Supporting information

Total Synthesis of Spirotenuipesines A and B

Mingji Dai,1 Isaac J. Krauss,2 Samuel J. Danishefsky*1,2

1Department of Chemistry, Columbia University, Havemeyer Hall, New York, NY 10027, USA;
2Laboratory for Bioorganic Chemistry, Sloan-Kettering Institute for Cancer Research Center, 1275 York Avenue, New York, NY 10065, USA;

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General Methods

All non-aqueous reactions were carried out in oven-dried glassware under a slight positive pressure of argon unless otherwise noted. All reagents were commercially available and used without further purification, unless indicated otherwise. Solvents were reagent grade and purified by standard techniques: THF was distilled from Na-benzophenone or filtered through a dry-solvent system; CH₂Cl₂ was distilled from CaH₂ or filtered through a dry-solvent system; all other solvents were “anhydrous” grade solvents, unless indicated otherwise. Reactions were magnetically stirred and monitored by thin layer chromatography on 0.25 mm plates. Preperative thin layer chromatography was performed with 0.50 mm or 1.0 mm plates. Flash chromatography was performed with silica gel 60 (particle size 32-63 µm), unless indicated otherwise. Yields reported are for isolated, spectroscopically pure compounds. CDCl₃ was allowed to stand over K₂CO₃ and 4 Å MS to neutralize and dry prior to NMR sample preparation. NMR spectra were recorded on 300 MHz, 400 MHz and 500 MHz spectrometers. Proton and Carbon chemical shifts were referenced to residual solvent peaks. Abbreviations for ¹H NMR: s = singlet, d = doublet, t = triplet, q = quartlet, m = multiplet, or br = broad.

Experimental Procedures and Spectra Data (Please also see reference 12 in the text (Dai, M. J.; Danishefsky, S. J. J. Am. Chem. Soc. 2007, 129, 3498.) for more experimental procedures and spectra data.)

To the solution of a mixture of esters 12a/12b (98 mg, 0.3141 mmol) in 3 mL CH₂Cl₂ was added DIBAL-H (0.35 mL, 0.35 mmol, 1.0 M in toluene) at -78 °C during 5 minutes. The reaction mixture was stirred at -78 °C for 20 minutes more before quenched with 0.1 mL saturated aqueous NH₄Cl and warmed up to room temperature. The resulting mixture was diluted with 20 mL Et₂O, stirred for 1.5 hours and treated with anhydrous MgSO₄ then filtrated through a plug of silica gel. After evaporation of the solvent, the crude aldehyde product was used directly in the next step.
To the solution of the above crude aldehyde in t-butyl alcohol (2 mL) and water (2 mL) was added NaClO2 (170 mg), NaH2PO4-H2O (260 mg) and 2-methyl-2-butene (1.26 mL, 2.0 M in THF) at room temperature. The resulting mixture was stirred for 5 hours before acidified to pH (1-2), then extracted with Ethyl acetate for 3 times. The organic layers were combined and dried over anhydrous MgSO4, filtered and concentrated under reduced pressure to generate the crude acid which was used to the next step without any purification.

A solution of the above crude acid in THF (5 mL) and water (5 mL) was slowly treated with NaHCO3 (79 mg, 0.94 mmol). After the gas evolution had subsided, the mixture was treated with potassium iodide (68 mg, 0.41 mmol), followed by iodine (104 mg, 0.41 mmol). The resulting dark mixture was stirred in the dark overnight, then quenched by addition of saturated aqueous NaS2O3 solution until the color disappeared, and extracted with ether for 3 times. The combined organic layers were washed twice with brine, dried over anhydrous MgSO4 and concentrated. The residue was purified by flash chromatography (Hexane / EA: 8 / 1) to give 58 mg A and 38 mg B in total 76% yield (three steps).

14a: 1H NMR (400MHz, CDCl3): δ 4.28 (quint, J = 6.0 Hz, 1H), 3.54 (d, J =11.2 Hz, 1H), 3.36 (d, J = 11.2 Hz, 1H), 2.68 (d, J = 18.4 Hz, 1H), 2.56 (dd, J =14.8, 6.0 Hz, 1H), 2.49 (d, J = 18.4 Hz, 1H), 2.10 (dd, J =13.6, 6.4 Hz, 1H), 1.96 (dd, J =14.4, 5.6 Hz, 1H), 1.87 (dd, J =13.6, 5.2 Hz, 1H), 1.39 (s, 3H), 0.87 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); 13C NMR (100MHz, CDCl3): δ 174.1, 94.0, 69.8, 52.0, 48.9, 46.8, 44.7, 25.9, 23.2, 18.1, 9.4, -4.6 (2C); HRMS (FAB) calcd for C15H28O3Si: 411.0853; found 411.0861.

14b: 1H NMR (400MHz, CDCl3): δ 4.29 (m, 1H), 3.42 (d, J =10.8 Hz, 1H), 3.37 (d, J = 10.8 Hz, 1H), 2.86 (d, J = 18.0 Hz, 1H), 2.58 (d, J =18.0 Hz, 1H), 2.37 (d, J = 15.2 Hz, 1H), 2.05 (d, J =14.0 Hz, 1H), 1.99 (dd, J =14.8, 4.8 Hz, 1H), 1.88 (dd, J =14.0, 4.8 Hz, 1H), 1.29 (s, 3H), 0.86 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); 13C NMR (100MHz, CDCl3): δ 174.4, 94.0, 70.9, 52.5, 49.0, 46.7, 45.8, 25.7, 23.7, 18.0, 10.2, -4.9, -5.1; HRMS (FAB) calcd for C15H28O3Si: 411.0853; found 411.0861.
A solution of 1/1 mixture of crude acids (12.4 mg, 0.044 mmol) in CH₂Cl₂ (2 mL) was treated with mCPBA (11.8 mg, 0.052 mmol) at 0 °C. The reaction mixture was stirred for overnight, then quenched by addition of saturated aqueous Na₂S₂O₃ solution, and extracted with ether for 3 times. The combined organic layers were washed twice with brine, dried over anhydrous MgSO₄ and concentrated. The residue was purified by flash chromatography (Hexane / EA: 8 / 1) to give 15a (3.8 mg) in about 30% yield without any detection of 15b.

¹H NMR (400MHz, CDCl₃): δ 4.34 (m, 1H), 3.84 (d, J =12.4 Hz, 1H), 3.75 (d, J = 12.4 Hz, 1H), 2.65 (d, J = 18.0 Hz, 1H), 2.45 (d, J =18.0 Hz, 1H), 2.27 (dd, J =14.8, 6.0 Hz, 1H), 1.98 (dd, J =13.6, 6.4 Hz, 1H), 1.77 (dd, J =13.6, 4.4 Hz, 1H), 1.71 (dd, J =14.8, 5.2 Hz, 1H), 1.40 (s, 3H), 0.85 (s, 9H), 0.02 (s, 6H); ¹³C NMR (100MHz, CDCl₃): δ 176.8, 97.7, 71.3, 64.5, 50.9, 46.8, 45.0, 43.9, 25.7, 22.9, 17.9, -4.9, -5.0; HRMS (FAB) calcd for C₁₅H₂₉O₄Si: 301.1835; found 301.1833.

To a solution of iodide 14 (154 mg, 0.376 mmol) in 30 ml toluene was added AIBN (62 mg, 0.376 mmol) and tributyltinhydride (328 mg, 0.3 ml, 1.13 mmol). The reaction mixture was heated to 60 °C and bubbled with dry air for 2 days (more AIBN and Bu₃SnH if necessary). The reaction was cooled to 0 °C, treated with 30 mg NaBH₄ in 8 ml ethanol and stirred for 2 hours before quenched with saturated aqueous NH₄Cl. The organic layer was separated. The aqueous layer was extracted with ether for 3 times. The combined organic layers were dried over anhydrous MgSO₄, filtered, concentrated and purified by flash chromatography (Hexane / EA: 4 / 1) to give 85 mg desired product in 75% yield.

¹H NMR (400MHz, CDCl₃): δ 4.34 (m, 1H), 3.84 (d, J =12.4 Hz, 1H), 3.75 (d, J = 12.4 Hz, 1H), 2.65 (d, J = 18.0 Hz, 1H), 2.45 (d, J =18.0 Hz, 1H), 2.27 (dd, J =14.8, 6.0 Hz, 1H), 1.98 (dd, J =13.6, 6.4 Hz,
1H, 1.77 (dd, J = 13.6, 4.4 Hz, 1H), 1.71 (dd, J = 14.8, 5.2 Hz, 1H), 1.40 (s, 3H), 0.85 (s, 9H), 0.02 (s, 6H); 13C NMR (100MHz, CDCl3): δ 176.8, 97.7, 71.3, 64.5, 50.9, 46.8, 45.0, 43.9, 25.7, 22.9, 17.9, -4.9, -5.0; HRMS (FAB) calcd for C15H29O4Si: 301.1835; found 301.1833.

To a solution of 15a (20 mg, 0.067 mmol) and PMB trichloroacetimidate (56 mg, 0.2 mmol) in 2 ml CH2Cl2 was added 10-camphorsulfonic acid (1.6 mg, 0.0067 mmol). The reaction mixture was stirred overnight before the solvent was removed. The residue was purified by flash chromatography (Hexane / EA: 20/1) to give 26 mg desired product in 93% yield.

1H NMR (400MHz, CDCl3): δ 7.24 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 4.49 (d, J = 11.6 Hz, 1H), 4.42 (d, J = 11.6 Hz, 1H), 4.37 (quint, J = 5.2 Hz, 1H), 3.80 (s, 3H), 3.63 (d, J = 10.8 Hz, 1H), 3.60 (d, J = 10.8 Hz, 1H), 2.65 (d, J = 17.2 Hz, 1H), 2.39 (d, J = 17.2 Hz, 1H), 2.31 (dd, J = 14.8, 6.4 Hz, 1H), 1.98 (dd, J = 13.6, 6.4 Hz, 1H), 1.75 (dd, J = 14.0, 4.4 Hz, 1H), 1.69 (dd, J = 14.8, 5.2 Hz, 1H), 1.36 (s, 3H), 0.85 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H); 13C NMR (100MHz, CDCl3): δ 176.4, 159.2, 129.8, 129.1, 113.8, 96.6, 73.3, 71.6, 71.5, 55.2, 50.7, 47.4, 44.9, 44.0, 25.7, 22.7, 17.9, -4.9, -5.0; HRMS (FAB) calcd for C23H35O5Si: 419.2254; found 419.2244.

To a solution of 16a (250 mg, 0.595 mmol) in 10 ml THF was added TBAF (1.0 M in THF, 1.2 mL, 1.2 mmol). The reaction mixture was stirred overnight before quenched with saturated aqueous NH4Cl. The mixture was extracted with ethyl acetate for 3 times and the combined organic phases were washed with brine, dried over MgSO4 and concentrated. The residue was purified by flash chromatography (Hexane / EA: 1/1, then 1/2) to give 159 mg desired product in 87% yield.

1H NMR (400MHz, CDCl3): δ 7.19 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 4.47 (d, J = 11.6 Hz, 1H), 4.43 (m, 1H), 4.40 (d, J = 11.6 Hz, 1H), 3.78 (s, 3H), 3.60 (s, 2H), 2.63 (d, J = 17.2 Hz, 1H), 2.48
To a toluene (2 mL) solution of 17 (24 mg, 0.078 mmol), PPh₃ (25 mg, 0.094 mmol) and benzoic acid (12 mg, 0.094 mmol) was added DIAD (19 mg, 18 µL, 0.094 mmol). The reaction mixture was stirred at room temperature for 3 hours. After evaporation of the solvent, the residue was purified on preparative TLC to give a mixture of desired ester contaminated with diisopropyl hydrazine-1,2-dicarboxylate which was dissolved in MeOH (3 mL) and treated with K₂CO₃ (11 mg, 0.078 mmol). After the reaction was stirred at room temperature for 7 hours, the solvent was removed and the residue was dissolved in ethyl acetate, which was washed with water and brine, then dried over anhydrous MgSO₄. After filtration and evaporation, the residue was purified by flash chromatography (Hexane / EA: 1/ 1, then 1 / 2) to give 23 mg desired product in 98% yield.

1H NMR (400MHz, CDCl₃): δ 7.20 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 4.48 (d, J = 11.6 Hz, 1H), 4.40 (d, J = 11.6 Hz, 1H), 4.37 (quint, J = 4.8 Hz, 1H), 3.78 (s, 3H), 3.58 (d, J = 10.8 Hz, 1H), 3.49 (d, J = 10.4 Hz, 1H), 2.63 (d, J = 18.0 Hz, 1H), 2.58 (d, J = 18.4 Hz, 1H), 2.09-2.02 (m, 2H), 1.97 (dd, J = 14.0, 6.0 Hz, 1H), 1.90 (dd, J = 13.6, 5.2 Hz, 1H), 1.20 (s, 3H); ¹³C NMR (100MHz, CDCl₃): δ 176.5, 159.2, 129.6, 129.1, 113.7, 96.3, 73.2, 71.3, 71.0, 55.2, 50.6, 47.1, 45.0, 42.6, 22.2; HRMS (FAB) calcd for C₁₇H₂₃O₅: 307.1545; found 307.1540.

To a solution of sm (85 mg, 0.28 mmol) and 2,6-lutidine (600 mg, 5.6 mmol) in 12 ml CH₂Cl₂ was added TBSOTf (592 mg, 2.24 mmol) slowly at 0°C. The reaction mixture was allowed to warm up to
room temperature and stirred overnight. The reaction was quenched with saturated aqueous NH₄Cl and extracted with ether for 3 times. The combined organic layers were washed with 1N HCl, saturated aqueous sodium bicarbonate, water and brine respectively, then dried over anhydrous MgSO₄, concentrated and purified by flash chromatography (Hexane / EA: 7/ 1) to give 111 mg desired product in 95% yield.

$^1$H NMR (400MHz, CDCl₃): δ 7.21 (d, $J = 8.4$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 4.49 (d, $J = 11.6$ Hz, 1H), 4.42 (d, $J = 11.6$ Hz, 1H), 4.32 (quint, $J = 5.2$ Hz, 1H), 3.80 (s, 3H), 3.56 (d, $J = 10.4$ Hz, 1H), 3.49 (d, $J = 10.8$ Hz, 1H), 2.67 (d, $J = 17.6$ Hz, 1H), 2.55 (d, $J = 17.6$ Hz, 1H), 2.04 (dd, $J = 15.2$, 4.0 Hz, 1H), 1.98 (dd, $J = 15.2$, 6.0 Hz, 1H), 1.89 (dd, $J = 13.6$, 5.2 Hz, 1H), 1.83 (dd, $J = 13.2$, 5.2 Hz, 1H), 1.26 (s, 3H), 0.86 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H); $^{13}$C NMR (100MHz, CDCl₃): δ 176.1, 159.2, 129.8, 129.2, 113.7, 95.6, 73.3, 71.8, 71.3, 55.2, 50.9, 46.6, 45.0, 43.5, 25.7, 22.5, 17.9, -4.9, -5.0; HRMS (FAB) calcd for C₂₃H₃₅O₅Si: 419.2254; found 419.2254.

To a solution of 34 (5 mg, 0.014 mmol) in dry pyridine was added a solution of OsO₄ (0.05 M, 1.1 equiv.) in toluene. The dark reaction mixture was stirred overnight, then 2 mL aqueous NaHSO₃ (1M) was added. After a further 90 min the mixture was diluted with 2 mL water and extracted with CHCl₃ (3 x 4 mL) and then with ethyl acetate (3 x 4 mL). The organic phases were combined and dried over MgSO₄. After evaporation of the solvent, the oily residue was used directly to the next step. Crude H NMR showed a 2.5/1 mixture of C-9 epimers. The major one was confirmed to be the undesired product after carry on all the way to the final 9-epi-spirotenuipesine.

To a solution of the above diol and pyridine in CH₂Cl₂ was added MsCl (1.2 equiv.) at 0 ºC. The solution was warmed to r.t. and stirred for 18 h, and quenched with saturated aqueous NaHCO₃ solution. The resulting mixture was extracted with ethyl acetate for 3 times, and the combined organic extracts were dried over
MgSO₄, filtered and concentrated. Flash chromatography of the residue on silica gel (Hexane/EA = 1/2) afforded a mixture of two isomers (5.3 mg) in 81% yield. This mixture was used directly in the next step without any further separation.

To a solution of the above mesylates in dry THF was added super-hydride (4.0 equiv.) at 0 °C. The reaction mixture was stirred for 45 min at this temperature and then quenched with saturated aqueous NH₄Cl. The resulting mixture was extracted with ethyl acetate for 3 times and the combined organic extracts were dried over MgSO₄, filtered and concentrated. Flash chromatography of the residue on silica gel (Hexane/EA = 2/1) afforded 36a (0.8 mg) and 36b (1.8 mg) in total 62% yield.

To a solution of PMB ether 36b (12 mg, 0.031 mmol) in 6 mL CH₂Cl₂ / buffer solution pH = 7.00 (18 / 1) was added DDQ (26 mg). The reaction was stirred at r.t. for 5 hours, then quenched with 3 mL saturated aqueous NaHCO₃, extracted with ethyl acetate (5 x 3 mL), dried over anhydrous MgSO₄, filtered, concentrated and purified on a silica gel column using Hexane/EtOAc (1 / 2 to 1 / 4) as the eluant to afford 9-epi-spirotenuipesine A 7.0 mg in 84% yield.

¹H NMR (400MHz, CDCl₃): δ 5.75 (dd, J = 10.0, 1H), 5.63 (d, J = 10.4, 1H), 4.96 (s, 1H), 4.74 (s, 1H), 3.86 (dd, J = 12.0, 4.8 Hz, 1H), 3.76 (dd, J = 12.4, 6.4 Hz, 1H), 2.47 (d, J = 13.2 Hz, 1H), 2.24 (dd, J = 11.6, 1H), 2.02 (d, J =13.6, 1H), 1.83-1.89 (m, 2H), 1.60-1.76 (m, 3H), 1.58 (br s, 1H), 1.51 (d, J = 11.6, 1H), 1.29 (s, 3H), 1.25 (m, 1H), 1.07 (s, 3H); ¹³C NMR (100MHz, CDCl₃): δ 134.8, 133.0, 102.5, 90.0, 76.1, 66.4, 64.8, 52.8, 49.1, 43.2, 41.0, 35.4, 29.7, 21.6, 15.7; HRMS (FAB) calcd for C₁₅H₂₃O₄⁺: 267.1596; found 267.1592.

To a suspension of CuI (1.73 g, 9.08 mmol) in Et₂O (90 mL) was added 2-propenylmagnesium bromide (0.5 M in THF, 100 mL, 50 mmol) at -78 °C. The resulting mixture was placed in a -30 °C bath for 15 minutes, then R-(-)-epichlorohydrin (3.56 mL, 45.4 mmol) was added dropwise. The mixture was stirred 30 minutes at -30 to -20 °C, by which time the initial yellow-orange color had turned to black. The
reaction was quenched with saturated aqueous NH₄Cl, washed with 4 x 20 mL H₂O to give 6.2 g chlorohydrin as a colorless oil, which by H NMR contained a small amount of THF but was otherwise pure. ¹H NMR (500 MHz, CDCl₃): δ 4.91 (s, 1H), 4.83 (s, 1H), 3.98 (m, 1H), 3.63 (dd, J = 11.1, 3.8 Hz, 1H), 3.53 (dd, J = 11.1, 6.4 Hz, 1H), 2.30 (m, 2H), 2.18 (d, J = 3.9 Hz, 1H), 1.78 (s, 3H).

The above crude chlorohydrin (6.2 g, ~45 mmol) was dissolved in 50 mL CH₂Cl₂, crushed NaOH pellets (3.6 g, 90 mmol) were added and the resulting suspension was stirred at room temperature for 24 hours (reaction was monitored by ¹H-NMR of aliquots). MgSO₄ was then added and the reaction mixture was filtered and concentrated at 30 ºC / 450 mmHg to remove almost all solvent. The remaining small amount of THF was removed by a short column of SiO₂, eluting with 5:1 pentane/Et₂O. Fractions were concentrated to remove almost all solvent at 30 ºC / 450 mmHg. The final 2-3 mL solvent was removed by evaporation under N₂ stream to give pure, solvent-free epoxide 45 2.6 g (58 % over 2 steps) as a colorless volatile oil. [α]²₂.⁸ D + 2.7 (c 1.17, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 4.83 (app s, 2H), 3.03 (m, 1H), 2.79 (dd, J = 4.8, 4.0 Hz, 1H), 2.50 (dd, J = 5.2, 2.8 Hz, 1H), 2.28 (dd, J = 15.2, 6.0 Hz, 1H), 2.19 (dd, J = 15.2, 5.2 Hz, 1H), 1.80 (s, 3H); ¹³C NMR (100MHz, CDCl₃): δ 141.2, 112.1, 51.1, 46.9, 40.8, 23.0; MS (APCI+) calcd for C₆H₁₁O (M+H): 99.07; found 99.23.

Magnesium turnings (1.24 g, 51.8 mmol) were flame-dried under an argon atmosphere. After cooling to room temperature, THF (5 mL) was added. To this mixture, was added 1,2-dibromoethane (50 µL) to activate the magnesium turnings. Neat 1-bromo-1-trimethylsilylethylene (1 g, 5.18 mmol) was added slowly (15 min). The reflux was maintained for another 30 min.

To a cold (-60ºC) solution of epoxide 45 (270 mg, 2.75 mmol) in THF (5 mL) was added copper (I) iodide (74.5 mg, 0.39 mmol). The above Grignard solution in THF was added quickly to the suspension. A THF rinse (3 mL) of the Grignard solution was also added to the suspension. After warming the reaction to -60ºC for 2 h, the mixture was quenched with aqueous saturated NH₄Cl. The mixture was
diluted with ether and washed with aqueous saturated NH₄Cl and brine, dried over MgSO₄, filtered, and concentrated. The residue was purified by flash chromatography (Hexane / EA: 12 / 1) to give the desired product (573 mg, 98%). [α]₂¹.₈ D + 13.5 (c 0.53, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 4.87 (s, 1H), 4.81 (s, 1H), 4.71 (s, 1H), 4.69 (s, 1H), 3.89 (m, 1H), 2.06-2.21 (m, 4H), 1.99 (s, 1H), 1.79 (s, 3H), 1.61 (d, J = 13.2 Hz, 1H), 1.55 (d, J = 13.2 Hz, 1H), 0.05 (s, 9H); ¹³C NMR (100MHz, CDCl₃): δ 144.5, 142.7, 113.0, 110.1, 66.5, 46.0, 45.5, 26.7, 22.5, -1.5; MS (APCI+) calcd for C₁₂H₂₃OSi (M-H): 211.16; found 211.23.

To a solution of the above material (124 mg, 0.585 mmol) in 3 mL DMF were added imidazole (80 mg, 1.17 mmol) and TBSCl (106 mg, 0.70 mmol) at 0°C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with 20 mL water, extracted with ether (3 x 20 mL). The combined organic phases were washed with water and brine respectively, dried over MgSO₄, and concentrated to give 48 (178 mg, 93%) without further purification. [α]₂¹.₃ D + 1.84 (c 1.24, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 4.78 (s, 1H), 4.72 (s, 1H), 4.63 (s, 1H), 4.58 (s, 1H), 3.93 (m, 1H), 2.08-2.24 (m, 4H), 1.74 (s, 3H), 1.55 (d, J = 13.6 Hz, 1H), 1.51 (d, J = 13.6 Hz, 1H), 0.89 (s, 9H), 0.05 (s, 6H), 0.02 (s, 9H); ¹³C NMR (100MHz, CDCl₃): δ 144.4, 142.9, 113.0, 109.9, 70.0, 46.1, 27.1, 25.9, 23.0, 18.1, -1.1, -1.4, -4.4, -4.5; MS (APCI+) calcd for C₁₈H₃₉OSi₂ (M+H): 327.2; found 327.4.

To a solution of 48 (56 mg, 0.17 mmol) in 3 ml CH₂Cl₂ was added PhSeCl (28 mg, 0.143 mmol) and catalytic amount of SnCl₂ at -78°C. The reaction was stirred at -78°C for 17 min, then warmed up to 0°C and stirred for another 23 min. After the solvent was removed, the residue was put on florisil column for 15 min. The selenide was washed off the column with Hexane / EA (10 / 1). After
concentration, the selenide was subsequently treated with 30% (wt.) H₂O₂ (162 mg, 1.43 mmol) and pyridine (23 µL) in CH₂Cl₂ (3 mL) at 0°C for 20 min. The reaction mixture was quenched with aqueous 20% Na₂S₂O₃, diluted with ether, washed with 20% Na₂S₂O₃, 1N HCl, aqueous saturated NaHCO₃ and brine, then dried over MgSO₄, filtered, concentrated and purified by flash chromatography (Hexane / EA: 8 / 1) to give desired product 10 (34 mg, 88% based on PhSeCl or 73% based on 48). [α]²³.³⁰ + 22.3 (c 0.93, CHCl₃); ¹H NMR (400MHz, CDCl₃): δ 5.11 (s, 1H), 4.90 (s, 1H), 4.80 (s, 1H), 4.73 (s, 1H), 4.05 (d, J = 6.40 Hz, 2H), 3.98 (m, 1H), 2.81 (t, J = 6.40 Hz, 1H), 2.26 (m, 4H), 1.73 (s, 3H), 0.90 (s, 9H), 0.08 (s, 6H); ¹³C NMR (100MHz, CDCl₃): δ 145.6, 142.2, 114.0, 113.3, 70.4, 66.4, 45.2, 41.1, 25.8, 22.8, 18.0, -4.66, -4.71; HRMS (FAB+) calcd for C₁₅H₃₁O₂Si: 271.2093; found 271.2079.

¹H NMR and ¹³C NMR Spectra
