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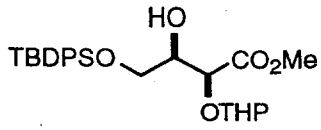
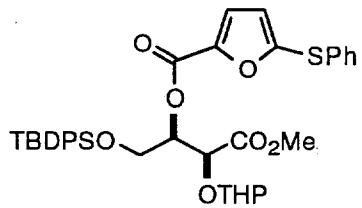


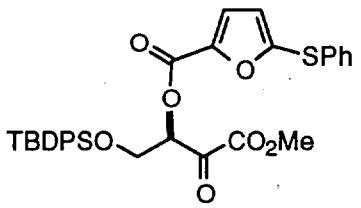
6

Methyl (2*S*,3*R*)-4-*tert*-butyldiphenylsiloxy-3-hydroxy-2-(tetrahydropyran-2-yloxy)butanoate (6). To a solution of tetrahydropyranyl ether **5**[10] (1.43 g, 5.5 mmol) in THF (10 mL) was added BH_3-SMe_2 (10~10.2 M; 0.54 mL, 5.7 mmol) dropwise at rt, and the solution was stirred for 2 h. This solution was cooled to 0 °C, and $NaBH_4$ (10 mg, 0.3 mmol) was added. The reaction mixture was then stirred at 0 °C for 1 h and then allowed to warm to rt over 1 h. After stirring at rt for an additional 1 h, MeOH (2 mL) was added dropwise, and the solution was stirred for an additional 30 min. The reaction mixture was concentrated under reduced pressure, and the residue was directly chromatographed (100% EtOAc) to afford 0.97 g of viscous oil containing diols. The mixture of diols (0.97 g) and imidazole (0.42 g, 6.2 mmol) were dissolved in CH_2Cl_2 (12 mL), whereupon *tert*-butylchlorodiphenylsilane (1.70 g, 1.6 mL, 6.2 mmol) was added at 0 °C. After stirring at 0 °C for 1 h, saturated $NaHCO_3$ solution (50 mL) and EtOAc (50 mL) were added to the reaction mixture. The layers were separated, and the organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with hexanes/EtOAc (4:1) to give 1.30 g (50% from **5**) of β-hydroxyester **6**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71-7.65 (comp, 4 H), 7.46-7.35 (comp, 6 H), 4.83-4.81 (m, 1 H), 4.62 (d, J = 2.7 Hz, 1 H), 4.12-4.05 (m, 1 H), 3.79-3.68 (comp, 3 H), 3.75 (s, 3 H), 3.48-3.42 (m, 1 H), 2.51 (d, J = 8.0 Hz, 1 H), 1.80-1.40 (comp, 6 H), 1.05 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 135.6, 133.2, 129.8, 127.8, 96.8, 72.8, 72.6, 63.9, 62.2, 52.1, 30.1, 26.8, 25.2, 19.2, 18.8; IR ($CHCl_3$) 3569, 1748, 1203, 1113 cm^{-1}; mass spectrum (CI) *m/z* 473.2348 [$C_{26}H_{37}O_6Si$ (M+1) requires 473.2359], 389, 311 (base), 233.



8

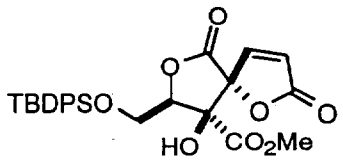
Methyl (2*S*,3*R*)-4-*tert*-butyldiphenylsiloxy-3-(5-phenylthio-2-furoyloxy)-2-(tetrahydropyran-2-yloxy)butanoate (8). β-Hydroxyester **6** (4.90 g, 10.4 mmol), 5-phenylthio-2-furoic acid **7**[11] (2.40 g, 10.9 mmol) and 4-dimethylaminopyridine (DMAP) (0.63 g, 5.2 mmol) were dissolved in CH_2Cl_2 (30 mL), whereupon dicyclohexylcarbodiimide (DCC) (2.57 g, 12.4 mmol) was added at 0 °C. The reaction mixture was stirred at rt for 5 h, and then Et_2O (100 mL) was added. Insoluble materials were removed by filtration. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with hexanes/EtOAc (5:1) to give 6.72 g (96%) of ester **8** as a viscous oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.70-7.64 (comp, 4 H), 7.40-7.17 (comp, 11 H), 7.16 (d, *J* = 3.4 Hz, 1 H), 6.63 (d, *J* = 3.4 Hz, 1 H), 5.59-5.53 (m, 1 H), 4.79 (br s, 1 H), 4.75 (d, *J* = 4.3 Hz, 1 H), 3.98 (dd, *J* = 5.7, 10.7 Hz, 1 H), 3.91 (dd, *J* = 6.1, 10.7 Hz, 1 H), 3.77-3.71 (m, 1 H), 3.68 (s, 3 H), 3.43-3.39 (m, 1 H), 1.80-1.40 (comp, 6 H), 1.02 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 157.1, 150.2, 146.6, 135.6, 133.7, 133.1, 133.0, 129.8, 129.7, 129.3, 127.8, 127.7, 127.5, 119.9, 118.8, 96.3, 74.3, 71.4, 61.9, 61.8, 52.2, 30.0, 26.7, 25.3, 19.2, 18.5; IR ($CHCl_3$) 1744; 1222, 1114 cm^{-1}; mass spectrum (CI) *m/z* 673.2301 [$C_{37}H_{41}O_8SiS$ (M+1) requires 673.2291], 591, 513, 427(base), 302.



9

Methyl (3*R*)-4-*tert*-butyldiphenylsiloxy-2-oxo-3-(5-phenylthio-2-furoyloxy)butanoate (9). To a solution of THP ether **8** (6.72 g, 10.0 mmol) in CH_2Cl_2 (50 mL) was added 1 M Me_2AlCl solution in hexanes (20.0 mL, 20.0 mmol) at -25 °C.[12] The reaction was allowed to warm to rt over 2 h and stirred at rt for 2 h. Saturated $KHCO_3$ solution (100 mL) was then added to the reaction solution at 0 °C. The mixture was filtered through Celite, and the filtrate was extracted with CH_2Cl_2 (2 x 100 mL). The extracts were dried (Na_2SO_4) and concentrated in vacuo. The residue was rapidly purified by flash chromatography eluting with hexanes/EtOAc (4:1) to afford 5.60 g (95%) of alcohol as powder (mp, 76-78 °C). To a solution of alcohol (5.60 g, 9.5 mmol) in CH_2Cl_2 (95

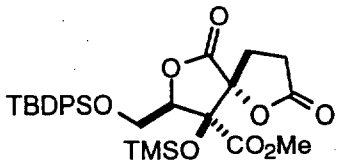
mL) was added Dess-Martin periodinane (8.04 g, 19.0 mmol) at 0 °C. The mixture was stirred at rt for 10 min, and then wet CH_2Cl_2 (350 μL of water in 350 mL of CH_2Cl_2) was added over 1 h. After stirring at rt for 20 min, ether (300 mL), saturated $NaHCO_3$ solution (150 mL) and 10% $Na_2S_2O_3$ solution (150 mL) were added to the mixture. The layers were separated. The organic layer was washed with saturated $NaHCO_3$ solution (1 x 150 mL), dried (Na_2SO_4) and concentrated under reduced pressure to give 5.50 g (99%) of α-ketoester **9**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.69-7.61 (comp, 4 H), 7.46-7.24 (comp, 11 H), 7.22 (d, *J* = 3.4 Hz, 1 H), 6.66 (d, *J* = 3.4 Hz, 1 H), 5.99 (dd, *J* = 3.4, 4.6 Hz, 1 H), 4.43 (dd, *J* = 4.6, 11.4 Hz, 1 H), 4.09 (dd, *J* = 3.4, 11.4 Hz, 1 H), 3.89 (s, 3 H), 0.99 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.1, 160.1, 156.9, 151.2, 145.7, 135.6, 135.4, 133.2, 132.6, 132.2, 130.0, 129.4, 127.9, 120.8, 118.6, 77.2, 63.2, 53.2, 26.5, 19.2; IR ($CHCl_3$) 1736, 1577, 1463, 1296, 1114 cm^{-1}; mass spectrum (CI) *m/z* 589.1729 [$C_{32}H_{33}O_7SiS$ (M+1) requires 589.1716] (base), 511, 279, 177.



10

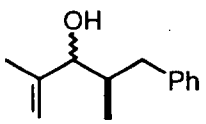
(5*R*,8*R*,9*S*)-8-(*tert*-Butyldiphenylsiloxymethyl)-9-hydroxy-9-methoxycarbonyl-1,7-dioxaspiro[4.4]non-3-ene-2,6-dione (10). To a solution of α-ketoester **9** (5.50 g, 9.3 mmol) in CH_2Cl_2 (14 mL) was added 1 M $TiCl_4$ solution in CH_2Cl_2 (28.5 mL, 28.5 mmol) dropwise at 0 °C. The reaction was stirred at 0 °C for 30 min and at rt for 1 h, and then poured into ice-cold water (150 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 150 mL). The extracts were washed with saturated $NaHCO_3$ solution (50 mL), dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash chromatography eluting with hexanes/EtOAc (3:1~2:1) to give 1.98 g (42%) of spirobislactone **10**, which contained one of other isomers in the ratio of 20:1 (by NMR): ^1H NMR (300 MHz, $CDCl_3$) δ 7.70-7.63 (comp, 5 H), 7.51-7.40 (comp, 6 H), 6.36 (d, *J* = 5.7 Hz, 1 H), 5.32 (s, 1 H), 4.94 (dd, *J* = 3.2, 4.3 Hz, 1 H), 4.26 (dd, *J* = 3.2, 11.8 Hz, 1 H), 4.18 (dd, *J* = 4.3, 11.8 Hz, 1 H), 3.84 (s, 3 H), 1.06 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 168.4, 167.0, 150.1, 135.7, 135.5, 131.8, 131.2, 130.5, 130.4, 128.1, 124.7, 89.3, 81.2, 79.8, 61.4, 54.0, 26.8, 19.2; IR ($CHCl_3$) 3310,

1803, 1747, 1206, 1100 cm^{-1}; mass spectrum (FAB) *m/z* 497.1631 [$C_{26}H_{29}O_8Si$ (M+1) requires 497.1632] 289, 197 (base), 165.



11

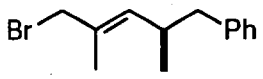
(5*R*,8*R*,9*S*)-8-*tert*-Butyldiphenylsiloxymethyl-9-methoxycarbonyl-9-trimethylsiloxy-1,7-dioxaspiro[4.4]nonane-2,6-dione (11). A solution of **10** (65 mg, 0.13 mmol) in EtOAc (2.6 mL) containing 20% $Pd(OH)_2$ on carbon (195 mg, 0.28 mmol) was stirred under 1 atm H_2 atomosphere at rt. After 18 h the catalyst was removed by filtration, and the filtrate was concentrated. The residue was purified by flash chromatography eluting with hexanes/EtOAc (2:1) to give 59 mg (90%) of reduced lactone. To a solution of the lactone (327 mg, 0.66 mmol) in CH_2Cl_2 (6.6 mL) containing imidazole (179 mg, 2.62 mmol) was added chlorotrimethylsilane (TMSCl) (142 mg, 166 μL, 1.31 mmol) at 0 °C, and the solution was stirred at rt for 1 h. The reaction mixture was diluted with EtOAc (50 mL), washed with water (50 mL), dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography eluting with hexanes/EtOAc (4:1) to give 309 mg (83%) of TMS ether **11** as a white crystals: mp, 142-145 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.67-7.65 (comp, 4 H), 7.43-7.36 (comp, 6 H), 5.01 (dd, *J* = 3.6, 7.5 Hz, 1 H), 3.89 (dd, *J* = 3.6, 11.6 Hz, 1 H), 3.75 (dd, *J* = 7.5, 11.6 Hz, 1 H), 3.74 (s, 3 H), 2.82-2.23 (comp, 4 H), 1.06 (s, 9 H), -0.02 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.2, 171.2, 168.1, 135.7, 135.6, 132.9, 132.6, 130.0, 127.9, 86.3, 83.5, 81.5, 62.5, 53.4, 27.2, 26.8, 23.4, 19.3, 1.4; IR ($CHCl_3$) 1796, 1748, 1216, 1113 cm^{-1}; mass spectrum (CI) *m/z* 571.2179 [$C_{29}H_{39}O_8Si_2$ (M+1) requires 571.2184] (base), 513, 493.



13

(4*R*)-3-Hydroxy-2,4-dimethyl-5-phenyl-1-pentene (13). To a suspension of magnesium (152 mg, 6.25 mmol) in THF (3 mL) was added a solution of 2-bromopropene (605 mg, 5.00

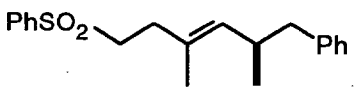
mmol) in THF (2 mL) at rt over 1 h, and the mixture was stirred at rt for 1 h and then cooled to 0 °C. A solution of aldehyde **12**[14] (380 mg, 2.56 mmol) in THF (5 mL) was added to the prepared Grignard reagent. The mixture was stirred at 0 °C for 10 min and at rt for 10 min, and then poured into water (20 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 40 mL). The extracts were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with hexanes/EtOAc (4:1) to give 366 mg (75%) of diastereomixture (~1:1) of alcohols **13**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.16 (comp, 5 H), 5.00-4.90 (comp, 2 H), 3.90-3.84 (comp, 1 H), 3.07 (dd, *J* = 3.4, 13.2 Hz, 0.5 H), 2.76 (dd, *J* = 6.0, 13.4 Hz, 0.5 H), 2.43 (dd, *J* = 8.6, 13.4 Hz, 0.5 H), 2.29 (dd, *J* = 10.0, 13.2 Hz, 0.5 H), 2.00-1.86 (comp, 1 H), 1.75 (s, 1.5 H), 1.70 (s, 1.5 H), 1.59 (br s, 1 H), 0.84 (d, *J* = 6.8 Hz, 1.5 H), 0.75 (d, *J* = 6.8 Hz, 1.5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.7, 146.5, 141.1, 141.0, 129.4, 129.1, 128.2, 128.1, 125.8, 125.7, 112.7, 111.3, 80.6, 77.9, 40.1, 38.2, 38.0, 37.6, 18.6, 17.4, 15.9, 13.4; IR ($CHCl_3$) 3606, 1650, 1602, 1495, 1453, 1010, 907 cm^{-1}; mass spectrum (CI) *m/z* 190.1352 [$C_{13}H_{18}O$ (M) requires 190.1358], 173 (base).



14

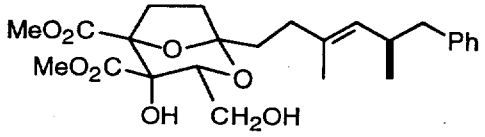
(4*R*)-1-Bromo-2,4-dimethyl-5-phenyl-2-pentene (14). To a solution of diastereomixture of alcohols **13** (366 mg, 1.92 mmol) and Et_3N (330 mg, 455 μL, 3.26 mmol) in CH_2Cl_2 (6 mL) was added methanesulfonyl chloride (330 mg, 223 μL, 2.88 mmol) at 0 °C. The reaction mixture was stirred at rt for 1 h and then poured into water (50 mL). The aqueous layer was extracted with EtOAc (1 x 50 mL), and the extract was washed with 1 N HCl (10 mL), dried (Na_2SO_4) and concentrated under reduced pressure to give 512 mg of crude mesylates. The mesylates were diluted with 2-butanone (10 mL) containing NaBr (395 mg, 3.84 mmol) and 18-crown-6 ether (50 mg, 0.19 mmol). The mixture was stirred at reflux for 6 h and then poured into a mixture of EtOAc (50 mL) and water (50 mL). The layers were separated, and the organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with 100% hexanes to give 395 mg (81%) of bromide **14**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.11 (comp, 5 H), 5.43 (d, *J* = 8.4 Hz, 1 H), 3.92 (s, 2 H), 2.65-2.54 (comp, 3 H), 1.54 (d, *J* = 1.3 Hz, 3 H), 0.97 (d, *J* = 6.4 Hz, 3 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.3, 136.6, 131.2, 129.3, 128.2, 125.9, 43.4, 41.9, 35.0, 20.2, 14.7; IR ($CHCl_3$) 1603, 1495, 1452 cm^{-1}; mass spectrum (CI) *m/z* 253.0592 [$C_{13}H_{18}Br$ (M+1) requires 253.0592], 173 (base).

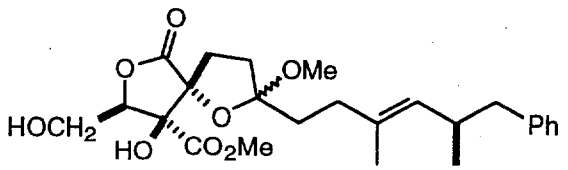


15

(2*R*)-2,4-Dimethyl-1-phenyl-6-phenylsulfonyl-3-hexene (15). To a suspension of KH (57 mg, 1.42 mmol) in THF (2 mL) was added a solution of methyl phenyl sulfone (244 mg, 1.56 mmol) in THF (2 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h, and then a solution of bromide **14** (180 mg, 0.71 mmol) in THF (1 mL) was added at 0 °C. The reaction mixture was stirred at rt for 10 h and then quenched by adding saturated NH_4Cl solution (20 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 30 mL). The extracts were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with hexanes/EtOAc (5:1) to give 208 mg (89%) of sulfone **15**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.93-7.25 (comp, 5 H), 7.24-7.05 (comp, 5 H), 4.95 (br d, *J* = 8.9 Hz, 1 H), 3.14-2.98 (m, 2 H), 2.61-2.40 (comp, 3 H), 2.32-2.27 (m, 2 H), 1.31 (d, *J* = 1.3 Hz, 3 H), 0.91 (d, *J* = 6.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7, 139.1, 133.7, 132.6, 130.0, 129.3, 129.2, 128.1, 128.0, 125.7, 55.2, 43.7, 34.6, 32.2, 20.6, 15.9; IR ($CHCl_3$) 1603, 1495, 1448, 1307, 1151, 1086 cm^{-1}; mass spectrum (CI) *m/z* 329.1584 [$C_{20}H_{25}O_2S$ (M+1) requires 329.1575], 187 (base), 143.



17



18a,b

(1*S*,3*R*,4*S*,5*R*)-1-[(5*R*)-3,5-Dimethyl-6-phenyl-3-hexen-1-yl]-4-hydroxy-3-hydroxymethyl-4,5-bis(methoxycarbonyl)-2,8-dioxabicyclo[3.2.1]octane (17) and (*5R,8R,9S*)-2-[(5*R*)-3,5-dimethyl-6-phenyl-3-hexen-1-yl]-9-hydroxy-8-(hydroxymethyl)-2-methoxy-9-methoxycarbonyl-1,7-dioxaspiro[4.4]nonane-6-one

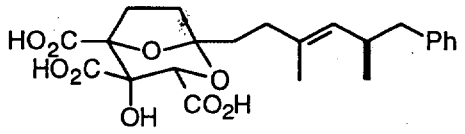
(18a,b). Sulfone **15** (138 mg, 0.42 mmol) was dissolved in THF (1 mL), whereupon 1.4 M BuLi solution in hexanes (0.60 mL, 0.84 mmol) was added at -78 °C. The solution was stirred at -78 °C for 1.5 h, and then a solution of bislactone **11** (239 mg, 0.42 mmol) in THF (2 mL) was added. The reaction was stirred at -78 °C for 1 h and then allowed to warm to 0 °C over 1 h. Saturated NH_4Cl solution (10 mL) was added to the reaction solution at 0 °C, and the aqueous layer was extracted with EtOAc (2 x 30 mL). The extracts were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was diluted with THF (8 mL), and the solution was added to aluminum amalgam, which was prepared from aluminum foil (1.56 g, 57.7 mmol) according to the literature procedure.[17] To the reaction mixture, HMPA (2 mL) and water (0.2 mL) were added, successively. The reaction mixture was stirred at rt for 3 h and then filtered through Celite, and the unreacted aluminum amalgam was washed with Et_2O (1 x 50 mL). The filtrate was washed with water (2 x 50 mL), dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by flash chromatography eluting with hexanes/EtOAc (3:1) to give 232 mg (73%) of desulfonylated compounds **16** as a mixture of hemiacetals and a ketone. Lactone **16** (49 mg, 0.065 mmol) was diluted in MeOH (5 mL) containing conc. H_2SO_4 (49 mg, 0.5 mmol), and the solution was stirred at rt for 40 h. Pyridine (119 mg, 121 μL, 1.5 mmol) was added to the solution, and the solvents were evaporated under reduced pressure. The residue was diluted with EtOAc (30 mL), washed with water (10 mL), dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography eluting with hexanes/EtOAc (1:2) to give 7.6 mg (25%) of dimethyl ester **17**, 9.5 mg (32%) of methyl acetal **18a** (less polar) and 9.8 mg (33%) of methyl acetal **18b** (more polar).

17: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.12 (comp, 5 H), 5.01 (d, J = 9.1 Hz, 1 H), 4.28 (t, J = 5.7 Hz, 1 H), 3.85 (s, 3 H), 3.79 (s, 3 H), 3.80-3.60 (m, 2 H), 3.12-3.03 (m, 1 H), 2.64-2.51 (comp, 3 H), 2.21-1.85 (comp, 7 H), 1.44 (d, J = 1.1 Hz, 3 H), 0.95 (d, J = 6.4 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 169.4, 141.1, 133.2, 130.6, 129.3, 128.0, 125.7, 109.0, 88.1, 75.1, 74.1, 61.6, 53.2, 52.8, 44.0, 35.4, 34.5, 33.5, 31.6, 29.3, 20.9, 16.1; IR ($CHCl_3$) 3538, 1737, 1439, 1268, 1229, 1124, 1036 cm^{-1}; mass spectrum (CI) *m/z* 463.2323 [$C_{25}H_{35}O_8$ (M+1) requires 463.2332] (base), 445.

18a (less polar): mp, 100-102 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25-7.11 (comp, 5 H), 4.98 (d, J = 8.4 Hz, 1 H), 4.84 (t, J = 4.4 Hz, 1 H), 4.54 (s, 1 H), 4.10-4.07 (m, 2 H), 3.86 (s, 3 H), 3.22 (s, 3 H), 2.70-1.64 (comp, 11 H), 1.41 (d, J = 1.2 Hz, 3 H), 0.96 (d, J = 6.4 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 170.9, 141.1, 133.3, 130.6, 129.3, 128.0, 125.6, 112.4, 87.6, 81.0, 78.9,

60.9, 53.4, 48.9, 44.0, 35.7, 34.6, 33.0, 31.7, 27.7, 22.7, 14.2; IR ($CHCl_3$) 3335, 1793, 1741, 1453, 1286, 1077, 1041, 1032 cm^{-1}; mass spectrum (CI) *m/z* 463.2335 [$C_{25}H_{35}O_8$ (M+1) requires 463.2332], 431 (base), 403.

18b (more polar): ^1H NMR (300 MHz, $CDCl_3$) δ 7.26-7.12 (comp, 5 H), 4.99 (d, *J* = 7.7 Hz, 1 H), 4.76 (t, *J* = 5.0 Hz, 1 H), 4.11 (s, 1 H), 3.98-3.93 (m, 2 H), 3.92 (s, 3 H), 3.12 (s, 3 H), 2.75-1.70 (comp, 11 H), 1.43 (d, *J* = 1.3 Hz, 3 H), 0.94 (d, *J* = 6.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.2, 171.4, 141.1, 133.2, 130.6, 130.5, 129.3, 128.0, 125.7, 112.6, 87.0, 80.1, 79.4, 61.1, 53.8, 49.2, 44.0, 35.5, 34.6, 34.3, 32.8, 29.3, 20.8, 16.3; IR ($CHCl_3$) 3498, 1792, 1744, 1453, 1288, 1058, 1032 cm^{-1}; mass spectrum (CI) *m/z* 463.2326 [$C_{25}H_{35}O_8$ (M+1) requires 463.2332], 431 (base), 403.



3

6,7-Dideoxysqualestatin H5 (3). Alcohol **17** (25 mg, 0.05 mmol) was disolved in CH_3CN (1 mL) containing water (2 mg, 0.11 mmol), whereupon *N*-methylmorphorine-*N*-oxide (NMO) (25 mg, 0.22 mmol) and tetrapropylammonium perruthenate (TPAP) (2 mg, 0.005 mmol) were added. The solution was stirred at rt for 5 h, and then EtOAc (30 mL) and 0.1 M HCl solution (10 mL) were added. The layers were separated, and the organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography eluting with CH_2Cl_2/MeOH (5:1) to give 23 mg (88%) of carboxylic acid. The carboxylic acid (10 mg, 0.021 mmol) was diluted in dioxane (1 mL) containing water (1.5 mg, 0.084 mmol), whereupon potasium *tert*-butoxide (24 mg, 0.21 mmol) was added. The reaction mixture was heated at reflux for 1 d, and then the solvent was evaporated. The residue was diluted with water (10 mL), and the aqueous layer was washed with Et_2O (1 x 10 mL), acidified by adding 0.1 N HCl solution (4 mL) and then extracted with EtOAc (2 x 20 mL). The extracts were dried (Na_2SO_4) and concentrated under reduced presure. The residue was purified by HPLC (C18 reverse phase column; eluent: MeOH/H_2O/AcOH, 400:100:1) to give 6.6 mg (70%) of 6,7-dideoxysqualestatin H5 (**3**): ^1H NMR (500 MHz, CD_3OD) δ 7.23-7.11 (comp, 5 H), 5.03 (d, *J* = 9.0 Hz, 1 H), 4.87 (s, 1 H), 3.19-3.15 (m, 1 H), 2.68-2.60 (m, 1 H), 2.58 (dd, *J* = 6.1, 13.0 Hz, 1 H), 2.47 (dd, *J* = 8.3, 13.0

Hz, 1 H), 2.21-1.83 (comp, 7 H), 1.42 (d, J = 1.1 Hz, 3 H), 0.95 (d, J = 6.6 Hz, 3 H); ^{13}C NMR (125 MHz, CD_3OD) δ 173.4, 172.4, 171.1, 142.4, 135.0, 131.7, 130.3, 129.0, 126.7, 109.9, 89.5, 76.2, 75.9, 45.1, 36.5, 35.9, 34.7, 32.2, 30.3, 21.4, 16.1; IR ($CHCl_3$) 3397, 1733, 1603, 1276, 1129 cm^{-1}; mass spectrum (FAB) *m/z* 447.1642 [$C_{23}H_{27}O_9$ (M-1) requires 447.1655] (base), 403.