Supporting Information

Efficient Stereochemical Relay En Route to Leucascandrolide A

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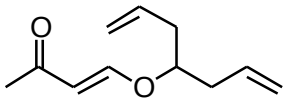
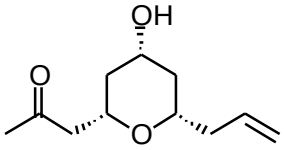
General. Dichloromethane (HPLC grade), benzene (ACS grade), toluene (HPLC grade), ethyl acetate (ACS grade), hexanes (ACS grade), and diethyl ether (anhydrous grade) were purchased from Fisher Scientific and used without further purification. Dicyclohexylboron chloride (1.0 M solution in hexane) was used from newly opened 100 mL bottles, purchased from Aldrich Chemical Company. Reactions were monitored by thin layer chromatography (TLC) using Whatman precoated silica gel plates. Flash column chromatography was performed over EM Science Laboratories silica gel (230-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DRX-400 and DMX-500 spectrometers. Infrared spectra (IR) were recorded with Nicolet FTIR spectrometer and are reported in reciprocal centimeter (cm^{-1}).



8

Vinylogous Ester 8. A 100-mL round-bottomed flask, equipped with magnetic stirring bar, 10 cm vigreux column, and distillation head was charged with heptadienol **7** (2.78 g, 24.8 mmol), 4-methoxy-3-butenone (3.00 g, 30 mmol, distilled prior to use), PPTS (60 mg, 1 mol%) and toluene (50 mL). The reaction mixture was heated for 5 h at gentle reflux allowing for a slow distillation of the methanol-toluene mixture (distillate temperature: 60-110 °C). The progress of the reaction was monitored by TLC. Upon completion, the solvent was removed under reduced pressure. The resulting dark-red oil was subjected to the bulb-to-bulb distillation (100-150 °C oven temperature, 0.5 mm Hg) to give 4.10 g (92% yield) of vinylogous ester **8**, as a pale-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.10 (s, 3H), 2.33 (t, 4H, *J* = 6.4 Hz), 3.97 (quintet, 1H, , *J* = 6.0 Hz), 5.10 (m, 4H), 5.60 (d, 1H, *J* = 12.6 Hz), 5.70 (ddt, 2H, *J*= 17.0 , 9.5, 7.0 Hz), 7.41 (d, 1H, *J* = 12.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.9, 38.1, 82.7, 107.7, 118.5, 132.6, 162.2, 197.4; IR (neat) 1633, 1600, 1192, 1142, 956, 916 cm^{-1}.

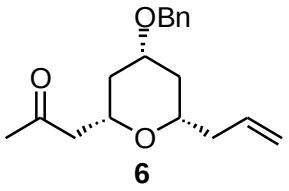


9

Alcohol 9. A dry 25-mL round-bottomed flask, flushed with nitrogen, was charged with vinylogous ester **8** (360 mg, 2.0 mmol) and CH_2Cl_2 (5 mL). This solution was cooled to 0 °C and treated with TFA (0.8 mL, 8 mmol). The flask was placed in the refrigerator at 5 °C for 2 days. The resulting trifluoroacetate was hydrolyzed by the slow addition into a solution of LiOH (520 mg, 12 mmol) in THF (20 mL) and water (5 mL). After 10 min at ambient temperature, the reaction mixture was partitioned between ethyl acetate (40 mL) and brine (30 mL). The aqueous layer was extracted with ethyl acetate (40 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Flash chromatography on silica gel (elution with ethyl acetate:hexane; 2:1, 3:1) afforded 305 mg of alcohol **9** (77% yield) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12 (m, 2H), 1.93 (m, 2H), 2.15 (s, 3H), 2.16 (m, 1H), 2.27 (dddt, 1H, *J* = 14.0, 6.5, 6.5, 1.0 Hz), 2.42 (dd, 1H, *J* = 16.0, 5.0 Hz), 2.72 (dd, 1H, *J* = 16.0, 8.0 Hz), 3.34 (dddd, 1H, *J* = 11.5, 6.5, 6.5, 2.0 Hz), 3.73 (dddd, 1H, *J* = 9.0, 8.0, 5.0, 2.0 Hz), 3.79 (dddd, 1H, *J* = 11.0, 11.0, 5.0, 5.0 Hz), 5.00 (d, 1H, *J* = 10.0 Hz), 5.03 (d, 1H, *J* = 17.0 Hz), 5.75 (dddd, 1H, *J* = 17.0, 10.0, 7.0,

7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.1, 40.2, 40.3, 40.7, 49.5, 67.7, 71.9, 75.1, 116.9, 134.4, 207.3; IR (neat) 3390, 2917, 1708, 1357, 1082, 1031, 914, 732 cm^{-1}.

Ketone 6. A solution of alcohol **9** (570 mg, 2.87 mmol), benzyl trochloroacetimidate (882 mg, 3.5 mmol) in CH_2Cl_2 (4 mL) and cyclohexane (2 mL) under nitrogen atmosphere was cooled to 0 °C, and treated with TfOH (60 μl). The reaction mixture was stirred for 30 min, then partitioned between ether (50 mL) and saturated aqueous solution of $NaHCO_3$ (10 mL). The aqueous layer was extracted with ether (50 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Flash chromatography on silica gel (elution with ether:hexane; 2:1) afforded 586 mg of ketone **6** (71% yield) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20 (m, 2H), 2.05 (m, 2H), 2.15 (s, 3H), 2.16 (m, 1H), 2.30 (m, 1H), 2.44 (dd, 1H, *J* = 16.0, 5.0 Hz), 2.72 (dd, 1H, *J* = 16.0, 8.0 Hz), 3.34 (m), 3.56 (dddd, 1H, *J* = 11.0, 11.0, 5.0, 5.0 Hz), 3.73 (dddd, 1H, *J* = 9.0, 8.0, 5.0, 2.0 Hz), 4.53 (s, 2H), 5.00-5.03 (m, 2H), 5.75 (dddd, 1H, *J* = 17.0, 10.0, 7.0, 7.0 Hz), 7.25-7.35 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 31.1, 37.4, 37.8, 40.4, 49.7, 69.6, 72.0, 74.3, 75.2, 116.9, 127.5, 128.4, 134.4, 138.4, 207.3; IR (neat) 2917, 2848, 1712, 1353, 1085, 1068, 912, 735, 697 cm^{-1}.



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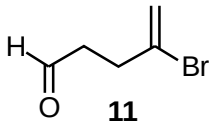
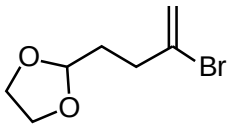
Aldehyde 11. Cyclohexylamine (20 g, 0.20 mol) was treated dropwise with acetaldehyde (11.2 mL, 0.20 mol) at -10 °C. The resulting white suspension was allowed to warm to ambient temperature, and treated with anhydrous Na_2SO_4 (4 g). The reaction mixture was stirred for 12 h, and filtered. The residue was subjected to distillation (54 °C, 33 mm Hg) to give 21 g (81% yield) of the desired imine as a colorless oil.

A solution of diethyl amine (10.3 mL, 100 mmol) in THF (120 mL) was treated at –78 °C with *n*-butyllithium (40 mL, 2.5 M solution in hexane). The resulting solution was stirred for 15 min, and treated with cyclohexyl imine (10.9 g, 87.2 mmol) in THF (50 mL), immediately followed by addition of HMPA (17.4 mL, 100 mmol). The reaction mixture was allowed to reach 0 °C, cooled to –78 °C and transferred via canula into a solution of 2,3-dibromopropene in THF (30 mL) at 0 °C, followed by slow warming to ambient temperature. The resulting solution was treated with 10% aqueous solution of tartaric acid (270 mL), stirred for 16 h, partitioned between ether (200 mL) and water (200 ml). The organic layer was separated, washed with water (300 mL), saturated aqueous solution of $NaHCO_3$ (200 mL), dried over anhydrous $MgSO_4$. Concentration under reduced pressure gave 12.4 g of the crude aldehyde **11** (74% yield), which was used for the next step without further purification.

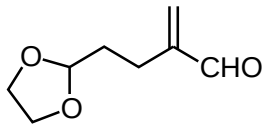


11

A 100-mL round-bottomed flask, equipped with the Dean-Stark trap was charged with aldehyde **11** (4.66 g, 28.6 mmol), ethylene glycol (1.86 g, 30 mmol), TsOH (50 mg) and benzene (50 mL). The resulting mixture was heated under a gentle reflux for 5 h, partitioned between ether (30 mL) and saturated aqueous solution of $NaHCO_3$ (50 mL). The aqueous layer was extracted with ether (30 mL), dried over anhydrous $MgSO_4$, filtered and concentrated. The resulting dark-brown oil was subjected to the bulb-to-bulb distillation (100 °C oven temperature, 2 mm Hg) to give 5.62 g (96% yield) of the corresponding acetal, as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (m, 2H), 2.54 (m, 2H), 3.84 (m, 2H), 3.95 (m, 2H), 4.88 (t, 1H, J = 4.5 Hz), 5.38 (d, 1H, J = 1.7 Hz), 5.59 (q, 1H, J = 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.3, 35.8, 65.0, 103.1, 116.8, 133.6; IR (neat) 2957, 2881, 1629, 1406, 1138, 1037, 886 cm^{-1}.

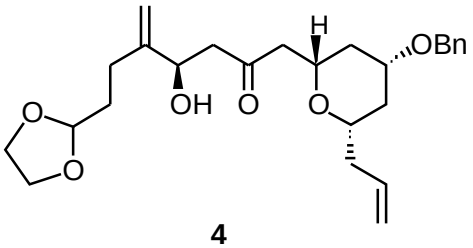


Aldehyde 5. A solution of vinyl bromide (3.70 g, 17.8 mmol), prepared in the previous step, in THF (50 mL) was treated dropwise with *n*-butyllithium (7.2 mL, 2.5 M in hexane) at –78 °C, followed by addition of dimethylformamide (6.9 mL) after a 20 min period. The reaction mixture was allowed to warm to ambient temperature, quenched by addition of water (200 mL), extracted with ether (2x300 mL), dried over anhydrous $MgSO_4$, filtered and concentrated. Flash chromatography on silica gel (elution with ether:hexane; 1:3, 1:1) afforded 0.81 g of starting bromide and 1.15 g of aldehyde **5** (53% yield) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.80 (m, 2H), 2.36 (t, 2H, J = 8.0 Hz), 3.83 (m, 2H), 3.94 (m, 2H), 4.86 (t, 1H, J = 4.5 Hz), 6.00 (s, 1H), 6.26 (s, 1H), 9.52 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.3, 31.7, 64.9, 103.7, 134.0, 149.5, 194.4; IR (neat) 2952, 2884, 1688, 1138, 1035, 945 cm^{-1}.



5

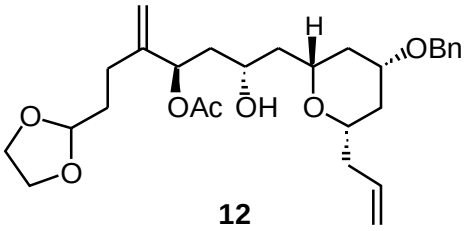
Ketone 4 Dicyclohexylboron chloride (2.5 mL of 1.0 M solution in hexane, 2.5 mmol) in ether (20 mL) was cooled to 0 °C, and treated with triethyl amine (0.39 mL, 2.8 mL), followed by addition of ketone **6** (473 mg, 1.64 mmol) in ether (6 mL). The resulting white suspension was stirred for 15 min at 0 °C, cooled to –78 C, and treated with aldehyde **5** (442 mg, 2.83 mmol) in ether (6 mL) over a 10 min period. The reaction mixture was stirred for 5 h at –78 C, quenched by addition of 21 mL of methanol:pH 7 buffer (6:1). Upon warming to ambient temperature, 9 mL of methanol-30% hydrogen peroxide (2:1) was added. The stirring was continued for 4 h. The resulting colorless solution was partitioned between ethyl acetate (100 mL) and saturated aqueous solution of $NaHCO_3$ (50 mL). The organic layer was washed with 10% solution of Na_2SO_3, dried over anhydrous $MgSO_4$, filtered and concentrated. Flash chromatography on silica gel (elution with ethyl acetate:hexane; 1:1) afforded 554 mg of ketone



4

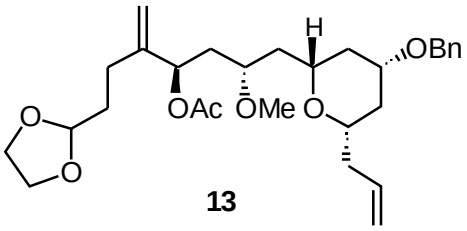
4 (76% yield) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20 (m, 3H), 1.84 (m, 2H), 2.05 (m, 2H), 2.06-2.30 (m, 4H), 2.43 (dd, 1H, *J* = 15.0, 4.5 Hz), 2.66 (dd, 1H, *J* = 17.0, 9.0 Hz), 2.75 (m, 2H), 3.33 (m, 1H), 3.55 (dddd, 1H, *J* = 11.0, 11.0, 5.0, 5.0 Hz), 3.75 (m, 1H), 3.83 (, 2H), 3.94 (m, 2H), 4.52 (m, 1H), 4.53 (s, 2H), 4.88 (m, 2H), 5.01 (d, 1H, *J* = 9 Hz), 5.03 (d, 1H, *J* = 16.5 Hz), 5.08 (s, 1H), 5.75 (dddd, 1H, *J* = 17.0, 10.0, 7.0, 7.0 Hz); 7.26-7.34 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.1, 32.1, 37.3, 37.8, 40.3, 49.4, 49.7, 64.9, 69.7, 70.3, 72.2, 74.2, 75.2, 104.0, 110.1, 117.1, 127.6, 128.4, 134.3, 138.4, 149.2, 209.8; IR (neat) 3451, 2916, 2849, 1710, 1352, 1069, 906, 733, 697 cm^{-1}.

Alcohol 12. A solution of ketone **4** (120 mg, 0.27 mmol) and acetaldehyde (48 mg, 1.1 mmol) in THF (3 mL) was cooled to –10 °C and treated with SmI_2 (0.80 mL, 0.1 M solution in THF). The reaction mixture was stirred for 15 min, quenched by addition of saturated aqueous solution of $NaHCO_3$ (15 mL), extracted with ethyl acetate (50 mL), dried over anhydrous $MgSO_4$, filtered and concentrated. Flash chromatography on silica gel (elution with ethyl acetate:hexane; 2:1) afforded 122 mg of alcohol **12** (93% yield) as a colorless oil. ^{1}H NMR (500 MHz, C_6D_6) δ 1.15 (m, 3H), 1.60 (dt, 1H, *J* = 14.0, 9.5 Hz), 1.72 (s, 3H), 1.65-1.85 (m, 4H), 1.95 (m, 1H), 2.00-2.10 (m, 3H), 2.40 (m, 2H), 2.95 (m, 1H), 3.18 (m, 2H), 3.33 (m, 1H), 3.35 (m, 2H), 3.52 (m, 2H), 3.77 (s, 1H), 3.95 (t, 1H, *J* = 9.0 Hz), 4.34 (d, 1H, *J* = 12.5 Hz), 4.36 (d, 1H, *J* = 12.5 Hz), 4.84 (t, 1H, *J* = 4.5 Hz), 4.89 (s, 1H), 4.98 (m, 2H), 5.15 (s, 1H), 5.66 (dddd, 1H, *J* = 17.0, 10.0, 7.0, 7.0 Hz); 5.87 (dd, 1H, *J* = 9.5, 2.5 Hz), 7.13 (t, *J* = 7.0 Hz), 7.22 (t, 2H, *J* = 7.0 Hz), 7. 34 (d, 2H, *J* = 7 Hz); ^{13}C NMR (125 MHz, C_6D_6) δ 20.7, 26.9, 32.7, 37.8, 38.8, 40.7, 42.6, 43.3, 64.8, 67.7, 69.4, 73.8, 74.3, 75.2, 76.5, 104.2, 110.4, 117.5, 127.5, 127.6, 128.6, 134,7, 139.6, 148.9, 169.6; IR (neat) 3492, 2917, 2860, 1736, 1642, 1368, 1236, 1070, 904, 736, 698 cm^{-1}.



12

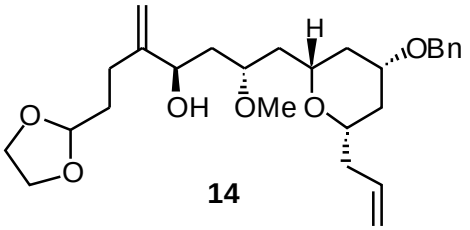
Methyl Ether 13. A solution of alcohol **12** (110 mg, 0.225 mmol), 2,6-di-*tert*-butylpyridine (0.76 mL, 3.37 mmol) and methyl triflate (0.323 mL, 2.25 mmol) was stirred for 14 h at ambient temperature, and quenched by addition of aqueous solution of ammonium hydroxide (10 mL). The product was extracted with ether (2x50 mL), dried over anhydrous $MgSO_4$, filtered and concentrated. The excess 2,6-di-*tert*-butylpyridine was removed by bulb-to-bulb distillation (80 °C, 0.5 mm Hg). Flash chromatography on silica gel (elution with ethyl acetate:hexane; 1:2) afforded 81 mg of methyl ether **13** (72% yield) as a colorless oil. ^{1}H NMR (500 MHz, C_6D_6) δ 1.19 (q, 1H, *J* = 11.5 Hz), 1.26 (q, 1H, *J* = 11.5 Hz), 1.43 (ddd, 1H, *J* = 14.0, 7.5, 3.5 Hz), 1.77 (s, 3H), 1.80-1.90 (m, 5H),



13

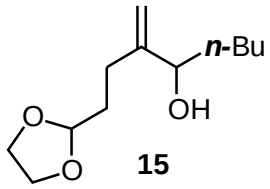
2.00-2.10 (m, 3H), 2.27 (m, 1H), 2.40 (m, 2H), 2.98 (m, 1H), 3.17 (s, 3H), 3.20-3.28 (m, 2H), 3.33 (m, 1H), 3.35 (m, 2H), 3.50 (m, 2H), 4.37 (s, 2H), 4.83 (t, 1H, *J* = 4.5 Hz), 4.89 (s, 1H), 5.03 (m, 2H), 5.17 (s, 1H), 5.84 (dd, 1H, *J* = 9.5, 2.5 Hz), 5.90 (m, 1H); 7.12 (t, *J* = 7.0 Hz), 7.22 (t, 2H, *J* = 7.0 Hz), 7. 35 (d, 2H, *J* = 7 Hz); ^{13}C NMR (125 MHz, C_6D_6) δ 20.7, 26.8, 32.7, 38.1, 39.0, 39.4, 39.8, 40.9, 56.5, 64.8, 69.4, 72.1, 73.8, 74.7, 74.8, 75.2, 104.2, 110.5, 116.6, 127.5, 127.6, 128.5, 135,5, 139.7, 148.8, 169.3; IR (neat) 2939, 2880, 1736, 1368, 1235, 1070, 906, 736, 698 cm^{-1}.

Alcohol 14. Lithium aluminum hydride (38 mg, 1 mmol) was suspended in ether (2 mL), cooled to –78 °C, and treated with methyl ether **13** (66 mg, 0.13 mmol) in ether (2 mL). The reaction mixture was stirred for 30 min at –78 °C, quenched by dropwise addition of water (0.2 mL). The resulting suspension was allowed to reach ambient temperature, vigorously stirred for 1 h, diluted with ether, dried with anhydrous Na_2SO_4, filtered and concentrated. Flash chromatography on silica gel (elution with ethyl acetate:hexane; 1:2) afforded 51 mg of alcohol **14** (86% yield) as a colorless oil. ^{1}H NMR (500 MHz, C_6D_6) δ 1.20 (q, 1H, *J* = 11.5 Hz), 1.26 (q, 1H, *J* = 11.5 Hz), 1.46 (ddd, 1H, *J* = 14.0, 7.5, 3.5 Hz), 1.80-1.85 (m, 4H), 1.93 (ddd, 1H, *J* = 14.0, 9.0, 4.5 Hz), 2.00-2.04 (m, 2H), 2.10 (m, 1H), 2.28 (m, 2H), 2.40 (m, 1H), 3.00 (m, 1H), 3.08 (s, 3H), 3.20-3.28 (m, 2H), 3.35 (m, 2H), 3.69 (m, 1H), 4.37 (s, 2H), 4.43 (m, 1H), 4.85 (t, 1H, *J* = 4.5 Hz), 4.95 (s, 1H), 5.04 (m, 2H), 5.33 (s, 1H), 5.86 (dddd, 1H, *J* = 17.0, 10.0, 7.0, 7.0 Hz), 7.12 (t, *J* = 7.0 Hz), 7.22 (t, 2H, *J* = 7.0 Hz), 7. 35 (d, 2H, *J* = 7 Hz); ^{13}C NMR (125 MHz, C_6D_6) δ 26.7, 33.0, 37.9, 39.0, 38.9, 39.3, 39.5, 40.9, 56.0, 64.8, 69.4, 72.3, 74.8, 75.2, 76.4, 104.4, 108.9, 116.8, 127.5, 127.6, 128.5, 135,3, 139.7, 152.2; IR (neat) 3452, 2942, 2878, 1642, 1354, 1071, 904, 736, 698 cm^{-1}.



14

Alcohol 15. Aldehyde **5** (312 mg, 2.0 mmol) in THF (10 mL) was cooled to –78 °C, and treated with *n*-butyllithium (0.88 mL, 2.5 M solution in hexane). After 15 min, the reaction was quenched by addition of saturated aqueous solution of $NaHCO_3$ (15 mL), extracted with ether (50 mL), dried over anhydrous $MgSO_4$, filtered and concentrated. Flash chromatography on silica gel (elution with ether:hexane; 2:1) afforded 380 mg of alcohol **15** (87% yield) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, 3H, *J* = 7.0 Hz), 1.20-1.38 (m, 4H), 1.53 (m, 2H), 1.78 (br s, 1H), 1.85 (m, 2H), 2.10 (m, 1H), 2.21 (m, 1H), 3.81 (m, 2H), 3.95 (m, 2H), 4.06 (t, 1H, *J* = 7.0 Hz), 4.83 (s, 1H), 4.87 (t, 1H, *J* = 4.5 Hz), 5.01 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 22.6, 25.3, 27.8, 32.2, 35.1, 64.9, 75.6, 104.2, 109.8, 151.1; IR (neat) 3439, 2953, 2870, 1692, 1409, 1135, 1031, 899, 731 cm^{-1}.



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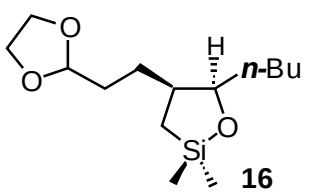
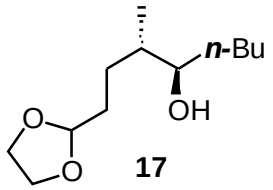
Silane 16. A solution of alcohol **15** (142 mg, 0.66 mmol) in CH_2Cl_2 (0.50 mL) was treated with tetramethyldisilazane (0.35 mL, 2.0 mmol). After 12 h, ^{1}H NMR analysis indicated complete consumption of the starting alcohol. The excess tetramethyldisilazane was removed under high vacuum. The resulting silyl ether was dissolved in C_6H_6 (7 mL) and treated with H_2PtCl_6 [30 μL, 0.05 M in THF, (0.3 mol%)]. After 30 min at 50 °C, ^{1}H NMR analysis indicated quantitative formation of the silacycle **16**, as 85:15 mixture of diastereomers. Major isomer: ^{1}H NMR (400 MHz, C_6D_6) δ 0.10 (s, 3H), 0.15 (s, 3H), 0.90 (t, 3H, *J* = 7.0 Hz), 1.20-1.90 (m, 10H), 2.00 (m, 1H), 3.39 (m, 2H), 3.56 (m, 2H), 3.99 (ddd, 1H, *J* = 10.4, 5.6, 3.2 Hz), 4.82 (t, 1H, *J* = 4.5 Hz); ^{13}C NMR (100 MHz, C_6D_6) δ 0.2, 1.2, 14.4, 16.2, 23.0, 26.9, 28.7, 31.4, 33.2, 42.5, 64.8, 104.8; IR (neat) 2953, 2871, 1408, 1250, 1033, 840, 796 cm^{-1}.



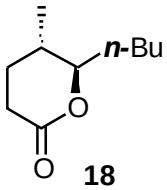
16

Alcohol 17. Cyclic silane **16**, obtained upon concentration of the crude hydrosilylation reaction mixture was treated with TBAF (2.6 mmol) in DMF (2.5 mL). The resulting solution was heated to 75 °C for 24 h. The excess DMF was removed by bulb-to-bulb distillation (50 °C, 0.5 mm Hg). Flash chromatography on silica gel (elution with ethyl acetate:hexane; 1:2) afforded 121 mg of alcohol **17** (82% yield from **15**) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (d, 3H, *J* = 7.0 Hz), 0.88 (t, 3H, *J* = 7.0 Hz), 1.20-1.90 (m, 10H), 2.74 (m, 1H), 3.41 (m, 1H), 3.82 (m, 2H), 3.95 (m, 2H), 4.83 (t, 1H, *J* = 4.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 15.2, 22.7, 26.0, 28.2, 31.6, 33.1, 38.6, 64.8, 75.7, 104.7.



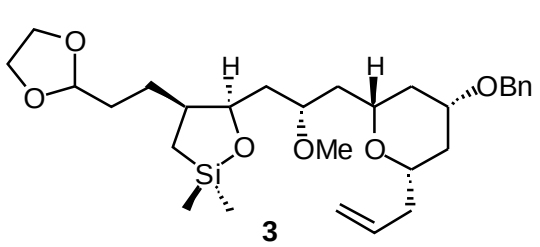
17

Lactone 18. A solution of alcohol **17** (110 mg, .50 mmol) in 6 mL of THF-water (5:1) containing a drop of concentrated H_2SO_4 was heated to 80 °C for 10 h, then partitioned between saturated aqueous solution of $NaHCO_3$ (1 mL), and ether (20 mL). The organic layer was separated, dried over anhydrous $MgSO_4$, filtered and concentrated. Flash chromatography on silica gel (elution with ether:pentane; 1:1) afforded 62 mg of the corresponding lactol as a colorless oil. The oxidation was conducted by addition of bromine (15 μL) to the solution of the lactol in acetic acid (0.4 mL) and water (0.64 mL). After 1 h, the reaction mixture was partitioned between saturated aqueous solution of $NaHCO_3$, and ether (20 mL). The organic layer was separated, dried over anhydrous $MgSO_4$, filtered and concentrated. Flash chromatography on silica gel (elution with ether:pentane; 1:1) afforded 61 mg of lactone **18** (86% from 17) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, 3H, *J* = 7.0 Hz), 0.97 (t, 3H, *J* = 7.0 Hz), 1.20-1.70 (m, 8H), 1.87 (m, 1H), 2.45 (ddd, 1H, *J* = 17.0, 10.0, 6.8 Hz), 2.60 (ddd, 1H, *J* = 17.0, 6.4, 4.4 Hz), 3.91 (ddd, 1H, *J* = 10.0, 8.0, 3.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 17.4, 22.6, 26.5, 27.8, 29.5, 32.2, 33.1, 85.9, 174.0.



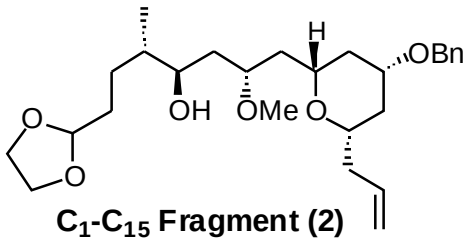
18

Silane 3. A solution of alcohol **13** (46 mg, 0.10 mmol) in $CDCl_3$ (0.50 mL) was treated with tetramethyldisilazane (0.10 mL, 0.56 mmol). After 15 min, ^{1}H NMR analysis indicated complete consumption of the starting alcohol. The excess tetramethyldisilazane was removed under high vacuum. The resulting silyl ether was dissolved in C_6D_6 (1 mL) and treated with H_2PtCl_6 (0.5 mol%). After 10 min at 57 °C, ^{1}H NMR analysis indicated quantitative formation of the silacycle **3**, as 87:13 mixture of diastereomers. Major isomer: ^{1}H NMR (500 MHz, C_6D_6) δ 0.11 (s, 3H), 0.17 (s, 3H), 0.48 (dd, 1H, *J* = 14.5, 11.0 Hz), 0.80 (dd, 1H, *J* = 14.5, 7.0 Hz), 1.25 (q, 1H, *J* = 11.5 Hz), 1.36 (q, 1H, *J* = 11.5 Hz), 1.46-2.38 (m, 2H), 3.10 (m, 1H), 3.33 (s, 3H), 3.20-3.28 (m, 2H), 3.28 (m, 2H), 3.35 (m, 2H), 3.90 (m, 1H), 4.38 (s, 2H), 4.50 (m, 1H), 4.85 (t, 1H, *J* = 4.5 Hz), 5.04 (m, 2H), 5.92 (m, 1H), 7.11 (t, *J* = 7.0 Hz), 7.21 (t, 2H, *J* = 7.0 Hz), 7. 34 (d, 2H, *J* = 7 Hz).



3

Alcohol 2. Cyclic silane **3**, obtained upon concentration of the crude hydrosilylation reaction mixture was treated with TBAF (0.4 mmol) in *d*-DMF (0.5 mL). The resulting solution was heated to 70 °C for 15 min. At this point, ^{1}H NMR analysis indicated complete consumption of the starting silane **3**. The excess DMF was removed by bulb-to-bulb distillation (50 °C, 0. 5 mm Hg). Flash chromatography on silica gel (elution with ethyl acetate:hexane; 1:1) afforded 24 mg of alcohol **2** (54% yield from **14**) as a colorless oil. ^{1}H NMR (500 MHz, C_6D_6) δ 0.93 (d, 3H, *J* = 6.5 Hz), 1.22 (q, 1H, *J* = 11.5 Hz), 1.28 (q, 1H, *J* = 11.5 Hz), 1.48-2.03 (m, H), 2.10 (m, 1H), 2.30 (m, 1H), 2.80 (br s, 1H), 3.00 (m, 1H), 3.07 (s, 3H), 3.26 (m, 2H), 3.36 (m, 2H), 3.56 (m, 2H), 3.67 (m, 1H), 3.78 (m, 1H), 4.37 (s, 2H), 4.85 (t, 1H, *J* = 4.5 Hz), 5.04 (m, 2H), 5.87 (dddd, 1H, *J* = 17.0, 10.0, 7.0, 7.0 Hz), 7.12 (t, *J* = 7.0 Hz), 7.22 (t, 2H, *J* = 7.0 Hz), 7. 35 (d, 2H, *J* = 7 Hz); ^{13}C NMR (125 MHz, C_6D_6) δ 15.4, 27.0, 32.2, 36.3, 37.9, 38.9, 39.3, 39.4, 40.9, 56.2, 64.8, 69.4, 72.4, 74.9, 75.2, 76.8, 105.2, 116.8, 127.5, 127.6, 128.5, 135,2, 139.7; IR (neat) 3470, 2919, 2870, 1354, 1071, 736, 697 cm^{-1}.



C_1-C_{15} Fragment (2)