Supporting Information

Total Synthesis of (+)-Sundiversifolide

Hiromasa Yokoe, Hiroyuki Sasaki, Tomoyuki Yoshimura, Mitsuru Shindo, Masahiro Yoshida and

Kozo Shishido*

*Graduate School of Pharmaceutical Sciences, The University of Tokushima, 1-78-1 Sho-machi,
Tokushima 770-8505, Japan and Institute for Materials Chemistry and Engineering, Kyusyu University,*

6-1 Kasugakoen, Kasuga 816-8580, Japan

shishido@ph.tokushima-u.ac.jp

General. All nonaqueous reactions were carried out under a positive atmosphere of argon in dried glassware unless otherwise indicated. Materials were obtained from commercial suppliers and used without further purification except when otherwise noted. Solvents were dried and distilled according to standard protocol. The phrase ‘residue upon workup’ refers to the residue obtained when the organic layer was separated and dried over anhydrous MgSO_4 and the solvent was evaporated under reduced pressure.

(*R*)-4-Benzyl-3-[(2*R*,3*S*)-3-hydroxy-2-methylhept-6-enoyl]oxazolidin-2-one (7**)**

To a stirred solution of Evans' propionate **6** (5.67 g, 24.3 mmol) in CH_2Cl_2 (50 mL) were added dropwise Bu_2BOTf (1.0 M solution in CH_2Cl_2 , 26.7 mL, 26.7 mmol) and Et_3N (4.57 mL, 32.5 mmol) at 0 °C, and stirring was continued for 10 min at the same temperature. 4-Penten-2-ol (**5**) (2.31 g, 27.5 mmol) in CH_2Cl_2 (11 mL) was added dropwise to the solution at –70 °C, and stirring was continued for 1.5 h at the same temperature. After further stirring was continued for 3.5 h at 0 °C, the reaction mixture was quenched with pH 7.0 phosphate buffer/MeOH (75 mL, 1/2 v/v) and 35% H_2O_2 aq./MeOH (65 mL, 1/2 v/v) successively, and stirring was continued for 1 h. After evaporation of the reaction solvent, the aqueous layer was extracted with AcOEt. The extracts were washed with sat. NaHCO_3 aq. and brine, and the residue upon workup was chromatographed on silica gel with hexane-AcOEt (70/30 v/v) as eluent to give aldol product **7** (7.15 g, 92%) as colorless needles; mp: 82.9 to 84.8 °C (recrystallized from benzene/hexane); $[\alpha]_{29}^{\text{D}} = -48.7^\circ$ (c 0.95, CHCl_3); IR (KBr) cm^{-1} : 3516, 2947, 1774, 1678, 916; ^1H NMR (400 MHz, CDCl_3): δ 1.27 (3H, d, $J = 7.2$ Hz), 1.46–1.71 (2H, m), 2.09–2.31 (2H, m), 2.79 (1H, brs), 2.90 (1H, brs), 3.24 (1H, dd, $J = 3.6$ and 13.6 Hz), 3.76 (1H, dq, $J = 2.8$ and 7.2 Hz), 3.94–4.01 (1H, m), 4.16–4.27 (2H, m), 4.68–4.74 (1H, m), 4.96–4.99 (1H, m), 5.03–5.08 (1H, dd, $J = 2.4$ and 16.9 Hz), 5.83 (1H, ddt, $J = 6.8, 10.4$ and 16.9 Hz), 7.31–7.17 (5H, m); ^{13}C NMR (100 MHz, CDCl_3): δ 10.6, 30.1, 32.9,

37.7, 42.1 55.0, 66.1, 70.8, 114.8, 127.2, 128.8, 128.8, 129.2, 129.2, 134.8, 137.9, 152.8, 177.1; HRMS (ESI) calcd for $C_{18}H_{24}NO_4$ ($M^+ + H$): 318.1705 found 318.1696; Anal. calcd for $C_{18}H_{23}NO_4$: C, 68.12; H, 7.30; N, 4.41 found C, 68.04; H, 7.31; N, 4.39.

(2*R*,3*S*)-3-Hydroxy-*N*-methoxy-*N*,2-dimethylhept-6-enamide (8)

To a stirred solution of *N,O*-dimethylhydroxylamine hydrochloride (13.7 g, 141 mmol) in CH_2Cl_2 (200 mL) was added dropwise Me_3Al (1.03 M in hexane, 139 mL, 143 mmol) over 40 min, and stirring was continued for 1 h at rt. After the solution was cooled to $-20\text{ }^\circ\text{C}$, the aldol product **7** (21.4 g, 67.4 mmol) in CH_2Cl_2 (228 mL) was added dropwise. The reaction temperature was slowly increased to rt during 5 h, and stirring was continued for 8 h at the same temperature. The reaction mixture was quenched with 10% tartaric acid aq. (428 mL), and extracted with CH_2Cl_2 . The combined extracts were washed with sat. NH_4Cl aq. and brine, and the residue upon workup was chromatographed on silica gel with hexane-AcOEt (70/30 v/v) as eluent to give Weinreb amide **8** (12.9 g, 95%) as a colorless oil; $[\alpha]_{30}^D = -9.81^\circ$ (c 1.05, $CHCl_3$); IR (KBr) cm^{-1} : 3438, 2939, 1639, 995, 913; ^1H NMR (400 MHz, $CDCl_3$) δ 1.18 (3H, d, $J = 7.2$ Hz), 1.39–1.47 (1H, m), 1.63–1.73 (1H, m), 2.08–2.17 (1H, m), 2.21–2.31 (1H, m), 2.86–2.91 (1H, m), 3.20 (3H, s), 3.71 (3H, s), 3.78 (1H, brs), 3.86–3.92 (1H, m), 4.97 (1H, ddt, $J = 1.2, 1.6$ and 10.4 Hz), 5.05 (1H, ddt, $J = 1.6, 2.0$ and 16.8 Hz), 5.84 (1H, ddt, $J = 6.8, 10.4$ and 16.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.4, 29.8, 31.4, 32.9, 38.7, 61.1, 70.7, 114.3, 138.0, 177.6; LRMS (EI) m/z 201 (M^+), 28 (base peak); HRMS (EI) m/z calcd for $C_{10}H_{19}NO_3$ (M^+): 201.1365 found 201.1356.

(4*R*,5*S*)-5-(*tert*-Butyldimethylsilyloxy)-4-methylnona-1,8-dien-3-one (4)

To a stirred solution of Weinreb amide **8** (450 mg, 1.73 mmol) and 2,6-lutidine (0.81 mL, 6.92 mmol) in CH_2Cl_2 (8 mL) was added TBSOTf (0.9 mL, 3.93 mmol) at 0 °C, and stirring was continued for 1 h at rt. The reaction mixture was added to MeOH, and extracted with CH_2Cl_2 . The extracts were washed with 1 N HCl, sat. Na_2CO_3 aq. and brine, and the residue upon workup was chromatographed on silica gel with hexane-AcOEt (90/10 v/v) as eluent to give the silyl ether (533 mg, 98%) as a colorless oil; $[\alpha]_{30}^{\text{D}} = +0.334^\circ$ (c 1.00, CHCl_3); IR (KBr) cm^{-1} : 2935, 1666, 998, 910; ^1H NMR (400 MHz, CDCl_3) δ 0.07 (6H, s), 0.96 (9H, s), 1.16 (3H, d, $J = 6.8$ Hz), 1.52–1.61 (2H, m), 2.08–2.14 (2H, m), 2.71–3.30 (1H, brs), 3.18 (3H, s), 3.70 (3H, s), 3.95 (1H, s), 4.92–4.94 (1H, m), 4.97–5.02 (1H, m) 5.81 (1H, ddt, $J = 6.4$, 10.0 and 16.8 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ -4.61, -4.50, 14.5, 18.1, 25.9, 25.9, 26.1, 28.5, 32.1, 34.8, 40.5, 61.3, 73.0, 114.1, 138.8, 176.4; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{34}\text{NO}_3\text{Si}$ ($\text{M}^+\text{+H}$): 316.2308 found 316.2299.

To a stirred solution of the silyl ether (1.0 g, 3.17 mmol) in THF (20 mL) was added dropwise vinylmagnesium bromide (1.32 M in THF, 14.4 mL, 19 mmol) at 0 °C, and stirring was continued for 1 h at the same temperature. The reaction mixture was quenched with 0.5 N HCl/THF (1/1 v/v), and evaporation of volatiles. The aqueous layer was extracted with CH_2Cl_2 , and the residue upon workup was chromatographed on silica gel with hexane-AcOEt (97/3 v/v) as eluent to give vinyl ketone **4** (827 mg, 92%) as a colorless oil; $[\alpha]_{30}^{\text{D}} = -36.3^\circ$ (c 1.00, CHCl_3); IR (KBr) cm^{-1} : 2935, 1664, 998, 910; ^1H NMR (400 MHz, CDCl_3) δ 0.02 (3H, s), 0.05 (3H, s), 0.88 (9H, s), 1.10 (3H, d, $J = 6.8$ Hz), 1.46–1.63 (2H, m), 2.05–2.10 (2H, m), 2.93 (1H, dt, $J = 5.2$ and 6.8 Hz), 3.98 (1H, dt, $J = 5.2$ and 5.6 Hz), 4.94–4.97 (1H, m), 5.03 (1H, m), 5.73–5.83 (2H, m), 6.22–6.27 (1H, m), 6.45–6.52 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ -4.57, -4.39, 11.7, 18.0, 25.6, 25.8, 25.9, 29.3, 34.2, 48.7, 72.7, 114.6, 127.5, 135.6, 138.1, 202.1; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{31}\text{O}_2\text{Si}$ ($\text{M}^+\text{+H}$): 283.2093 found 283.2085.

(6*S*,7*R*,*Z*)-6-(*tert*-Butyldimethylsilyloxy)-7-methylcyclohept-2-enone (10)

To a stirred solution of vinyl ketone **4** (7.26 g, 25.7 mmol) in degassed CH₂Cl₂ (1.3 L) was added 2nd generation Grubbs' catalyst **9** (1.1 g, 1.29 mmol) at rt, and stirring was continued at reflux for 4 h. The reaction mixture was concentrated and the residue was chromatographed on silica gel with hexane-AcOEt (95/5 v/v) as eluent to give cycloheptenone **10** (6.2 g, 95%) as a colorless oil; $[\alpha]_{29}^D = +34.1^\circ$ (c 0.87, CHCl₃); IR (KBr) cm⁻¹: 2954, 1682; ¹H NMR (400 MHz, CDCl₃) δ 0.07 (3H, s), 0.08 (3H, s), 0.90 (9H, s), 1.16 (3H, d, $J = 6.8$ Hz), 1.72 (1H, m), 1.95 (1H, dddd, $J = 3.0, 3.0, 6.0,$ and 14.8 Hz), 2.33 (1H, m), 2.70 (1H, dddd, $J = 2.8, 4.4, 10.8$ and 16.4 Hz), 2.86 (1H, dq, $J = 6.8$ and 6.8 Hz), 3.71 (1H, ddd, $J = 2.8, 2.8$ and 6.8 Hz), 6.00 (1H, dd, $J = 3.2$ and 7.6 Hz), 6.67 (1H, ddd, $J = 2.8, 4.0$ and 11.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ -4.66, -4.38, 14.3, 18.0, 25.1, 25.8, 35.7, 54.7, 73.0, 132.5, 146.8, 203.7; HRMS (ESI) m/z calcd for C₁₄H₂₇O₂Si (M⁺+H): 255.1780 found 255.1778.

(1*S*,6*S*,7*S*,*Z*)-6-(*tert*-Butyldimethylsilyloxy)-7-methylcyclohept-2-enol (3)

To a stirred solution of vinyl ketone **10** (652 mg, 2.56 mmol) in Et₂O (13 mL) was added dropwise Red-Al® (3.3 M in toluene, 1.16 mL, 3.84 mmol) at -78 °C, and stirring was continued for 1.5 h at the same temperature. The reaction mixture was quenched with sat. NaHCO₃ aq., and filtered through a Celite pad. The residue upon workup was chromatographed on silica gel with CH₂Cl₂ as eluent to give allyl alcohol **3** (484 mg, 74%) and the *1R*-epimer (7.2 mg, 1%); **3**: colorless needles, mp: 51.6 to 52.8 °C

(recrystallized from hexane); $[\alpha]_{27}^D = +48.6^\circ$ (c 0.58, CHCl_3); IR (KBr) cm^{-1} : 3346, 3034, 2937, 1084; ^1H NMR (400 MHz, CDCl_3) δ 0.05 (3H, s), 0.07 (3H, s), 0.91 (9H, s), 0.94 (3H, d, $J = 7.2$ Hz), 1.39 (1H, brd, $J = 3.6$ Hz), 1.49 (1H, m), 1.66 (1H, dddd, $J = 2.0, 2.0, 12.8$, and 14.4 Hz), 1.79 (1H, dddd, $J = 2.0, 6.0, 8.2$ and 14.4 Hz), 1.92–1.95 (1H, m), 2.45–2.55 (1H, m), 3.84 (1H, ddd, $J = 2.4, 6.0$ and 6.0 Hz), 4.99 (1H, brs), 5.50 (1H, brd, $J = 10.8$ Hz), 5.74 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ –4.69, –4.69, 11.5, 18.0, 21.0, 25.9, 25.9, 25.9, 28.9, 45.0, 69.6, 73.5, 129.2, 136.0; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{29}\text{O}_2\text{NaSi}$ ($\text{M}^+ + \text{Na} + \text{H}$): 280.1813 found 280.1835. *1R*-epimer of **3**: colorless oil; $[\alpha]_{27}^D = -13.4^\circ$ (c 0.52, CHCl_3); IR (KBr) cm^{-1} : 3418, 3020, 2929, 1074; ^1H NMR (400 MHz, CDCl_3) δ 0.09 (3H, s), 0.12 (3H, s), 0.91–0.93 (12H, m), 1.62–1.69 (1H, m), 1.81 (1H, ddt, $J = 2.4, 12.4$, and 14.4 Hz), 1.92–2.00 (1H, m), 2.25–2.32 (1H, m), 2.62–2.67 (1H, m), 4.01 (1H, dt, $J = 2.0$ and 5.0 Hz), 4.04–4.09 (1H, m), 4.21 (1H, d, $J = 7.6$ Hz), 5.80 (1H, ddt, $J = 2.4, 6.0$ and 11.6 Hz), 5.89 (1H, ddd, $3.6, 7.6$ and 11.6 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ –4.70, –5.00, 15.6, 18.2, 22.0, 25.8, 25.8, 25.8, 29.9, 42.5, 73.3, 77.9, 132.9, 133.1; HRMS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{28}\text{O}_2\text{SiNa}$ ($\text{M} + \text{Na}^+$): 279.1756 found 279.1761.

2-[(1*R*,4*S*,5*S*,*Z*)-5-(*tert*-Butyldimethylsilyloxy)-4-methylcyclohept-2-enyl]-*N,N*-dimethylacetamide
(**11**)

A solution of the allyl alcohol (473 mg, 1.84 mmol) and *N,N*-dimethylacetamide dimethylacetal (1.62 mL, 11.1 mmol) in toluene (9.4 mL) was refluxed under a Dean-Stark water separation for 30 h. The reaction mixture was concentrated, and the residue was chromatographed on silica gel with hexane-AcOEt (80/20 v/v) as eluent to give amide **11** (575 mg, 96%) as a colorless oil; $[\alpha]_{28}^D = +69.3^\circ$ (c 1.00, CHCl_3); IR (KBr) cm^{-1} : 2994, 2929, 2857, 1649; ^1H NMR (400 MHz, CDCl_3) δ 0.032 (3H, s), 0.03 (3H, s), 0.89 (9H,

s), 1.05 (3H, d, $J = 6.8$ Hz), 1.30 (1H, ddt, $J = 2.8, 9.6$ and 13.2 Hz), 1.62–1.66 (1H, m), 1.74 (1H, ddt, $J = 2.8, 10.0$, and 12.8 Hz), 2.04–2.11 (1H, m), 2.34 (2H, ddt, $J = 7.2, 15.2$ and 16.8 Hz), 2.42–2.49 (1H, m), 2.69–2.79 (1H, m), 2.94 (3H, s), 3.01 (3H, s), 3.16 (1H, dt, $J = 3.6$ and 9.6 Hz), 5.27 (1H, ddd, $J = 2.0, 2.4$ and 11.2 Hz), 5.52 (1H, ddd, $J = 2.0, 2.4$ and 11.2 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ –4.83, –4.52, 17.9, 19.4, 25.7, 25.7, 25.7, 32.1, 35.0, 35.5, 37.0, 39.8, 40.7, 40.9, 73.5, 134.2, 136.5, 171.3; HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{36}\text{NO}_2\text{Si}$ ($\text{M}^+ + \text{H}$): 326.2515 found 326.2515.

(3a*R*,6*S*,7*S*,8a*R*)-6-(*tert*-Butyldimethylsilyloxy)-7-methyloctahydro-2*H*-cyclohepta[*b*]furan-2-one
(12)

To a stirred solution of amide **11** (1.16 g, 3.56 mmol) in THF/ H_2O (9/1 v/v, 23 mL) was added iodine (1.8 g, 7.13 mmol) at rt, and stirring was continued for 12 h at the same temperature. the reaction mixture was treated with $\text{Na}_2\text{S}_2\text{O}_3$, and extracted with Et_2O . The residue upon workup was chromatographed on silica gel with hexane-AcOEt (85/15 v/v) as eluent to give iodolactone (1.34 g, 89%) as colorless needles; mp: 121.9 to 122.1 °C (recrystallized from hexane); $[\alpha]_{27}^{\text{D}} = +98.0^\circ$ (c 1.09, CHCl_3); IR (KBr) cm^{-1} : 2931, 2859, 1774; ^1H NMR (400 MHz, CDCl_3) δ 0.06 (3H, s), 0.08 (3H, s), 0.91 (9H, s), 1.24 (3H, d, $J = 7.2$ Hz), 1.60–1.74 (3H, m), 1.97–2.01 (1H, m), 2.24 (1H, dd, $J = 5.6$, and 20.0 Hz), 2.44–2.50 (1H, m), 2.89 (1H, dd, $J = 10.4$ and 20.0 Hz), 3.12–3.21 (1H, m), 3.65 (1H, dt, $J = 4.4$ and 4.4 Hz), 4.12 (1H, dd, $J = 8.8$ and 10.8 Hz), 5.24 (1H, dd, $J = 7.6$ and 10.8 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ –4.98, –4.79, 17.9, 20.9, 25.8, 25.8, 25.8, 25.9, 31.6, 35.2, 37.7, 37.7, 48.7, 74.3, 85.2, 174.3; HRMS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{30}\text{O}_3\text{SiI}$ ($\text{M}^+ + \text{H}$): 425.1009 found 425.1008; Anal. calcd for $\text{C}_{16}\text{H}_{29}\text{O}_3\text{SiI}$: C, 45.28; H, 6.89 found C, 45.13; H, 6.84.

To a stirred solution of iodolactone (215 mg, 0.51 mmol) in benzene (4 mL) were added Bu₃SnH (0.42 mL, 1.56 mmol) and AIBN (8.3 mg, 0.051 mmol) at rt, and stirring was continued for 1 h at reflux. After treatment with NaF (10 mg), the reaction mixture was filtered through a Celite pad and concentrated. The residue was chromatographed on silica gel with hexane-AcOEt (80/20 v/v) as eluent to give lactone **12** (151 mg, quant.) as a colorless oil; $[\alpha]_{25}^D = +36.0^\circ$ (c 1.12, CHCl₃); IR (KBr) cm⁻¹: 2953, 1780; ¹H NMR (400 MHz, CDCl₃) δ 0.05 (6H, s), 0.88 (9H, s), 1.04 (3H, d, $J = 6.4$ Hz), 1.28–1.64 (4H, m), 1.71–1.81 (2H, m), 1.94–2.01 (1H, m), 2.14–2.22 (1H, m), 2.70–2.75 (2H, m), 3.14 (1H, dt, $J = 4.0$ and 10.0 Hz), 4.70 (1H, ddd, $J = 1.2, 2.8$ and 3.6 Hz); ¹³C NMR (100 MHz, CDCl₃) δ -4.55, -4.04, 18.0, 21.3, 25.9, 25.9, 25.9, 26.0, 34.5, 35.7, 36.5, 37.7, 38.3, 78.9, 82.8, 176.2; LHMS (EI) m/z 298 (M⁺), 107 (base peak); HRMS (EI) m/z calcd for C₁₆H₃₀O₃Si (M⁺): 298.1964 found 298.1956.

(3a*R*,6*S*,7*S*,8a*R*)-2-Methoxy-7-methyloctahydro-2*H*-cyclohepta[*b*]furan-6-ol (13**)**

To a stirred solution of lactone **12** (905 mg, 3.03 mmol) in CH₂Cl₂ (18 mL) was added dropwise DIBAL-H (0.94 M in THF, 4.0 mL, 3.76 mmol) at -78 °C, and stirring was continued for 1 h at the same reaction temperature. The reaction mixture was quenched with the minimum amount of water, and filtered thorough a Celite pad. To a stirred solution of the residue upon workup in MeOH (50 mL) was added TsOH·H₂O (57.6 mg, 0.303 mmol), and stirring was continued for 1.5 h at reflux. The reaction mixture was diluted with sat. NaHCO₃ aq., and extracted with AcOEt. The combined extracts were washed with sat. NH₄Cl aq. and brine, and the residue upon workup was chromatographed on silica gel with hexane-AcOEt (70/30 v/v) as eluent to give methyl acetal **13** (514 mg, 1:4 diastereomixture, 2 steps 85%) as colorless needles; mp: 65.6 to 66.1 °C (recrystallized from hexane); IR (KBr) cm⁻¹: 3427, 2929, 2830;

^1H NMR (400 MHz, CDCl_3) δ 1.09 (0.6H, d, $J = 6.4$ Hz), 1.10 (2.4H, d, $J = 6.4$ Hz), 1.23–1.78 (7H, m), 2.01–2.09 (2.6H, m), 2.27–2.42 (0.6H, m), 2.49–2.60 (0.8H, m), 3.09–3.16 (1H, m), 3.31 (0.6H, s), 3.32 (2.4H, s), 4.22–4.28 (1H, m), 4.87–4.91 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 20.8, 26.1, 26.8, 35.4, 37.1, 37.3, 37.5, 38.4, 38.5, 39.1, 40.1, 40.5, 40.8, 54.2, 54.8, 78.3, 80.2, 82.4, 103.5, 104.8; LRMS (EI) m/z 199 (M^+), 71 (base peak); Anal. calcd for $\text{C}_{11}\text{H}_{20}\text{O}_3$: C, 65.97; H, 10.07 found C, 65.67; H, 9.99.

(3a*R*,7*S*,8a*R*)-2-Methoxy-7-methylhexahydro-2*H*-cyclohepta[*b*]furan-6(7*H*)-one (2)

To a stirred solution of methyl acetal **13** (100 mg, 0.50 mmol) in CH_2Cl_2 (7 mL) was added Dess-Martin periodinane (318 mg, 0.75 mmol) at 0 °C, and stirring was continued for 1 h at rt. The reaction mixture was added sat. NaHCO_3 aq./sat. $\text{Na}_2\text{S}_2\text{O}_3$ aq. (1/1 v/v), and extracted with CH_2Cl_2 . The combined extracts were washed with brine, and the residue upon workup was chromatographed on silica gel with hexane-AcOEt (60/40 v/v) as eluent to give ketone **2** (97 mg, 1:4 diastereomixture, 98%) as a colorless oil; IR (KBr) cm^{-1} : 2935, 2830, 1703; ^1H NMR (400 MHz, CDCl_3) δ 1.10 (0.6H, d, $J = 6.8$ Hz), 1.11 (2.4H, d, $J = 6.8$ Hz), 1.57–2.00 (5.2H, m), 2.14 (0.8H, dd, $J = 8.0$ and 13.2 Hz), 2.26–2.75 (4H, m), 3.33 (0.6H, s), 3.34 (2.4H, s), 4.34–4.45 (1H, s), 4.93–4.96 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 17.0, 17.1, 25.5, 25.6, 34.2, 35.8, 39.0, 39.4, 39.7, 40.0, 41.7, 42.3, 42.4, 42.7, 54.3, 54.8, 78.9, 81.3, 103.3, 104.7; LRMS (EI) m/z 198 (M^+), 69 (base peak); HRMS (EI) m/z calcd for $\text{C}_{11}\text{H}_{18}\text{O}_3$ (M^+): 198.1256 found 198.1245.

Ethyl 2-[(3a*R*,7*S*,8a*R*)-2-methoxy-7-methyltetrahydro-2*H*-cyclohepta[*b*]furan-6(7*H*,8*H*,8a*H*)-ylidene]acetate (14)

To a stirred solution of lithium dicyclohexylamide [prepared in situ from dicyclohexylamine (0.102 mL, 0.514 mmol) and BuLi (1.46 M in hexane, 0.352 mL, 0.514 mmol) at -78°C] in THF (3.5 mL) was added ethyl trimethylsilylacetate (0.094 mL, 0.514 mmol) at -78°C , and stirring was continued for 10 min at the same temperature. Then ketone **2** (48 mg, 0.242 mmol) in THF (3.5 mL) was added dropwise to the solution, and stirring was continued for 1 h at the same temperature. After further stirring for 2 h at -25°C , the reaction mixture was quenched with sat. NH_4Cl aq. at rt and extracted with Et_2O . The combined extracts were washed with brine, and the residue upon workup was chromatographed on silica gel with benzene-AcOEt (80/20 v/v) as eluent to give α,β -unsaturated ester **14** (64.8 mg, 1:1:4:4 distereomixture, 99%) as a colorless oil; IR (KBr) cm^{-1} : 2935, 1714, 1637; ^1H NMR (400 MHz, CDCl_3) δ 1.10–1.14 (3H, m), 1.28 (3H, t, $J = 7.2$ Hz), 1.56–2.96 (10H, m), 3.30–3.33 (3H, m), 3.89–4.22 (3H, m), 4.86–4.92 (1H, m), 5.62–5.70 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 14.2, 20.9, 21.0, 25.6, 26.2, 27.5, 27.9, 31.5, 31.7, 35.4, 35.6, 36.6, 37.4, 38.2, 38.3, 39.6, 39.7, 39.9, 40.0, 54.3, 54.8, 59.4, 59.5, 77.6, 78.5, 81.2, 103.4, 103.5, 114.8, 114.9, 117.3, 165.6, 166.3, 166.4, 166.5; LRMS (EI) m/z 268 (M^+), 44 (base peak); HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{24}\text{O}_4$ (M^+): 268.1675 found 268.1687.

Ethyl 2-[(3a*R*,7*S*,8a*R*,*Z*)-2-methoxy-7-methyl-3,3a,4,7,8,8a-hexahydro-2*H*-cyclohepta[*b*]-furan-6-yl]acetate (15)

To a stirred solution of LDA [prepared in situ from diisopropylamine (0.026 mL, 0.187 mmol) and BuLi

(1.56 M in hexane, 0.12 mL, 0.187 mmol) at 0 °C] in THF (0.5 mL) was added dropwise α,β -unsaturated ester **14** (10.0 mg, 0.0373 mmol) in THF (0.5 mL) at -78 °C, and stirring was continued for 30 min at the same temperature. The reaction mixture was quenched with sat. NH_4Cl aq. at the same temperature, and extracted with Et_2O . The combined extracts were washed with brine, and the residue upon workup was chromatographed on silica gel with hexane-AcOEt (89/11 v/v) as eluent to give β,γ -unsaturated ester **15** (6.4 mg, 1:4 diastereomixture, 64%) with recovered **14** (3.6 mg, 36%) as a colorless oil; IR (KBr) cm^{-1} : 2933, 1733; ^1H NMR (400 MHz, CDCl_3) δ 1.10 (3H, d, $J = 2.8$ Hz), 1.25 (3H, t, $J = 6.1$ Hz), 1.54–1.60 (1H, m), 1.76–2.02 (4H, m), 2.26–2.39 (2H, m), 2.60–2.78 (2H, m), 2.83 (1H, d, $J = 15.3$ Hz), 3.03 (1H, d, $J = 15.1$ Hz), 3.30 (3H, s), 4.12 (2H, q, $J = 7.0$ Hz), 4.24–4.29 (1H, m), 4.94–4.95 (1H, m), 5.52–5.56 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 14.2, 21.0, 27.7, 28.6, 35.0, 35.2, 36.8, 38.5, 39.3, 39.4, 39.9, 40.4, 42.7, 54.2, 54.8, 60.4, 78.6, 81.1, 103.9, 105.2, 126.5, 127.0, 137.9, 172.0; LRMS (EI) m/z 291 ($\text{M}+\text{Na}^+$), 176 (base peak); HRMS (EI) m/z calcd for $\text{C}_{15}\text{H}_{24}\text{O}_4\text{Na}$ ($\text{M}+\text{Na}^+$): 291.1572 found 291.1577.

2-[(3a*R*,7*S*,8a*R*,*Z*)-2-Methoxy-7-methyl-3,3a,4,7,8,8a-hexahydro-2*H*-cyclohepta[*b*]furan-6-yl]ethanol (16**)**

To a stirred solution of β,γ -unsaturated ester **15** (145 mg, 0.55 mmol) in THF (3 mL) was added dropwise DIBAL-H (0.94 M in THF, 2.7 mL, 2.53 mmol) at -78 °C, and stirring was continued for 1 h at the same temperature. The reaction mixture was quenched with the minimum amount of water, and filtered thorough a Celite pad. The residue upon evaporation was chromatographed on silica gel with hexane-AcOEt (60/40 v/v) as eluent to give alcohol **16** (115 mg, 1:4 diastereomixture, 93%) as a colorless oil; IR (KBr) cm^{-1} : 3411, 2932; ^1H NMR (400 MHz, CDCl_3) δ 1.12 (2H, d, $J = 6.8$ Hz), 1.13 (1H, d, $J = 6.8$ Hz), 1.35–1.38 (1H, m), 1.53–1.60 (1.33H, m), 1.78–2.01 (3.67H, m), 2.11–2.33 (4H, m), 2.55–2.77

(1H, m), 3.31–3.34 (3H, s), 3.56–3.69 (2H, m), 4.17–4.23 (1H, m), 4.90–4.95 (1H, m), 5.48–5.51 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 21.3, 27.5, 28.5, 34.7, 35.6, 36.8, 38.5, 39.2, 39.5, 39.7, 39.8, 40.7, 54.3, 55.0, 60.8, 78.8, 81.2, 104.0, 105.3, 124.5, 124.9, 140.6, 140.8; LRMS (EI) m/z 226 (M^+), 93 (base peak); HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{22}\text{O}_3$ (M^+): 226.1569 found 226.1573.

(3a*R*,7*S*,8a*R*)-2-Methoxy-7-methyl-6-methyleneoctahydro-2*H*-cyclohepta[*b*]furan (17)

To a stirred solution of ketone **2** (150 mg, 0.76 mmol) in Et_2O (1 mL) was added dropwise $\text{TMSCH}_2\text{MgCl}$ (1.0 M in Et_2O , 2.3 mL, 2.27 mmol) at 0 °C, and stirring was continued for 10 min at the same temperature. The reaction mixture was quenched with sat. NH_4Cl aq., and extracted with AcOEt . The combined extracts were washed with brine. The residue upon workup in THF (0.5 mL) was added dropwise to the stirred solution of KH (30 wt % in oil; 50 mg) in THF (0.5 mL) at 0 °C, and stirring was continued for 3 h at reflux. The reaction mixture was treated with sat. NH_4Cl aq., and extracted with AcOEt . The combined extracts were washed with brine, and the residue upon workup was chromatographed on silica gel with hexane- AcOEt (85/15 v/v) as eluent to give alkene **17** (150 mg, 1:4 diastereomixture, quant.) as a colorless oil; IR (KBr) cm^{-1} : 2929, 1255, 979, 913; ^1H NMR (400 MHz, CDCl_3) δ 1.11 (0.6H, d, $J = 7.2$ Hz), 1.12 (2.4H, d, $J = 7.2$ Hz), 1.43–1.78 (4H, m), 1.83–1.92 (1H, m), 1.96–2.09 (2H, m), 2.23–2.32 (1H, m), 2.44–2.60 (2H, m), 3.30 (2.4H, s), 3.32 (0.6H, s), 4.24–4.30 (1H, m), 4.65–4.69 (2H, m), 4.87 (0.2H, dd, $J = 2.0$ and 5.6 Hz), 4.91 (0.8H, d, $J = 4.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 21.3, 21.4, 29.7, 30.0, 35.0, 36.7, 37.8, 38.3, 39.3, 39.7, 40.3, 40.6, 42.1, 44.0, 54.3, 54.8, 79.3, 103.7, 108.8, 109.1, 154.3; LRMS (EI) m/z 196 (M^+), 41 (base peak); HRMS (EI) m/z calcd for $\text{C}_{10}\text{H}_{20}\text{O}_2$ (M^+): 196.1463 found 196.1451.

Synthesis of **16** by Alder-ene reaction using MAPH

To a stirred solution of MAPH [prepared in situ from 2,6-diphenylphenol (738 mg, 3.0 mmol) and Me_3Al (1.03 M in hexane, 1.5 mL, 1.5 mmol) at rt] in CH_2Cl_2 (1 mL) was added trioxane (45 mg, 0.48 mmol) in CH_2Cl_2 (0.5 mL) at 0 °C. After stirring was continued for 1 h at the same temperature, alkene **17** (10 mg, 0.05 mmol) in CH_2Cl_2 (0.5 mL) was added to the solution at –78 °C, and stirring was continued for 12 h at the same reaction temperature. The reaction mixture was quenched with sat. NaHCO_3 aq. and extracted with CH_2Cl_2 . The combined extracts were washed with 1 N NaOH aq. and brine, and the residue upon workup was chromatographed on silica gel with hexane-AcOEt (50/50 v/v) as eluent to give alcohol **16** (7.9 mg, 1:4 diastereomixture, 70%) as a colorless oil.

(3*aR*,7*S*,8*aR*,*Z*)-6-[2-(*tert*-butyldiphenylsilyloxy)ethyl]-7-methyl-3,3*a*,4,7,8,8*a*-hexahydro-2*H*-cyclohepta[*b*]furan-2-one (**18**)

To a stirred solution of alcohol (44.0 mg, 0.195 mmol) in CH_2Cl_2 (1 mL) were successively added imidazole (27 mg, 0.39 mmol), TBDPSCl (0.056 mL, 0.215 mmol) and DMAP (71 mg, 0.585 mmol) at 0 °C, and stirring was continued for 30 min at rt. The reaction mixture was treated with water, and extracted with CH_2Cl_2 . The combined extracts were washed with brine. The residue upon workup was dissolved in AcOH/acetone/ H_2O (8/1/1 v/v/v, 8.8 mL) and stirring was continued for 20 h at rt. The reaction mixture was extracted with Et_2O , and combined extracts were washed with brine. To a solution of the residue upon workup in CH_2Cl_2 (2 mL) were successively added 4A MS (225 mg), NMO (57 mg, 0.488 mmol) and TPAP (7.0 mg, 0.02 mmol) at rt, and stirring was continued for 1 h at the same reaction temperature. The resulting mixture was filtered through a Celite pad, and the residue upon evaporation of the reaction solvent was chromatographed on silica gel with hexane-AcOEt (90/10 v/v) as eluent to give lactone **18**

(67.4 mg, 3 steps 77%.) as a colorless oil; $[\alpha]_{28}^D = -8.89^\circ$ (c 1.01, CHCl_3); IR (KBr) cm^{-1} : 3070, 3049, 2931, 1775; ^1H NMR (400 MHz, CDCl_3) δ 1.04–1.06 (12H, m), 1.90–2.38 (8H, m), 2.59 (1H, dd, $J = 9.2$ and 17.8 Hz), 2.72–2.82 (1H, m), 3.66–3.70 (2H, m), 4.53–4.58 (1H, m), 5.37 (1H, dd, $J = 5.0$ and 8.7 Hz), 7.36–7.45 (6H, m), 7.64–7.66 (4H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 19.2, 20.8, 26.9, 26.9, 26.9, 27.5, 34.5, 34.8, 35.7, 37.3, 39.6, 63.2, 81.4, 122.0, 127.5, 127.5, 127.5, 127.5, 129.5, 129.5, 133.6, 133.6, 135.4, 135.4, 135.4, 135.4, 142.3, 176.4; LRMS (FAB) m/z 471 ($\text{M}+\text{Na}^+$), 176 (base peak); HRMS (FAB) m/z calcd for $\text{C}_{28}\text{H}_{36}\text{O}_3\text{SiNa}$ ($\text{M}+\text{Na}^+$): 471.2331 found 471.2350.

(3*R*,3*aR*,7*S*,8*aR*,*Z*)-6-[2-(*tert*-butyldiphenylsilyloxy)ethyl]-3,7-dimethyl-3,3*a*,4,7,8,8*a*-hexahydro-2*H*-cyclohepta[*b*]furan-2-one (19)

To a stirred solution of LiTMP [prepared in situ from tetramethylpiperidine (0.019 mL, 0.11 mmol) and BuLi (1.56 M in hexane, 0.071 mL, 0.11 mmol) at -78°C] in THF (0.5 mL) was added HMPA (0.019 mL, 0.11 mmol) at 0°C , and stirring was continued for 10 min at the same temperature. Lactone **18** (10 mg, 0.022 mmol) was then added to the solution at -78°C , and stirring was continued for 2 h at the same temperature. To the solution was added methyl iodide (1.5 μL , 0.024 mmol) at -78°C , and stirring was continued for 4 h at the same temperature. The reaction temperature was then raised to -40°C , and stirring was continued for 1 h at the same temperature. The reaction mixture was quenched with sat. NH_4Cl aq. and extracted with Et_2O . The combined extracts were washed with brine, and the residue upon workup was chromatographed on silica gel with hexane-AcOEt (95/5 v/v) as eluent to give methyl lactone **19** (9.7 mg, 95%) as a colorless oil; $[\alpha]_{23}^D = -10.2^\circ$ (c 0.86, CHCl_3); IR (KBr) cm^{-1} : 3070, 3049,

2932, 1773; ^1H NMR (400 MHz, CDCl_3) δ 1.05–1.06 (12H, m), 1.24 (3H, d, $J = 16.3$ Hz), 1.79–2.38 (9H, m), 3.66–3.71 (2H, m), 4.41–4.46 (1H, m), 5.36 (1H, dd, $J = 5.7$ and 8.5 Hz), 7.36–7.46 (6H, m), 7.65–7.67 (4H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 19.2, 20.5, 26.4, 26.9, 26.9, 26.9, 35.2, 35.3, 39.3, 39.5, 45.0, 63.3, 79.2, 121.0, 127.5, 127.5, 127.5, 127.5, 129.5, 129.5, 133.6, 133.6, 135.4, 135.4, 135.4, 135.4, 142.6, 179.2; LRMS (EI) m/z 485 ($\text{M}+\text{Na}^+$), 135 (base peak); HRMS (EI) m/z calcd for $\text{C}_{29}\text{H}_{38}\text{O}_3\text{SiNa}$ ($\text{M}+\text{Na}^+$): 485.2488 found 485.2471.

(3*R*,3*aR*,7*S*,8*aR*,*Z*)-6-(2-hydroxyethyl)-3,7-dimethyl-3,3*a*,4,7,8,8*a*-hexahydro-2*H*-cyclohepta[*b*]furan-2-one (20)

To a stirred solution of methyl lactone **19** (27 mg, 0.058 mmol) in THF (1 mL) was added TBAF (1.0 M in toluene, 0.12 mL, 0.12 mmol) at rt, and stirring was continued for 30 min at the same temperature. The reaction mixture was treated with water and extracted with AcOEt. The combined extracts were washed with brine, and the residue upon workup was chromatographed on silica gel with hexane-AcOEt (70/30 v/v) as eluent to give *epi*-sundiversifolide **20** (13 mg, quant.) as a colorless oil; $[\alpha]_{23}^{\text{D}} = -10.2^\circ$ (c 0.86, CHCl_3); IR (KBr) cm^{-1} : 3503, 1764; ^1H NMR (400 MHz, CDCl_3) δ 1.16 (3H, d, $J = 7.2$ Hz), 1.22–1.36 (4H, m), 1.85–2.09 (2H, m), 2.15–2.49 (7H, m), 3.62–3.69 (2H, m), 4.47–4.52 (1H, m), 5.47–5.50 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 20.6, 26.3, 35.2, 35.3, 39.3, 39.5, 45.0, 61.0, 79.0, 121.5, 142.4, 179.2; LRMS (FAB) m/z 225 ($\text{M}+\text{H}^+$), 136 (base peak); HRMS (FAB) m/z calcd for $\text{C}_{13}\text{H}_{21}\text{O}_3$ ($\text{M}+\text{H}^+$): 225.1491 found 225.1492.

Sundiversifolide (**1**)

To a stirred solution of LDA [prepared in situ from diisopropylamine (9 μ L, 0.069 mmol) and BuLi (1.57 M in hexane, 0.04 mL, 0.069 mmol) at -78 $^{\circ}$ C] in THF (0.7 mL) was added dropwise *epi*-sundiversifolide **20** (3.1 mg, 0.014 mmol) in THF (0.5 mL) at -78 $^{\circ}$ C. After stirring was continued for 30 min at the same temperature, phenol (1.0 M in THF, 0.11 mL, 0.11 mmol) was added to the solution at once at the same temperature. The reaction mixture was extracted with AcOEt and the combined extracts were washed with brine. The residue upon workup was chromatographed on silica gel with hexane-AcOEt (60/40 v/v) as eluent to give sundiversifolide (**1**) (2.2 mg, 71%) with recovered **20** (0.8 mg, 26%) as a colorless oil; $[\alpha]_{25}^D = +34^{\circ}$ (*c* 0.4, CHCl_3); IR (KBr) cm^{-1} : 3503, 1763; ^1H NMR (400 MHz, CD_3OD) δ 1.11 (3H, d, $J = 7.2$ Hz), 1.15 (3H, d, $J = 6.8$ Hz), 1.87–1.96 (1H, m), 1.99–2.04 (2H, m), 2.10–2.24 (2H, m), 2.32–2.44 (2H, m), 2.72–2.80 (1H, m), 2.86–2.94 (1H, m), 3.50–3.63 (2H, m), 4.67–4.73 (1H, m), 5.54–5.55 (1H, m); ^{13}C NMR (100 MHz, CD_3OD) δ 11.1, 22.0, 22.9, 34.1, 38.2, 40.2, 41.2, 43.5, 62.2, 82.4, 125.1, 143.4, 181.5; LRMS (FAB) m/z 225 ($\text{M}+\text{H}^+$), 136 (base peak); HRMS (FAB) m/z calcd for $\text{C}_{13}\text{H}_{21}\text{O}_3$ ($\text{M}+\text{H}^+$): 225.1491 found 225.1507.

7

8

8

S19

S21

S43

DFILE
 COMNT
 DATIM
 EXMOD
 OBNUC
 OBFRQ
 OBSET
 OBFIN
 POINT
 FREQU
 CLPNT
 TODAT
 CLFRQ
 SCANS
 ACQTM
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 PW1
 PW2
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 P11
 P12
 P13
 IRNUC
 CTEMP
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 EXREF
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 512
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 16
 0.282 sec
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 0.551 ms
 1300.00 ms
 1H
 25.9 c
 C6D6
 0.00 ppm
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 15