Representative procedure for the alkylation reaction: Preparation of 9. LDA was prepared by adding BuLi (4.68 mL, 7.5 mmol, 1.6 M in hexanes) to a solution of diisopropylamine (1.23 mL, 8.8 mmol) in 9 mL of THF, at –78 °C. The solution was stirred 15 min at 0 °C and then cooled again to –78 °C. A solution of **8** (1.2 g, 3.4 mmol) in THF (6 mL) was added to the LDA solution and the mixture was stirred for 30 min at –78 °C. MeI (1.05 mL, 17 mmol) in HMPA (3.5 mL) was then added to the dienolate solution. The reaction mixture was stirred for 2 hours, while the temperature was allowed to rise to 0 °C and quenched with saturated aquous NH_4Cl solution. The aqueous phase was extracted with ethyl ether (3x20 mL), the combined organic phases were dried ($MgSO_4$) and concentrated. Purification of the residue by medium pressure column chromatography (5/95 AcOEt/hexane) afforded **9** (1.28g, 99%) as a viscous colourless oil. $[\alpha]_D^{20}$-99.9 (2.02, $CHCl_3$). ^{1}H NMR ($CDCl_3$), 300 MHz: δ 3.35 (3H, s), 3.23 (3H, s), 2.93-2.70 (4H, m), 1.66 (3H, s), 1.54 (3H, s), 1.48 (3H, s), 1.39 (3H, s), 1.28 (3H, t, J=7.4 Hz), 1.21 (3H, t, J=7.4 Hz). ^{13}C NMR ($CDCl_3$), 75 MHz: δ 203.6, 201.0, 100.7, 100.4, 84.3, 82.0, 48.6, 47.8, 25.6, 25.3, 22.8, 22.5, 19.5, 19.2, 14.8, 14.1. m/z 349.0 $[M\text{-}Et]^+$.

Compound 10: $[\alpha]_D^{20}$-29.9 (0.29, $CHCl_3$). ^{1}H NMR ($CDCl_3$), 300 MHz: δ 4.91 (1H, s), 3.30 (3H, s), 3.27 (3H, s), 3.09 (2H, dd, J=17.3 Hz, J=2.4 Hz), 2.96-2.76 (4H, m), 1.81 (3H, t, J=2.4 Hz), 1.39 (3H, s), 1.35 (3H, s), 1.28 (3H, t, J=7.4 Hz), 1.24 (3H, t, J=7.4 Hz). ^{13}C NMR ($CDCl_3$), 75 MHz: δ 199.0, 198.4, 100.7, 99.9, 81.4, 78.8, 74.0, 73.1, 51.6, 48.5, 29.3, 22.9, 22.1, 17.7, 17.5, 14.4, 14.1, 3.6.

Compound 11: $[\alpha]_D^{20}$-14.3 (0.44, $CHCl_3$). ^{1}H NMR ($CDCl_3$), 300 MHz: δ 7.32 (2H, d, J=8.6 Hz), 6.79 (2H, d, J=8.7 Hz), 3.99 (1H, s), 3.79 (3H, s), 3.32 (3H, s), 3.32 (1H, d, J=14.1 Hz), 3.18 (1H, d, J=14.3 Hz), 2.97-2.82 (4H, m), 2.88 (3H, s), 1.34 (3H, s), 1.31 (3H, s), 1.28 (3H, t, J=7.4 Hz), 1.27 (3H, t, J=7.4 Hz). ^{13}C NMR ($CDCl_3$), 75 MHz: δ 199.3, 198.8, 158.5, 131.9, 128.0, 113.7, 113.0, 100.3, 99.6, 83.0, 73.2, 55.2, 51.6, 48.0, 42.4, 22.9, 22.1, 17.5, 14.4, 14.1. m/z 440.9 $[M\text{-}2xMe]^+$.

Compound 12: $[\alpha]_D^{20}$-41.2 (2.37, $CHCl_3$). ^{1}H NMR ($CDCl_3$), 300 MHz: δ 4.92 (2H, d, J=12.1 Hz), 4.48 (1H, s), 3.28 (3H, s), 3.28 (3H, s), 3.25 (3H, s), 2.95 (1H, d, J=14.1 Hz), 2.91-2.80 (4H, m), 2.55 (1H, d, J=14.0 Hz), 1.89 (3H, s), 1.38 (3H, s), 1.30 (3H, s), 1.27 (3H, t, J=7.4 Hz), 1.25 (3H, t, J=7.2 Hz). ^{13}C NMR ($CDCl_3$), 75 MHz: δ 200.0, 198.5, 141.6, 115.9, 100.5, 99.4, 82.6, 73.4, 51.6, 48.4, 45.2, 23.9, 22.8, 22.1, 17.7, 17.6, 14.4, 14.1.

Compound 13: $[\alpha]_D^{20}$-216.0 (0.20, $CHCl_3$). ^{1}H NMR ($CDCl_3$), 300 MHz: δ 3.56 (2H, dd, J= 16.2 Hz, J=2.6 Hz), 3.51 (3H, s), 3.35 (2H, dd, J=17.1 Hz, J=2.6 Hz), 3.28 (3H, s), 3.11-2.70 (4H, m),

2.11 (1H, t, J=2.6 Hz), 2.00 (1H, t, J=2.6 Hz), 1.56 (3H, s), 1.47 (3H, s), 1.31 (3H, t, J=7.4 Hz), 1.21 (3H, t, J=7.4 Hz). ^{13}C NMR ($CDCl_3$), 75 MHz: δ 203.0, 201.0, 101.6, 100.8, 81.6, 79.0, 72.6, 70.9, 48.7, 29.4, 27.5, 23.3, 22.9, 19.5, 19.1, 14.7, 13.9.

Compound 14: $[\alpha]_D^{20}$-51.5 (0.40, $CHCl_3$). ^{1}H NMR ($CDCl_3$), 300 MHz: δ 4.90 (1H, s), 3.30 (3H, s), 3.27 (3H, s), 3.17 (2H, dd, J=17.0 Hz, J=2.6 Hz), 2.92-2.83 (4H, m), 2.10 (1H, t, J=2.6 Hz), 1.40 (3H, s), 1.35 (3H, s), 1.28 (3H, t, J=7.4 Hz), 1.24 (3H, t, J=7.4 Hz). ^{13}C NMR ($CDCl_3$), 75 MHz: δ 199.0, 198.1, 100.9, 100.0, 80.8, 78.5, 73.9, 71.3, 51.7, 48.5, 29.0, 23.1, 22.1, 17.1, 17.4, 14.4, 14.1.

Compound 15: $[\alpha]_D^{20}$-10.8 (1.06, $CHCl_3$). ^{1}H NMR ($CDCl_3$), 300 MHz: δ 5.82-5.73 (2H, m), 5.03 (4H, d, J=12.8 Hz), 3.33 (6H, s), 3.18 (2H, dd, J=15.1 Hz, J=5.8 Hz), 2.77 (4H, q, J=7.3 Hz), 2.66 (2H, dd, J=14.7 Hz, J=7.08 Hz), 1.47 (6H, s), 1.22 (6H, t, J=7.3 Hz). ^{13}C NMR ($CDCl_3$), 75 MHz: δ 201.6, 132.6, 118.4, 100.2, 83.2, 51.3, 39.6, 23.0, 18.9, 14.0.

Compound 16: $[\alpha]_D^{20}$-72.9 (1.57, $CHCl_3$). ^{1}H NMR ($CDCl_3$), 300 MHz: δ 7.42-7.37 (2H, m), 7.26-7.22 (3H, m), 3.98 (1H, s), 3.39 (1H, d, J=14.1 Hz), 3.33 (3H, s), 3.25 (2H, d, J=14.1 Hz), 2.84 (3H, s), 2.97-2.80 (4H, m), 1.34 (3H, s), 1.30 (3H, s), 1.28-1.25 (6H, m). ^{13}C NMR ($CDCl_3$), 75 MHz: δ 199.2, 198.8, 135.9, 131.0, 127.6, 126.7, 100.3, 99.6, 82.8, 73.2, 51.6, 47.9, 43.2, 22.9, 22.1, 17.5, 14.4, 14.1.

Compound 17: $[\alpha]_D^{20}$-75.7 (0.63, CH_2Cl_2). ^{1}H NMR ($CDCl_3$), 300 MHz: δ 7.16 (s, 5H), 3.74 (1H, d, J=12.8 Hz), 3.69 (s, 3H), 3.50 (s, 3H), 3.11 (1H, d, J=12.8 Hz), 2.86 (4H, q, J=7.4 Hz), 2.78-2.67 (4H, m), 1.64 (s, 3H), 1.51 (s, 3H), 1.49 (s, 3H), 1.26 (3H, t, J=7.4 Hz), 1.13 (3H, t, J=7.4 Hz). ^{13}C NMR ($CDCl_3$), 75 MHz: δ 202.5, 135.8, 131.1, 127.3, 126.2, 100.5, 100.4, 84.8, 82.8, 50.3, 50.2, 41.4, 24.9, 23.5, 23.3, 20.1, 19.6, 14.2, 14.0.

Compound ent-11: $[\alpha]_D^{20}$+15.0 (1.2, $CHCl_3$). All other data was identical to **11**.

Compound 18: To a solution of **ent-11** (0.300 g, 0.63 mmol) in CH_2Cl_2 (3 mL) was added TFA (0.350 mL, 4.44 mmol) and a catalytic quantity of H_2O. After refluxing for 3 h, the reaction mixture was evaporated and purified by medium pressure column chromatography (2/8 AcOEt/hex). Diol **18** was obtained as a very viscous colourless oil (0.223 g, 98%). $[\alpha]_D^{20}$-44.2 (1.04, $CHCl_3$). ^{1}H NMR ($CDCl_3$), 300 MHz: δ 7.12 (2H, d, J=8.6 Hz), 6.80 (2H, d, J=8.7 Hz), 4.43 (1H, s), 3.77 (3H, s), 3.22 (1H, d, J=13.9 Hz), 3.12 (1H, d, J=13.9 Hz), 2.95-2.76 (4H, m), 1.26 (3H, t, J=7.4 Hz), 1.19 (3H, t, J=7.4 Hz). ^{13}C NMR ($CDCl_3$), 75 MHz: δ 204.2, 201.4, 158.8, 131.7, 125.7, 113.7, 84.2, 79.6, 55.1, 40.5, 23.2, 14.2, 14.1.

4'-O-methyl-piscidic acid dimethylester 2: To a solution of **18** (0.200 g, 0.56 mmol) in MeOH (1.5 mL) was added MeONa (0,440 g, 1.67 mmol) and the reaction mixture was stirred for 15 min and quenched with saturated aquous NH_4Cl solution. The aqueous phase was extracted with ethyl acetate (3 x 10 mL), the combined organic phases were dried ($MgSO_4$) and concentrated. Purification of the residue by recrystalisation (Hex/AcOEt) afforded **2** (0.158 g, 95%) as white crystals. $[\alpha]_D^{20}$+42.8 (1.02, $CHCl_3$), (isolated natural product, $[\alpha]_D^{24}$+44 ± 2, c=0.60, $CHCl_3$[7]; synthesised product, $[\alpha]_D^{25}$+46 ± 2, c=1.01, EtOH[7]). Mp= 105-106 °C (lit.[7] 107-108 °C). ^{1}H NMR ($CDCl_3$), 300 MHz: δ 7.08 (2H, d, J=8.6 Hz), 6.80 (2H, d, J=8.7 Hz), 4.54 (1H, s), 3.78 (3H, s), 3.76 (3H, s), 3.74 (3H, s), 3.28 (1H, d, J=13.9 Hz), 3.03 (1H, d, J=13.9 Hz). ^{13}C NMR ($CDCl_3$), 75 MHz: δ 173.3, 171.6, 158.7, 131.0, 126.9, 113.7, 113.6, 80.1, 75.1, 55.1, 52.8, 40.5.

Compound ent-12: $[\alpha]_D^{20}$+42.0 (1.5, $CHCl_3$). All other data was identical to **12**.

Compound 20: To a solution of **ent-12** (0.150 g, 0.37 mmol) in CH_2Cl_2 (2 mL) was added TFA (0.199 mL, 2.59 mmol) and a catalytic quantity of H_2O. After refluxing for 2 h, the reaction mixture was evaporated and purified by preparative TLC (4/6 AcOEt/hex). Diol **20** was obtained as a very viscous colourless oil (0.107 g, 99%). $[\alpha]_D^{20}$+3.12 (0.96, $CHCl_3$). ^{1}H NMR ($CDCl_3$), 300 MHz: δ 4.97 (1H, t, J=1.7 Hz), 4.84 (1H, d, J=0.93 Hz), 4.36 (1H, s), 2.95-2.84 (4H, m), 2.74 (1H, d, J=13.6 Hz), 2.64 (1H, d, J=13.7 Hz), 1.75 (3H, s), 1.265 (3H, t, J=7.4 Hz), 1.264 (3H, t, J=7.4 Hz). ^{13}C NMR ($CDCl_3$), 75 MHz: δ 204.5, 200.9, 140.0, 116.9, 83.1, 80.0, 43.3, 24.1, 23.4, 23.2, 14.2, 14.0.

Compound 21: To a solution of **20** (0.100 g, 0.34 mmol) in MeOH (1 mL) was added MeONa (5.5 mg, 1.02 mmol) and the reaction mixture was stirred for 15 min and quenched with saturated aquous NH_4Cl solution. The aqueous phase was extracted with ethyl acetate (3 x 10 mL), the combined organic phases were dried ($MgSO_4$) and concentrated. Purification of the residue by preparative TLC (4/6 AcOEt/Hex) afforded **21** (0.71 g, 95%) as very viscous colourless oil. $[\alpha]_D^{20}$+45.1 (0.49, $CHCl_3$). ^{1}H NMR ($CDCl_3$), 400 MHz: δ 4.89 (1H, t, J=1.5 Hz), 4.75 (1H, s), 4.44 (1H, s), 3.81 (3H, s), 3.77 (3H, s), 2.80 (1H, d, J=13.9 Hz), 2.64 (1H, d, J=13.8 Hz), 1.75 (3H, s). ^{13}C NMR ($CDCl_3$), 100 MHz: δ 173.7, 171.6, 140.8, 115.5, 79.8, 75.5, 52.83, 52.8, 42.8, 23.8.

Compound 22: A solution of **21** (0.070 g, 0.30 mmol) in AcOEt (1 mL) was added to Pd/C 10% (8 mg, 2.5 mol%) in AcOEt (1 mL). The reaction mixture was hydrogenated at 50 atm for 24h. The mixture was filtrated, the solvents evaporated and the residue was purified by preparative TLC (1/1 AcOEt/Hex) to afford **22** as a very viscous oil (0.062 g, 88%). $[\alpha]_D^{20}$ +29.5 (0.22, $CHCl_3$). ^{1}H NMR

($CDCl_3$), 400 MHz: δ 4.32 (1H, s), 3.82 (3H, s), 3.76 (3H, s), 2.04 (1H, dd, J=14.2 Hz, J=5.8 Hz), 1.77-1.66 (2H, m), 0.96 (3H, d, J=6.6 Hz), 0.84 (3H, d, J=6.6 Hz). ^{13}C NMR ($CDCl_3$), 100 MHz: δ 174.7, 171.6, 79.3, 76.1, 52.9, 52.7, 43.0, 24.1, 24.0, 23.2.