Supporting information

Total Synthesis of Spirotenuipesines A and B

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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. Preparative 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 C₁₅H₂₈O₃SiI: 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 C₁₅H₂₈O₃SiI: 411.0853; found 411.0861.

A solution of 1/1 mixture of crude acids (12.4 mg, 0.044 mmol) in CH_2Cl_2 (2 mL) was treated with *m*CPBA (11.8 mg, 0.052 mmol) at 0°C . The reaction mixture was stirred for overnight, then quenched by addition of saturated aqueous NaS_2O_3 solution, and extracted with ether for 3 times. The combined organic layers were washed twice with brine, dried over anhydrous MgSO_4 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, CDCl_3): 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); ^{13}C NMR (100MHz, CDCl_3): 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 $\text{C}_{15}\text{H}_{29}\text{O}_4\text{Si}$: 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 Bu_3SnH if necessary). The reaction was cooled to 0°C , treated with 30 mg NaBH_4 in 8 ml ethanol and stirred for 2 hours before quenched with saturated aqueous NH_4Cl . The organic layer was separated. The aqueous layer was extracted with ether for 3 times. The combined organic layers were dried over anhydrous MgSO_4 , filtered, concentrated and purified by flash chromatography (Hexane / EA: 4 / 1) to give 85 mg desired product in 75% yield.

^1H NMR (400MHz, CDCl_3): 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); ^{13}C NMR (100MHz, CDCl_3): 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 $\text{C}_{15}\text{H}_{29}\text{O}_4\text{Si}$: 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 CH_2Cl_2 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, CDCl_3): 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); ^{13}C NMR (100MHz, CDCl_3): 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 $\text{C}_{23}\text{H}_{35}\text{O}_5\text{Si}$: 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 NH_4Cl . The mixture was extracted with ethyl acetate for 3 times and the combined organic phases were washed with brine, dried over MgSO_4 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, CDCl_3): 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

(br, 1H), 2.37 (d, $J=17.2$ Hz, 1H), 2.33 (dd, $J=14.8$, 6.4 Hz, 1H), 2.03 (dd, $J=14.4$, 6.4 Hz, 1H), 1.76 (dd, $J=14.4$, 4.8 Hz, 1H), 1.72 (dd, $J=15.2$, 5.2 Hz, 1H), 1.34 (s, 3H); ^{13}C NMR (100MHz, CDCl_3): δ 176.5, 159.1, 129.6, 129.1, 113.7, 96.6, 73.2, 71.1, 70.7, 55.1, 50.2, 47.3, 44.7, 43.0, 22.6; HRMS (FAB) calcd for $\text{C}_{17}\text{H}_{22}\text{O}_5$: 306.1467; found 306.1478.

To a toluene (2 mL) solution of 17 (24 mg, 0.078 mmol), PPh_3 (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 K_2CO_3 (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 MgSO_4 . 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, CDCl_3): 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); ^{13}C NMR (100MHz, CDCl_3): 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 $\text{C}_{17}\text{H}_{23}\text{O}_5$: 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 CH_2Cl_2 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 NH_4Cl 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 MgSO_4 , concentrated and purified by flash chromatography (Hexane / EA: 7/ 1) to give 111 mg desired product in 95% yield.

^1H NMR (400MHz, CDCl_3): 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, CDCl_3): 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 $\text{C}_{23}\text{H}_{35}\text{O}_5\text{Si}$: 419.2254; found 419.2254.

To a solution of 34 (5 mg, 0.014 mmol) in dry pyridine was added a solution of OsO_4 (0.05 M, 1.1 equiv.) in toluene. The dark reaction mixture was stirred overnight, then 2 mL aqueous NaHSO_3 (1M) was added. After a further 90 min the mixture was diluted with 2 mL water and extracted with CHCl_3 (3 x 4 mL) and then with ethyl acetate (3 x 4 mL). The organic phases were combined and dried over MgSO_4 . 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 CH_2Cl_2 was added MsCl (1.2 equiv.) at 0 °C. The solution was warmed to r.t. and stirred for 18 h, and quenched with saturated aqueous NaHCO_3 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 NH_4Cl , washed with 4 x 20 mL H_2O to give 6.2 g chlorohydrin as a colorless oil, which by ^1H NMR contained a small amount of THF but was otherwise pure. ^1H NMR (500 MHz, CDCl_3): 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 CH_2Cl_2 , 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). MgSO_4 was then added and the reaction mixture was filtered and concentrated at 30 °C / 450 mmHg to remove almost all solvent. The remaining small amount of THF was removed by a short column of SiO_2 , eluting with 5:1 pentane/ Et_2O . Fractions were concentrated to remove almost all solvent at 30 °C / 450 mmHg. The final 2-3 mL solvent was removed by evaporation under N_2 stream to give pure, solvent-free epoxide 45 2.6 g (58 % over 2 steps) as a colorless volatile oil. $[\alpha]^{22.8}_{\text{D}} + 2.7$ (c 1.17, CHCl_3); ^1H NMR (400 MHz, CDCl_3): 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); ^{13}C NMR (100MHz, CDCl_3): δ 141.2, 112.1, 51.1, 46.9, 40.8, 23.0; MS (APCI+) calcd for $\text{C}_6\text{H}_{11}\text{O}$ ($\text{M}+\text{H}$): 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-trimethylsilylmethylethene (1 g, 5.18 mmol) was added slowly (15 min). The reflux was maintained for another 30 min.

To a cold (-60°C) 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 -60°C for 2 h, the mixture was quenched with aqueous saturated NH_4Cl . The mixture was

diluted with ether and washed with aqueous saturated NH_4Cl and brine, dried over MgSO_4 , filtered, and concentrated. The residue was purified by flash chromatography (Hexane / EA: 12 / 1) to give the desired product (573 mg, 98%). $[\alpha]^{21.8}_{\text{D}} + 13.5$ (c 0.53, CHCl_3); ^1H NMR (400 MHz, CDCl_3): 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); ^{13}C NMR (100MHz, CDCl_3): 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 $\text{C}_{12}\text{H}_{23}\text{OSi}$ (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. $[\alpha]^{21.3}_D + 1.84$ (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.) H_2O_2 (162 mg, 1.43 mmol) and pyridine (23 μL) in CH_2Cl_2 (3 mL) at 0°C for 20 min. The reaction mixture was quenched with aqueous 20% $\text{Na}_2\text{S}_2\text{O}_3$, diluted with ether, washed with 20% $\text{Na}_2\text{S}_2\text{O}_3$, 1N HCl, aqueous saturated NaHCO_3 and brine, then dried over MgSO_4 , 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). $[\alpha]^{23.3}_{\text{D}} + 22.3$ (c 0.93, CHCl_3); ^1H NMR (400MHz, CDCl_3): 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); ^{13}C NMR (100MHz, CDCl_3): 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 $\text{C}_{15}\text{H}_{31}\text{O}_2\text{Si}$: 271.2093; found 271.2079.

```

NAME MD-II-251-1
EXPNO 1
PROCNO 1
Date_ 20051121
Time 14.54
INSTRUM spect
PROBHD 5 mm Multinuc1
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 19
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 128
DM 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 2.50 usec
PL1 0.00 dB
SFO1 399.9225995 MHz
SI 32768
SF 399.9200111 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00

```

7.260

```

NAME          MD-11-251-1
EXPNO         2
PROCNO        1
Date_         20051121
Time          14.55
INSTRUM       spect
PROBHD        5 mm Multinucl
PULPROG       zgpg30
TD            32768
SOLVENT       Aceton
NS            2435
DS            0
SWH           22075.055 Hz
FIDRES        0.673677 Hz
AQ            0.7422452 sec
RG            16384
DW            22.650 usec
DE            6.00 usec
TE            300.0 K
D1            0.25000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

===== CHANNEL f1 =====
NUC1          13C
P1            17.50 usec
PL1           -1.00 dB
SFO1          100.5699800 MHz

===== CHANNEL f2 =====
CPOPRG2       waltz16
NUC2          1H
PCPD2         96.25 usec
PL2           0.00 dB
PL12          23.00 dB
PL13          23.00 dB
SFO2          399.9215997 MHz
ST            65536
SF            100.5599740 MHz
WDW           EM
SSB           0
LB            3.00 Hz

```

```

NAME MD-IV-87-2
EXPNO 1
PROCNO 1
Date_ 20060711
Time 18.46
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 15
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 25.4
DE 83.400 usec
TE 6.00 usec
TD 300.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCMRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 2.50 usec
PL1 0.00 dB
SFO1 399.9225995 MHz
SI 32768
SF 399.9200115 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00

```

NAME MD-IV-87-2
 EXPNO 2
 PROCNO 1
 Date_ 20060711
 Time 18.50
 INSTRUM spect
 PROBD 5 mm Multinuc1
 PULPROG zgpg30
 TD 32768
 SOLVENT Aceton
 NS 224
 DS 0
 SWH 22075.055 Hz
 FIDRES 0.673677 Hz
 AQ 0.7422452 sec
 RG 16384
 DW 22.650 usec
 DE 6.00 usec
 TE 300.0 K
 D1 0.25000000 sec
 d11 0.03000000 sec
 DELTA 0.15000001 sec
 MCREST 0.00000000 sec
 MCWRR 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 17.50 usec
 PL1 -1.00 dB
 SFO1 100.5699800 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 96.25 usec
 PL2 0.00 dB
 PL12 23.00 dB
 PL13 23.00 dB
 SFO2 399.9215997 MHz
 SI 65536
 SF 100.5599703 MHz
 WDW EM

97.713
 77.315
 76.997
 76.679
 71.272
 64.489
 50.907
 46.840
 44.973
 43.947
 25.685
 22.882
 17.859
 -4.925
 -4.974

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

NAME MD-IV-123-3
EXPNO 1
PROCNO 1
Date_ 20060815
Time 2.29
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 19
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 128
DE 83.400 usec
TE 6.00 usec
D1 300.0 K
D1 1.00000000 sec
MCWRR 0.01500000 sec
===== CHANNEL f1 =====
NUC1 1H
P1 2.50 usec
PL 0.00 dB
SFO1 399.925995 MHz
SI 32768
SF 399.9200113 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00

7.288
7.260
7.224
7.202
6.880
6.859

4.505
4.476
4.460
4.438
4.409
4.380
4.366
4.354
3.802
3.777
3.617
3.612
2.674
2.631
2.408
2.364
2.333
2.318
2.297
2.281
2.005
1.989
1.970
1.954
1.777
1.766
1.742
1.732
1.719
1.706
1.682
1.669
1.577
1.357
0.854
0.071
0.020
0.017

NAME MD-TV-135
EXENO 1
PROCNO 1
Date_ 20060818
Time 2.16
INSTRUM spect
PROBHD 5 mm Multinuc1
PULPROG zg
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 5995.204 Hz
FIDRES 0.182959 Hz
AQ 2.7329011 sec
RG 22.6
DW 83.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCMRK 0.01500000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 2.50 usec
PL 0.00 dB
SFO1 399.9225995 MHz
SI 32768
SF 399.9200113 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00

7.260
7.200
7.179
6.860
6.838

4.484
4.456
4.427
4.410
4.381

3.775
3.599

2.653
2.610
2.474
2.396
2.352
2.337
2.316
2.300

2.055
2.038
2.019
2.003

1.784
1.772
1.748
1.735
1.710
1.697
1.335
1.236

NAME AD-IV-135
 EXPNO 2
 PROCNO 1
 Date_ 20060818
 Time 2.19
 INSTRUM spect
 PROBD 5 mm Multinucl
 PULPROG zgpg30
 TD 32768
 SOLVENT Aceton
 NS 399
 DS 0
 SMH 22075.055 Hz
 FIDRES 0.673677 Hz
 AQ 0.7422452 sec
 RG 16384
 DW 22.650 usec
 DE 6.00 usec
 TE 300.0 K
 D1 0.25000000 sec
 d11 0.03000000 sec
 DELTA 0.15000001 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
 NUCL1 13C
 P1 17.50 usec
 PL1 -1.00 dB
 SFO1 100.5699800 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUCL2 1H
 PCPD2 96.25 usec
 PL2 0.00 dB
 PL12 23.00 dB
 PL13 23.00 dB
 SFO2 399.9215997 MHz
 SI 65536
 SF 100.5599780 MHz
 WDW EM

176.471
 159.135
 129.559
 129.077
 113.716
 96.653
 77.317
 76.998
 76.680
 73.205
 71.125
 70.739
 55.139
 50.196
 47.311
 44.741
 43.013
 22.635

NAME MD-IV-143-2
 EXPNO 1
 PROCNO 1
 Date_ 20060822
 Time 3.10
 INSTRUM spect
 PROBD 5 mm Multinucl
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 11
 DS 0
 SWH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 57
 DW 83.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.00000000 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
 NUCL1 1H
 P1 2.50 usec
 PL1 0.00 dB
 SFO1 399.922595 MHz
 SI 32768
 SF 399.9200111 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

7.260
 7.208
 7.187
 6.865
 6.844

4.490
 4.461
 4.417
 4.387
 4.373
 4.360
 3.783
 3.589
 3.563
 3.506
 3.479

2.605
 2.051
 2.035
 2.019
 1.996
 1.982
 1.962
 1.948
 1.927
 1.914
 1.892
 1.880
 1.195

NAME MS-IV-143-2
 EXPRNO 2
 PROCNO 1
 Date_ 20060822
 Time 3.14
 INSTRUM spect
 PROBD 5 mm Multinucl
 PULPROG zgpg30
 TD 32768
 SOLVENT Aceton
 NS 271
 DS 0
 SWH 22075.055 Hz
 FIDRES 0.673677 Hz
 AQ 0.7422452 sec
 RG 16384
 DW 22.650 usec
 DE 6.00 usec
 TE 300.0 K
 D1 0.25000000 sec
 d11 0.03000000 sec
 DELTA 0.15000001 sec
 MCREST 0.00000000 sec
 MCWRR 0.01500000 sec

===== CHANNEL f1 =====
 NUCL 13C
 P1 17.50 usec
 PL1 -1.00 dB
 SFO1 100.5699800 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 96.25 usec
 PL2 0.00 dB
 PL12 23.00 dB
 PL13 23.00 dB
 SFO2 399.9215997 MHz
 ST 65536
 SF 100.5599753 MHz
 WDW EM

129.638
 129.134
 113.725
 96.309
 77.316
 76.998
 76.680
 73.213
 71.251
 71.035
 55.167
 50.610
 47.051
 44.956
 42.638
 22.225

NAME MD-V-49
 EXTNO 1
 PROCNO 1
 Date_ 20070110
 Time 22.36
 INSTRUM spect
 PROBD 5 mm Multinucl
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 32
 DS 0
 SMH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 287.4
 DW 83.400 usec
 DE 6.00 usec
 TE 300.0 K
 D1 1.0000000 sec
 MCREST 0.0000000 sec
 MCWPRK 0.0150000 sec

===== CHANNEL f1 =====
 NUCL1 1H
 P1 2.50 usec
 PL1 0.00 dB
 SFO1 399.9225995 MHz
 SI 32768
 SF 399.9200115 MHz
 WDW EM
 SSB 0
 LB 0.20 Hz
 GB 0
 PC 1.00

NAME MD-V-49
 EXPNO 2
 PROCNO 1
 Date_ 20070110
 Time 22.41
 INSTRUM spect
 PROBD 5 mm Multinucl
 PULPROG zgpg30
 TD 32768
 SOLVENT Aceton
 NS 37541
 DS 0
 SWH 22075.055 Hz
 FIDRES 0.673677 Hz
 AQ 0.7422452 sec
 RG 16384
 DN 22.650 usec
 DE 6.00 usec
 TR 300.0 K
 D1 0.25000000 sec
 d11 0.03000000 sec
 DELTA 0.15000001 sec
 MCREST 0.00000000 sec
 MCWRR 0.01500000 sec

===== CHANNEL f1 =====
 NUCL1 13C
 P1 17.50 usec
 PL1 -1.00 dB
 SFO1 100.5699800 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 96.25 usec
 PL2 0.00 dB
 PL12 23.00 dB
 PL13 23.00 dB
 SFO2 399.9215997 MHz
 SI 65536
 SF 100.5599662 MHz
 WDW EM

```

NAME      ND-V-79-sm1
EXPNO     1
PROCNO    1
Date_     20070129
Time      21.00
INSTRUM   spect
PROBHD    5 mm Multicnuc1
PULPROG   zg
TD         32768
SOLVENT   CDCl3
NS         8
DS         0
SWH        5995.204 Hz
FIDRES     0.182959 Hz
AQ         2.7329011 sec
RG         128
DM         83.400 usec
DE         6.00 usec
TE         300.0 K
D1         1.00000000 sec
MCRBST     0.00000000 sec
MCWRK     0.01500000 sec

===== CHANNEL f1 =====
NUC1       1H
P1         2.50 usec
PL1        0.00 dB
SFO1       399.9225995 MHz
SI         32768
SF         399.9200115 MHz
WDW        EM
SSB        0
LB         0.20 Hz
GB         0
PC         1.00

```

NAME MD-V-79-sm1
 EXPNO 2
 PROCNO 1
 Date_ 20070129
 Time 21.02
 INSTRUM spect
 PROBHD 5 mm Multinucl
 PULPROG zgpg30
 TD 32768
 SOLVENT Aceton
 NS 5570
 DS 0
 SWH 22075.055 Hz
 FIDRES 0.673677 Hz
 AQ 0.7422452 sec
 RG 16384
 DW 22.650 usec
 DE 6.00 usec
 TE 300.0 K
 D1 0.2500000 sec
 d11 0.0300000 sec
 DELTA 0.1500001 sec
 MCREST 0.0000000 sec
 MCWRRK 0.0150000 sec

===== CHANNEL f1 =====
 NUC1 ¹³C
 P1 17.50 usec
 PL1 -1.00 dB
 SFO1 100.5699800 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 ¹H
 PCPD2 96.25 usec
 PL2 0.00 dB
 PL12 23.00 dB
 PL13 23.00 dB
 SFO2 399.9215997 MHz
 SI 65536
 SF 100.5599662 MHz
 WDW EM

```

===== CHANNEL f1 =====
NWCL          1H
P1            2.50 usec
PL            0.00 db
SP01          399.9225995 MHz
SI            32768
SF            399.9200000 MHz
MIDW          EM
SSB            0
LB            0.20 Hz
GB            0
PC            1.00

```

$$\begin{array}{r} \diagup 0.192 \\ \diagup 0.116 \\ \diagup 0.046 \\ \diagup -0.101 \end{array}$$

NAME MD-V-79
EXPNO 2
PROCNO 1
Date_ 20070129
Time 22.44
INSTRUM spect
PROBHD 5 mm Multinuc1
PULPROG zgpg30
TD 32768
SOLVENT Aceton
NS 204
DS 0
SWH 22075.055 Hz
FIDRES 0.673677 Hz
AQ 0.7422452 sec
RG 16384
DW 22.650 usec
DE 6.00 usec
TE 300.0 K
D1 0.25000000 sec
d11 0.03000000 sec
DELTA 0.15000001 sec
MCREST 0.00000000 sec
MCWRR 0.01500000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 17.50 usec
PL1 -1.00 dB
SFO1 100.5699800 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 96.25 usec
PL2 0.00 dB
PL12 23.00 dB
PL13 23.00 dB
SFO2 399.9215997 MHz
SI 65536
SF 100.5599710 MHz
WDW EM

[illegible]

carbon NMR

———— 145.595
———— 142.218

114.039
113.274

77.316
76.997
76.680
70.374
66.424

————— 45.161
————— 41.073

$$\begin{array}{r} \text{—————} 25.798 \\ \text{—————} 22.842 \\ \text{—————} 18.022 \end{array}$$
$$\begin{array}{l} \nearrow -4.660 \\ \searrow -4.715 \end{array}$$