oil (17.5 mg, 77%) $[\alpha]_{\text{D}}^{23}$ -89.7 (c 0.8, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 4.33-4.19 (m, 2H), 3.14 (d, $J=3.0$ Hz, 1H), 2.70-2.36 (m, 4H), 1.18 (s, 3H), 1.16 (s, 3H), 0.86 (s, 9H), 0.07 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (75

MHz, CDCl₃) δ 212.3, 66.7, 64.6, 53.8, 53.5, 26.7, 25.1, 23.1, 18.9, -3.5, -4.0; mass spectrum (ESI) m/z 283.5, [M+Na]⁺.

Sb was prepared using the same procedure for **Sa**. Yield: 84%; $[\alpha]_D^{23}$ -151.0 (*c* 1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.30 (m, 10H), 5.14 (m, 2H), 3.33 (d, *J*=3.0 Hz, 1H), 2.90-2.80 (m, 3H), 2.50 (dd, *J*=3.6, 14.7 Hz, 1H), 0.82 (s, 9H), -0.01 (s, 3H), -0.21 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 209.7, 144.0, 142.6, 128.5, 128.3, 127.6, 127.5, 125.7, 125.6, 71.9, 69.6, 54.1, 53.3, 25.7, 18.0, -4.7, -5.2; mass spectrum (ESI) m/z 407.5, [M+Na]⁺.

Sc was prepared using the same procedure for **Sa**. Yield: 90%; $[\alpha]_D^{23}$ -32.5 (*c* 1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.30 (m, 10H), 4.52 (s, 2H), 4.48 (s, 2H), 4.31 (m, 1H), 4.22 (m, 1H), 3.42 (m, 2H), 3.30 (dd, *J*=6.0, 9.6 Hz, 1H), 2.96 (d, *J*=3.6 Hz, 1H), 2.63 (m, 4H), 0.81 (s, 9H), 0.02 (s, 3H), 0.00 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 209.2, 138.0, 137.9, 128.4, 128.3, 127.73, 127.70, 127.6, 74.0, 73.33, 73.26, 73.2, 67.9, 66.6, 48.6, 47.3, 25.8, 17.9, -4.6, -5.0; mass spectrum (ESI) m/z 495.7, [M+Na]⁺.

Sd was prepared using the same procedure for **Sa**. Yield: 87%; $[\alpha]_D^{23}$ -91.8 (*c* 0.7, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.39-7.23 (m, 10H), 5.16 (dd, *J*=8.7, 3.6 Hz, 1H), 4.55 (s, 2H), 4.27 (m, 1H), 3.44 (m, 2H), 3.01-2.52 (m, 5H), 0.82 (s, 9H), -0.01 (s, 3H), -0.20 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 209.1, 114.2, 137.8, 128.4, 128.3, 127.8, 127.7, 127.4, 125.7, 75.4, 73.1, 71.8, 66.5, 54.3, 47.8, 26.2, 25.6, 18.0, -4.9, -5.3; mass spectrum (ESI) m/z 467.3, [M+K]⁺.

Se was prepared using the same procedure for **Sa**. Yield: 89%; $[\alpha]_D^{23}$ -58.0 (*c* 0.5, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.29 (m, 10H), 5.06 (m, 1H), 4.46 (s, 2H), 4.31 (m, 1H), 3.40 (dd, *J*=4.8, 9.6 Hz, 1H), 3.30 (d, *J*=3.0 Hz, 1H), 3.29 (dd, *J*=6.0, 9.6 Hz, 1H), 2.82-2.78 (m, 2H), 2.62-2.59 (m, 2H), 0.80 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 209.9, 142.7, 138.0, 128.5, 128.4,

127.7, 127.6, 125.6, 73.9, 73.3, 69.6, 68.0, 52.8, 48.7, 25.8, 18.0, -4.6, -5.0; mass spectrum (ESI) m/z 467.6, $[M+K]^+$.

Sf was prepared using the same procedure for **Sa**. Yield: 95%; $[\alpha]_D^{23}$ -64.9 (c 0.8, $CHCl_3$); 1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.27 (m, 5H), 4.51 (s, 2H), 4.38-4.30 (m, 1H), 3.95-3.91 (m, 1H), 3.39 (ddd, $J=31.5, 9.6, 4.8$ Hz, 2H), 3.03 (d, $J=3.0$ Hz, 1H), 2.66-2.48 (m, 4H), 1.55-1.39 (m, 2H), 0.92 (t, $J=7.5$ Hz, 3H), 0.86 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.8, 137.9, 128.3, 128.2, 127.6, 73.9, 73.3, 68.7, 68.0, 50.4, 48.6, 29.1, 25.7, 18.0, 9.8, -4.6, -4.9; mass spectrum (ESI) m/z 403.5, $[M+Na]^+$.

Sg was prepared using the same procedure for **Sa**. Yield: 90%; $[\alpha]_D^{23}$ -41.8 (c 1.0, $CHCl_3$); 1H NMR (300 MHz, $CDCl_3$) δ 7.35-7.29 (m, 5H), 4.55 (s, 2H), 4.30-4.22 (m, 1H), 4.13-4.09 (m, 1H), 3.46 (ddd, $J=14.7, 9.9, 4.8$ Hz, 2H), 3.03 (d, $J=3.6$ Hz, 1H), 2.69-2.43 (m, 4H), 1.51-1.43 (m, 2H), 0.86 (t, $J=7.2$ Hz, 3H), 0.85 (s, 9H), 0.05 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.9, 137.7, 128.2, 127.5, 127.4, 73.1, 72.9, 69.7, 66.4, 49.9, 47.3, 30.1, 25.6, 17.7, 9.0, -4.9, -5.0; mass spectrum (ESI) m/z 403.4, $[M+Na]^+$.

(5a): To a well stirred solution of (-)-**3a** (30 mg, 0.09mmol) in CH_2Cl_2 (2 mL) was added DMP (40 mg, 0.09 mmol) and $NaHCO_3$ (84 mg, 1mmol) at room temperature. The mixture was stirred for another 10 min, quenched with saturated aqueous $Na_2S_2O_3$ (1 mL) and the layers were separated. The aqueous phase was extracted with Et_2O (3×10 mL), and the combined organic layers were dried over Na_2SO_4 , filtered and flash chromatograph (hexanes/ethyl acetate, 93:7) gave **5a** as colorless oil (28 mg, 93%). $[\alpha]_D^{23}$ -28.8 (c 1.0, $CHCl_3$); 1H NMR (300 MHz, $CDCl_3$) δ 4.25 (m, 1H), 3.34 (d, $J=15.6$ Hz, 1H), 3.10 (d, $J=15.6$ Hz, 1H), 2.82-2.79 (m, 4H), 2.47 (dd, $J=7.5, 15.0$ Hz, 1H), 2.23 (s, 3H), 2.16 (dd, $J=3.3, 15.0$ Hz, 1H), 2.00-1.90 (m, 2H), 1.23 (d, $J=6.3$ Hz, 3H), 0.88 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.6, 66.4, 51.2, 49.0, 47.1, 32.1, 26.5, 26.4, 26.0, 25.7, 24.8, 18.0, -3.9, -4.0; mass spectrum (ESI) m/z 371.5, $[M+Na]^+$.

5b was prepared using the same procedure for **5a**. Yield: 85%; $[\alpha]_D^{23}$ -57.9 (*c* 1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 8.29 (m, 2H), 7.96-7.45 (m, 8H), 5.45 (dd, *J*=3.6, 8.4 Hz, 1H), 4.23 (d, *J*=16.5 Hz, 1H), 3.90 (d, *J*=16.5 Hz, 1H), 3.39 (dd, *J*=8.4, 15.0 Hz, 1H), 3.25-3.05 (m, 4H), 2.88 (dd, *J*=3.6, 15.0 Hz, 1H), 2.33 (m, 2H), 1.09 (s, 9H), 0.38 (s, 3H), 0.00 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 195.5, 145.5, 137.7, 132.8, 128.3, 128.2, 128.1, 127.3, 126.6, 73.8, 49.9, 46.3, 45.9, 26.4, 26.3, 25.8, 24.9, 17.9, -4.3, -4.4; mass spectrum (ESI) *m/z* 495.5, [M+Na]⁺.

5c was prepared using the same procedure for **5a**. Yield: 90%; $[\alpha]_D^{23}$ -15.2 (*c* 0.75, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.27 (m, 10H), 4.52 (s, 2H), 4.47 (s, 2H), 4.10 (m, 1H), 4.07 (s, 2H), 3.28 (m, 2H), 3.10 (dd, *J*=15.3, 27.3 Hz, 2H), 2.68 (m, 4H), 2.50 (dd, *J*=3.6, 15.0 Hz, 1H), 2.27 (dd, *J*=6.6, 15.3 Hz, 1H), 1.88 (m, 2H), 0.79 (s, 9H), 0.05 (s, 3H), 0.00 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 204.1, 138.2, 137.2, 128.4, 128.3, 128.0, 127.9, 127.6, 127.5, 76.1, 74.8, 73.2, 73.1, 69.4, 49.1, 47.1, 43.2, 26.6, 26.3, 25.9, 24.6, 18.0, -4.0, -4.0; mass spectrum (ESI) *m/z* 583.4, [M+Na]⁺.

5d was prepared using the same procedure for **5a**. Yield: 77%; $[\alpha]_D^{23}$ -36.9 (*c* 1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.70-7.60 (m, 10H), 5.39 (dd, *J*=3.6, 8.1 Hz, 1H), 4.89 (s, 2H), 4.36 (s, 2H), 3.68 (d, *J*=15.9 Hz, 1H), 3.39 (d, *J*=15.9 Hz, 1H), 3.08 (m, 4H), 3.06 (dd, *J*=8.1, 15.0 Hz, 1H), 2.72 (dd, *J*=3.6, 15.0 Hz, 1H), 2.23 (m, 2H), 1.14 (s, 9H), 0.37 (s, 3H), 0.00 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 204.1, 145.5, 137.2, 128.4, 128.2, 128.0, 127.9, 127.4, 126.6, 75.9, 73.3, 73.2, 49.1, 47.6, 46.2, 26.4, 25.9, 24.8, 18.0, -4.4, -4.5; mass spectrum (ESI) *m/z* 539.3, [M+Na]⁺; 555.5, [M+K]⁺.

5e was prepared using the same procedure for **5a**. Yield: 80%; $[\alpha]_D^{23}$ -38.1 (*c* 0.7, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.95-7.92 (m, 2H), 7.55-7.23 (m, 8H), 4.48 (s, 2H), 4.24 (m, 1H), 3.73 (d, *J*=16.2 Hz, 1H), 3.58 (d, *J*=16.2 Hz, 1H), 3.52-3.36 (m, 2H), 2.96-2.50 (m, 6H), 1.88 (m, 2H), 0.76 (s, 9H), 0.05 (s, 3H), 0.00 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 195.6, 138.3, 137.9, 132.9, 128.4, 128.3, 128.2, 127.6, 127.5, 74.8, 73.2, 69.8, 50.0, 46.4, 42.1, 26.6, 26.2, 25.9, 24.8, 18.0, -3.9, -4.1; mass spectrum (ESI) *m/z* 539.4, [M+Na]⁺.

5f was prepared using the same procedure for **5a**. Yield: 72%; $[\alpha]_D^{23}$ -18.3 (*c* 0.6, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.30-7.20 (m, 5H), 4.46 (dd, *J*=12.3 Hz, 2H), 4.20-4.11 (m, 1H), 3.36 (ddd, *J*=23.6, 9.6, 4.9 Hz, 2H), 3.00 (dd, *J*=34, 16 Hz, 2H), 2.89-2.62 (m, 4H), 2.56-2.20 (m, 4H), 1.92-1.78 (m, 2H), 0.95 (t, *J*=7 Hz, 3H), 0.78 (s, 9H), 0.05 (s, 3H), -0.01 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 206.9, 136.3, 128.3, 127.6, 127.5, 74.8, 73.2, 69.6, 50.6, 49.1, 42.4, 37.7, 26.6, 26.2, 26.0, 24.8, 18.1, 14.3, 1.0, -3.9; mass spectrum (ESI) *m/z* 491.4, [M+Na]⁺.

5g was prepared using the same procedure for **5a**. Yield: 84%; $[\alpha]_D^{23}$ -24.4 (*c* 0.5, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.28 (m, 5H), 4.53 (s, 2H), 4.06 (s, 2H), 4.05 (m, 1H), 3.23 (d, *J*=15.3 Hz, 1H), 3.09 (d, *J*=15.3 Hz, 1H), 2.86-2.63 (m, 4H), 2.25 (dd, *J*=6.9, 15.0 Hz, 1H), 2.14 (dd, *J*=3.9, 15.0 Hz, 1H), 1.88 (m, 2H), 1.60-1.40 (m, 2H), 0.83 (t, *J*=7.5 Hz, 3H), 0.80 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 204.2, 137.2, 128.4, 128.0, 127.9, 76.1, 73.2, 70.6, 49.1, 46.5, 44.6, 31.4, 26.6, 26.4, 26.0, 24.7, 18.1, 8.7, -3.8, -4.6; mass spectrum (ESI) *m/z* 491.4, [M+Na]⁺.

Procedure A (obtained from (-)-**Sa** by DMP oxidation): To a well stirred solution of (-)-**Sa** (28 mg, 0.11 mmol) in CH₂Cl₂ (2 mL) was added DMP (50 mg, 0.12 mmol) and NaHCO₃ (84 mg, 1 mmol) at room temperature. The mixture was stirred for another 15 min, quenched with saturated aqueous Na₂S₂O₃ (1 mL) and the layers were separated. The aqueous phase was extracted with Et₂O (3 × 10

mL), and the combined organic layers were dried over Na₂SO₄, filtered and concentrated. Flash chromatograph (hexanes/ethyl acetate, 50:1) gave (-)-**4a** as colorless oil (26 mg, 94%).

Procedure B (obtained from (-)-**5a** by dithiane group removal): To a well stirred solution of (-)-**5a** (28 mg, 0.08 mmol) in CH₃CN/H₂O (6 mL/2 mL) was added HgCl₂ (109 mg, 0.4 mmol) and CaCO₃ (80 mg, 0.8 mmol). The reaction mixture was stirred at room temperature until (-)-**5a** disappeared (monitored by TLC). Et₂O (20 mL) was added to the mixture and filtered through celite. The aqueous phase was extracted with Et₂O (3 × 5 mL), and the combined organic phases were dried over Na₂SO₄, filtered and concentrated *in vacuo*. Flash chromatograph (hexanes/ethyl acetate 50:1) gave (-)-**4a** as colorless oil (12.4 mg, 60%).

[α]_D²³ -99.0 (*c* 0.5, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 5.53 (s, 1H), 4.27-4.21 (m, 1H), 2.43-2.24 (m, 2H), 2.07 (s, 3H), 1.20 (d, *J*=6.0 Hz, 3H), 0.87 (s, 10H), 0.06 (s, 3H), 0.01 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 192.6, 190.4, 101.6, 66.3, 48.3, 25.7, 25.3, 24.2, 18.0, -4.6, -5.1; mass spectrum (ESI) *m/z* 281.5, [M+Na]⁺.

Yield: (Procedure A: 96%, Procedure B: 80%)

Procedure C: Compound (-)-**4b** was also obtained from (-)-**3a** directly upon treatment with NBS: to a well stirred solution of NBS (310 mg, 1.74 mmol) in 10 mL acetone/water (97:3) was slowly added a solution of (-)-**3a** (47.2 mg, 0.1 mmol) in acetone (1 mL) via syringe in 20 min at 0 °C. The mixture was stirred for 2h at 0 °C. The reaction was then quenched with saturated aqueous NaHSO₃ (3 mL) and the layers were separated. The aqueous phase was extracted with Et₂O (3 × 5 mL), and the organic layers were dried over Na₂SO₄, filtered and concentrated. Flash chromatograph provided (-)-**4b** (26 mg, 68%).

[α]_D²³ -78.2 (*c* 1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 8.14 (m, 2H), 7.73-7.60 (m, 8H), 6.45 (s, 1H), 5.46 (dd, *J*=3.9, 9.0 Hz, 1H), 3.04 (dd, *J*=9.0, 13.5 Hz, 1H), 2.90 (dd, *J*=3.9, 13.5 Hz, 1H), 1.08 (s, 10H), 0.24 (s, 3H), 0.11 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 192.8, 184.1, 144.5, 135.0, 132.3, 128.6, 128.3, 127.0, 125.6, 98.2, 72.5, 50.8, 25.7, 18.1, -4.8, -5.3; mass spectrum (ESI) *m/z* 405.5, [M+Na]⁺; HRMS (ES⁺) *m/z* 405.1877 [(M+Na)⁺; calcd for C₂₃H₃₀O₃SiNa: 405.1862].

Yield: (Procedure A: 97%, Procedure B: 80%); $[\alpha]_D^{23}$ -57.5 (*c* 1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.32 (m, 10H), 5.88 (s, 1H), 4.54 (d, *J*=12.6 Hz, 4H), 4.24 (m, 1H), 4.04 (s, 2H), 3.46 (dd, *J*=5.1, 9.6 Hz, 1H), 3.38 (dd, *J*=5.1, 9.6 Hz, 1H), 2.61 (dd, *J*=4.5, 14.1 Hz, 1H), 2.41 (dd, *J*=8.4, 14.1 Hz, 1H), 0.83 (s, 10H), 0.03 (s, 3H), 0.00 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 192.8, 190.4, 138.1, 137.2, 128.5, 128.3, 127.95, 127.90, 127.75, 127.62, 127.57, 98.6, 74.2, 73.3, 73.2, 71.2, 69.0, 43.7, 25.7, 18.0, -4.6, -5.2; mass spectrum (ESI) *m/z* 493.7, [M+Na]⁺.

Yield: (Procedure A: 84%, Procedure B: 75%); $[\alpha]_D^{23}$ -110.3 (*c* 0.3, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.38-7.26 (m, 10H), 5.86 (s, 1H), 5.11 (dd, *J*=6.0, 4.2 Hz, 1H), 4.57 (s, 2H), 4.06 (s, 2H), 2.69-2.52 (m, 2H), 0.83 (s, 9H), -0.03 (s, 3H), -0.18 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 193.6, 189.8, 144.6, 137.4, 128.8, 128.7, 128.0, 126.0, 125.9, 109.9, 99.0, 73.5, 72.6, 50.0, 29.9, 25.9, -4.5, -5.1; mass spectrum (ESI) *m/z* 449.3, [M+Na]⁺.

Yield: (Procedure A: 89%, Procedure B: 79%); $[\alpha]_D^{23}$ -69.0 (*c* 0.33, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.87 (d, *J*=6.9 Hz, 2H), 7.50-7.34 (m, 8H), 6.23 (s, 1H), 4.57 (s, 2H), 4.37 (m, 1H), 3.50-3.40 (m, 2H), 2.73 (dd, *J*=4.2, 13.8 Hz, 1H), 2.56 (dd, *J*=8.1, 13.8 Hz, 1H), 0.85 (s, 10H), 0.06 (s, 3H), 0.02 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 193.6, 183.8, 138.2, 135.0, 132.3, 128.6, 128.3, 127.6, 127.0, 98.0, 74.3, 73.3, 69.2, 44.7, 25.7, 18.0, -4.6, -5.1; mass spectrum (ESI) *m/z* 465.5, [M+K]⁺.

Yield: (Procedure A: 95%, Procedure B: 80%); $[\alpha]_D^{23}$ -60.0 (*c* 1.1, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.35-7.28 (m, 5H), 5.53 (s, 1H), 4.54 (s, 2H), 4.30-4.25 (m, 1H), 3.48-3.36 (m, 2H), 2.60-2.26 (m, 4H), 1.12 (t, *J*=7.5 Hz, 3H), 0.86 (s, 9H), -0.01 (s, 3H), -0.03 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 196.4, 190.6, 138.3, 128.5, 127.7, 127.6, 100.7, 74.4, 73.5, 69.2, 43.9, 31.9, 25.9, 18.2, 9.7, -4.4, -5.0; mass spectrum (ESI) *m/z* 401.3, [M+Na]⁺.

Yield: (Procedure A: 88%, Procedure B: 75%); $[\alpha]_D^{23}$ -54.6 (*c* 1.0, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.38-7.34 (m, 5H), 5.89 (s, 1H), 4.60 (s, 2H), 4.07 (m, 3H), 2.41 (d, *J*=6.3 Hz, 2H), 1.56-1.51 (m, 2H), 0.90 (t, *J*=7.2 Hz, 3H), 0.88 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 193.1, 190.6, 137.1, 128.4, 127.9, 127.7, 98.4, 73.2, 71.2, 70.8, 45.4, 30.4, 25.7, 17.9, 9.2, -4.7, -5.0; mass spectrum (ESI) *m/z* 401.4, [M+Na]⁺.

6a was prepared using the same procedure for **6b**. Yield: 95%. Experimental data of (+)-**6a** (optical rotation value and NMR) are the same as reported in the literature: *Agric. Biol. Chem.* **1987**, 51, 2001.

(+)-6b: To a well stirred solution of (-)-**4b** (50 mg, 0.13 mmol) in CH₂Cl₂ (4 mL) was added 10 μ L (14.8 mg, 0.13 mmol) of TFA. The mixture was stirred overnight and quenched with saturated aqueous NaHCO₃ (3 mL) and diluted with Et₂O (10 mL). The layers were separated. The aqueous phase was extracted with Et₂O (3 $\times$ 5 mL) and the combined organic layers were dried over Na₂SO₄, filtered and concentrated. Flash chromatograph (hexanes/ethyl acetate, 10:1) provide (+)-**6b** (31 mg, 93%). $[\alpha]_D^{23}$ +111.1 (*c* 1.0, MeOH); ¹H NMR (300 MHz, CDCl₃) δ 7.62 (m, 2H), 7.30 (m, 8H), 5.95 (s, 1H), 5.42 (dd, *J*=3.3, 13.8 Hz, 1H), 2.79 (dd, *J*=14.1, 17.1 Hz, 1H), 2.58 (dd, *J*=3.6, 16.8 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 192.9, 170.2, 138.2, 132.5, 131.7, 128.8, 128.7, 128.6, 126.6, 102.2, 80.9, 42.9; mass spectrum (ESI) *m/z* 251.4, [M+H]⁺, HRMS (ES⁺) *m/z* 273.0899 [(M+Na)⁺; calcd for C₁₇H₁₄O₂Na: 273.0891].

6c was prepared using the same procedure for **6b**. Yield: 95%; $[\alpha]_D^{23}$ +110.0 (*c* 0.5, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.27 (m, 10H), 5.60 (s, 1H), 4.51 (m, 5H), 4.00 (dd, *J*=15.6, 26.4 Hz, 2H), 3.63 (m, 2H), 2.64 (dd, *J*=14.1, 17.1 Hz, 1H), 2.32 (dd, *J*=3.3, 16.8 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 192.5, 173.3, 137.7, 137.3, 128.8, 128.3, 128.2, 128.0, 127.9, 103.6, 78.7, 73.8, 73.5, 70.8, 68.4, 38.3;

mass spectrum (ESI) m/z 361.4, $[M+Na]^+$, HRMS (ES^+) m/z 361.1422 $[(M+Na)^+]$; calcd for $C_{21}H_{22}O_4Na$: 361.1416].

6d was prepared using the same procedure for **6b**. Yield: 90%; $[\alpha]_D^{23} +71.6$ (c 0.55, $CHCl_3$); 1H NMR (300 MHz, $CDCl_3$) δ 7.42-7.32 (m, 10H), 5.78 (s, 1H), 5.41 (dd, $J=14.1, 3.6$ Hz, 1H), 4.60 (d, $J=1.8$ Hz, 2H), 4.16 (dd, $J=16.2, 0.9$ Hz, 2H), 2.88 (dd, $J=16.5, 2.7$ Hz, 1H), 2.64 (ddd, $J=17.2, 3.6, 2.4$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.5, 173.5, 138.1, 137.3, 129.2, 129.1, 128.7, 128.3, 128.0, 126.4, 103.9, 81.4, 73.5, 68.5, 43.2; mass spectrum (ESI) m/z 317.2, $[M+Na]^+$, HRMS (ES^+) m/z 317.1162 $[(M+Na)^+]$; calcd for $C_{19}H_{18}O_3Na$: 317.1154].

6e was prepared using the same procedure for **6b**. Yield: 95%; $[\alpha]_D^{23} -210.0$ (c 0.3, $CHCl_3$); 1H NMR (300 MHz, $CDCl_3$) δ 7.70-7.67 (m, 2H), 7.43-7.26 (m, 8H), 5.95 (d, $J=0.9$ Hz, 1H), 4.75-4.66 (m, 1H), 4.59 (d, $J=2.7$ Hz, 2H), 3.76 (m, 2H), 2.72 (dd, $J=13.8, 17.1$ Hz, 1H), 2.43 (ddd, $J=0.9, 3.3, 16.8$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.9, 170.0, 137.6, 132.5, 131.7, 128.6, 128.5, 127.9, 127.7, 126.6, 102.1, 78.4, 73.5, 70.7, 37.9; mass spectrum (ESI) m/z 333.3, $[M+K]^+$, HRMS (ES^+) m/z 317.1169 $[(M+Na)^+]$; calcd for $C_{19}H_{18}O_3Na$: 317.1154].

6f was prepared using the same procedure for **6b**. Yield: 97%; $[\alpha]_D^{23} +231.9$ (c 0.9, $CHCl_3$); 1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.30 (m, 5H), 5.34 (d, $J=0.9$ Hz, 1H), 4.66-4.51 (m, 3H), 3.70 (dd, $J=4.2, 2.1$ Hz, 2H), 2.65 (dd, $J=16.8, 14.1$ Hz, 1H), 2.39-2.26 (m, 3H), 1.37 (t, $J=7.5$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.9, 178.9, 137.8, 128.7, 128.1, 127.9, 103.4, 73.7, 70.9, 37.8, 28.0, 10.8; mass spectrum (ESI) m/z 269.3, $[M+Na]^+$, HRMS (ES^+) m/z 269.1145 $[(M+Na)^+]$; calcd for $C_{15}H_{18}O_3Na$: 269.1154].

6g was prepared using the same procedure for **6b**. Yield: 89%; $[\alpha]_D^{23} +147.9$ (*c* 0.7, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.37-7.27 (m, 5H), 5.66 (s, 1H), 4.59 (dd, *J*=14.1, 12.0 Hz, 2H), 4.33 (m, 1H), 4.04 (ddd, *J*=26.1, 15.3, 1.2 Hz, 2H), 2.54-2.39 (m, 2H), 1.87-1.66 (m, 2H), 1.02 (t, *J*=7.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 193.2, 173.5, 137.4, 128.7, 128.2, 128.0, 103.5, 81.1, 73.4, 68.5, 41.2, 27.7, 9.5; mass spectrum (ESI) *m/z* 269.2, [M+Na]⁺, HRMS (ES⁺) *m/z* 269.1160 [(M+Na)⁺; calcd for C₁₅H₁₈O₃Na: 269.1154].

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