Metal-Catalyzed di-*tert*-Butylsilylene Transfer: Synthesis and Reactivity of Silacyclopropanes

Jelena Cirakovic, Tom G. Driver, and K. A. Woerpel*

*Department of Chemistry, University of California,
Irvine, California, 92697-2025*

Supporting Information

Contents:

I. Preparation of Alkene 11	s-2
II. Silacyclopropane Formation	s-3
III. Synthesis of Oxasilacyclopentanes from Alkenes	s-4
IV. Construction of 1,3-Diols from Oxasilacyclopentanes	s-10
V. References	s-12
VI. Spectral Data	s-13

General. ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature using Bruker DRX 500 or DRX 400 MHz spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane standard on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. High resolution mass spectra were acquired on a VG Analytical 7070E or Fisons Autospec spectrometer, and were obtained by peak matching. Microanalyses were performed by Atlantic Microlab, Atlanta, GA. GC analyses were performed on an Agilent 6850 GC system gas chromatograph. Analytical thin layer chromatography was performed on EM Reagents 0.25 mm silica gel 60-F plates. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on EM silica gel (SiO_2) 60 (230-400) mesh, or gravity column chromatography on Fisher neutral alumina Broeckman activity I (60 – 325) mesh. HPLC Osmonics polypropylene 0.45 micron filters were used. The reactions were carried out under an atmosphere of argon, in glassware which had been flame dried under vacuum, or in an Innovative Technologies nitrogen atmosphere dry box. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. Toluene, Et_2O , and CH_2Cl_2 were dried by filtration through alumina according to the procedure of Grubbs.¹ Metal salts and cyclohexene di-*tert*-butyl silacyclopropane **1** were stored in an Innovative Technologies nitrogen atmosphere dry box.

I. Preparation of Alkene 11

Spectral data for compounds **2a-j**, and **3-10** have already been reported.²

Alkene 11. To a cooled ($-78\text{ }^{\circ}\text{C}$) solution of *n*-BuLi (10.40 mL of 2.0 M solution of *n*-BuLi in hexanes, 20.80 mmol) in THF (80 mL) was introduced propyne until the solution became milky white. $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (3.16 mL, 27.10 mmol) was then added dropwise. After 10 minutes, *cis*-2,3-epoxybutane was added dropwise and the mixture was left stirring at $-78\text{ }^{\circ}\text{C}$ for 45 minutes. The mixture was then quenched with saturated aqueous NH_4Cl and allowed to reach room temperature. The two layers that formed were separated. Water layer was extracted once with MTBE (20 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. Purification by flash chromatography (pentane: Et_2O = 91:9) yielded the product **s-1** as a colorless oil (1.450 g, 92%): ^1H NMR (CDCl_3 , 400 MHz) δ 3.57 (q, J = 6.0, 1H), 2.39 (m, 1H), 1.98 (br s, 1H), 1.82 (d, J = 2.4, 3H), 1.22 (d, J = 6.0, 3H), 1.16 (d, J = 7.2, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 79.8, 78.7, 70.9, 34.9, 20.8, 17.6, 3.5; IR (thin film) 3406, 2975, 2921, 1451, 1376, 1101 cm^{-1} .

Alcohol **s-1** obtained was then further utilized in the next step. To a cooled ($-78\text{ }^{\circ}\text{C}$) suspension of potassium hydride (0.299 g, 7.455 mmol) and 18-c-6 (0.002 g, 0.007 mmol) in THF (10 mL) was added **s-1** (0.497 g, 4.430 mmol) as a solution in THF (5 mL). After 10 minutes, TIPSCl (1.39 mL, 6.49 mmol) was added and the mixture was left to reach room temperature overnight. The reaction mixture was then diluted with Et_2O (20 mL), the reagents were quenched with 0.01 M HCl (5 mL), and the layers were separated. The organic extract was washed once with brine (20 mL), dried over Na_2SO_4 , and concentrated. Purification by gravity alumina column chromatography (pentane) afforded the product **s-2** as a colorless oil (1.180 g, 99%): ^1H NMR (CDCl_3 , 400 MHz) δ 4.04 (dq, J = 6.2, 4.3, 1H), 2.57 (qdd, J = 7.0, 4.3, 2.4, 1H), 1.78 (d, J = 2.4, 3H), 1.18 (d, J = 6.2, 3H), 1.11 (d, J = 7.0, 3H), 1.06 (s, 18H and 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 81.7, 76.7, 70.6, 35.6, 19.0, 18.6, 18.1, 13.9, 12.4; IR (thin film) 2943, 2867, 1463, 1378, 1108, 1016 cm^{-1} ; HRMS (CI/isobutene) m/z calcd for $\text{C}_{16}\text{H}_{33}\text{OSi}$ ($\text{M}+\text{H}$)⁺ 269.2301, found 269.2302. Anal. Calcd for $\text{C}_{16}\text{H}_{32}\text{OSi}$: C, 71.57; H, 12.01. Found C, 71.61; H, 12.10.

TIPS ether **s-2** obtained was reduced in the following manner: alkyne **s-2** (0.219 g, 0.816 mmol) was added to a suspension of Lindlar catalyst ($\text{Pd} \cdot \text{CaCO}_3(\text{Pb})$, 0.074 g, 0.030 mmol of Pd) in benzene (10 mL). A balloon of hydrogen was attached to the flask through the septum and the reaction mixture was left stirring overnight. The mixture was then filtered through a plug of Celite and concentrated. Purification by flash chromatography (pentane) afforded the product **11** as a colorless oil (0.216 g, 98%): ^1H NMR (500 MHz, CDCl_3) δ 5.47 (m, 1H), 5.31 (m, 1H), 3.90 (qd, J = 6.2, 3.8, 1H), 2.62 (m, 1H), 1.63 (dd, J = 6.8, 1.7, 3H), 1.09 (s, 18H and 6H), 0.99 (d, J = 6.8, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 133.4, 123.6, 71.6, 38.7, 19.7, 18.2, 15.2, 13.0, 12.7; IR (thin film) 3014, 2961, 1464, 1374, 1104, 883 cm^{-1} ; HRMS (CI/isobutene) m/z calcd for $\text{C}_{13}\text{H}_{27}\text{OSi}$ ($\text{M} - i\text{-Pr}$)⁺ 227.1831, found 227.1827. Anal. Calcd for $\text{C}_{16}\text{H}_{34}\text{OSi}$: C, 71.04; H, 12.67. Found C, 71.15; H, 12.76.

II. Silacyclopropane formation

Silacyclopropane 12. To a cooled ($-20\text{ }^{\circ}\text{C}$) suspension of AgOTf (0.001 g, 0.004 mmol) in 0.7 mL of 0.019 M solution of PhSiMe₃ in *d*₈-toluene, contained in an NMR tube, was added alkene **11** (0.049 g, 0.181 mmol). The solution of cyclohexene silacyclopropane **1** (0.034 g, 0.152 mmol) in 0.3 mL of 0.019 M solution of PhSiMe₃ in *d*₈-toluene was cooled to $-20\text{ }^{\circ}\text{C}$ and added to the NMR tube. After 12 h, the reagents were quenched with TMEDA (0.010 mL) and the reaction mixture was analyzed by ¹H and ²⁹Si NMR spectroscopy. Silacyclopropane **12** was formed in 79% as a 89:11 mixture of isomers. The ²⁹Si NMR spectrum was obtained to verify the formation of product silacyclopropane and to determine the diastereoselectivity of the reaction. The yield of the reaction was obtained through comparison of the area of the standard PhSiMe₃ peak at 0.20 ppm and the area of the *t*-Bu peak of the product:

²⁹ Si NMR peaks (ppm) rel. external TMS standard ^a	Relative ratio of ²⁹ Si NMR peaks	Product 12 <i>t</i> -Bu ppm (area) ^b	Standard (equiv., area) ^b	%yield ^b
-51.02, -54.02	11 : 89	1.15 (4.85) ^c 1.00 (7.56)	PhSiMe ₃ (0.129, 1.00)	79

^a The ²⁹Si NMR spectrum of **1** contains one peak at -54.6 ppm . ^b As determined by ¹H NMR analysis of product mixture relative to an internal standard of PhSiMe₃. Yield = (equiv. standard)(area of *t*-bu peak)/(area of standard). ^c *t*-Bu peak with smaller area used in the yield calculation.

2,3-*cis*-Dimethyl-1,1-di-*tert*-butylsilacyclopropane (3).³ Cold ($-78\text{ }^{\circ}\text{C}$) *cis*-butene (ca. 1 mL, excess), was added by cannula to a cooled ($0\text{ }^{\circ}\text{C}$) Schlenk flask that contained a suspension of AgOC(O)CF₃ (0.007 g, 0.032 mmol) in CH₂Cl₂ (12 mL). A solution of cyclohexene silacyclopropane **1** (0.709 g, 3.159 mmol) in CH₂Cl₂ (3 mL) was added dropwise, and the reaction mixture was allowed to reach room temperature overnight. The crude reaction mixture was filtered through Celite 545 under an atmosphere of argon (Schlenk filtration) and the cake was washed four times with freshly distilled hexanes ($5 \times 10\text{ mL}$). The filtrate was concentrated *in vacuo*. Purification by bulb-to-bulb distillation afforded the silacyclopropane **3** as a colorless oil (0.418 g, 67%): ¹H NMR (400 MHz, CDCl₃) δ 1.28 (m, 6H), 1.19 (s, 9H), 1.02 (s, 9H), 0.94 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 31.5, 29.8, 9.9, 9.5; IR (thin film): 2988, 2860, 1474, 1388, 1364 cm⁻¹; HRMS (CI/isobutene) *m/z* calcd for C₁₂H₂₆Si (M)⁺ 198.1804, found 198.1795.

2,3-*trans*-Dimethyl-1,1-di-*tert*-butylsilacyclopropane (4).³ The procedure for **3** was followed using ca. 1 mL of *trans*-2-butene, 0.800 g of cyclohexene silacyclopropane **1** (3.564 mmol), and 0.008 g of AgOC(O)CF₃ (0.036 mmol). Purification by bulb-to-bulb distillation afforded the silacyclopropane **4** as a colorless oil (0.565 g, 80%): ¹H NMR (400 MHz, CDCl₃) δ 1.33 (m, 6H), 1.12 (s, 18H), 0.51 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 30.7, 19.6, 16.9, 16.4; IR (thin film): 2966, 2859, 1473, 1455, 1388, 1363 cm⁻¹; HRMS (CI/isobutene) *m/z* calcd for C₁₂H₂₆Si (M)⁺ 198.1804, found 198.1808.

2-Butyl-1,1-di-*tert*-butyl silacyclopropane (13) To a cooled (0 °C) suspension of AgOC(O)CF₃ (0.004 g, 0.018 mmol) in CH₂Cl₂ (10 mL) was added 1-hexene (0.90 mL, 7.20 mmol). A solution of **1** (0.814 g, 3.626 mmol) in CH₂Cl₂ (2 mL) was then added dropwise and the reaction mixture was allowed to reach room temperature overnight. The reaction mixture was filtered through Celite 545 under an atmosphere of argon (Schlenk filtration) and the cake was washed with freshly distilled hexanes (5 × 10 mL). The filtrate was then concentrated *in vacuo*. Purification by bulb-to-bulb distillation afforded the product as a colorless oil (0.739 g, 90%): ¹H NMR (500 MHz, CDCl₃) δ 1.66 – 1.61 (m, 1H), 1.58 – 1.52 (m, 1H), 1.42 (m, 1H), 1.37 – 1.29 (m, 3H), 1.13 (s, 9H), 1.05 (s, 9H), 0.89 (t, *J* = 7.0, 3H), 0.76 (ddd, *J* = 16.5, 12.1, 8.4, 1H), 0.66 (dd, *J* = 12.1, 10.3, 1H), 0.35 (dd, *J* = 10.3, 8.7, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 34.7, 34.1, 31.8, 30.7, 29.8, 22.6, 18.9, 14.3, 14.0, 3.2; IR (thin film): 2966, 2857, 1474, 1459, 1388, 1363, 1012 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₄H₃₀Si (M)⁺ 226.2117, found 226.2116.

III. Synthesis of oxasilacyclopentanes from alkenes

Spectral data for compounds **14a-g** have already been reported.²

Oxasilacyclopentane 15a. To a cooled (0 °C) Schlenk flask that contained the suspension of AgOC(O)CF₃ (0.004 g, 0.018 mmol) in CH₂Cl₂ (5 mL) was added 1-hexene (0.070 mL, 0.559 mmol) and the reaction mixture was stirred for 10 minutes. A solution of **1** (0.064 g, 0.285 mmol) in CH₂Cl₂ (2 mL) was added dropwise and the mixture was left stirring for 2 h. The mixture was then cooled to -78 °C, and benzaldehyde (0.060 mL, 0.590 mmol) was then added followed by ZnBr₂ (0.018 mg, 0.080 mmol) and the mixture was allowed to reach room temperature overnight. The mixture was then diluted with CH₂Cl₂ (5 mL) and washed with brine (5 mL). The water layer was then extracted with CH₂Cl₂ (5 mL). The combined organic extracts were filtered through a cotton plug and concentrated to afford the product as a 65:35 mixture of diastereomers as determined by GC analysis. Purification by flash chromatography (pentane:EtOAc = 99:1) afforded the product as a colorless oil (0.062 g, 73%): IR (thin

film) 3028, 2930, 1473, 1458, 1041, 824 cm^{-1} ; HRMS (CI/isobutene) m/z calcd for $\text{C}_{21}\text{H}_{35}\text{OSi}$ ($\text{M} - \text{H}$)⁺ 331.2457, found 331.2442. Anal. Calcd for $\text{C}_{21}\text{H}_{36}\text{OSi}$: C, 75.84; H, 10.91. Found C, 75.82; H, 11.06. Selected data for major diastereomer: ^1H NMR (400 MHz, CDCl_3) δ 7.28 (m, 5H), 4.76 (dd, $J = 11.2, 4.0$, 1H), 2.36 (ddd, $J = 11.8, 6.1, 3.9$, 1H), 2.04 (dd, $J = 7.6, 6.8$, 1H), 1.67 (m, 2H), 1.32 (m, 5H), 1.08 (s, 9H), 1.02 (s, 9H), 0.83 (t, $J = 7.0$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 128.2, 126.8, 125.5, 125.0, 79.3, 43.5, 33.5, 29.8, 28.6, 28.5, 28.1, 25.9, 22.7, 14.1. Selected data for minor diastereomer: ^1H NMR (400 MHz, CDCl_3) δ 7.28 (m, 5H), 5.02 (t, $J = 6.6$, 1H), 1.66 (m, 2H), 1.32 (m, 6H), 1.07 (s, 9H), 0.98 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 128.2, 128.1, 126.8, 126.7, 78.1, 47.8, 33.6, 33.0, 30.5, 27.8, 27.7, 13.4

Oxasilacyclopentane (15b). To a cooled ($-15\text{ }^\circ\text{C}$) suspension of $\text{AgOC}(\text{O})\text{CF}_3$ (0.003 g, 0.015 mmol) in 2 mL of toluene was added, dropwise, a solution containing cyclohexene silacyclopropane **1** (0.048 g, 0.214 mmol) and 0.036 mL of allylbenzene (0.267 mmol) in 0.5 mL of toluene. After 90 minutes, the resultant dark suspension was added, dropwise, to a cold ($-78\text{ }^\circ\text{C}$) suspension of ZnI_2 (0.014 g, 0.446 mmol) in 0.7 mL of toluene. Freshly distilled crotonaldehyde (0.037 mL, 0.446 mmol) was added dropwise. The resultant suspension was allowed to slowly warm to $22\text{ }^\circ\text{C}$. After 5 h, the reaction mixture was passed through silanized silica gel and concentrated *in vacuo* to afford **15b** as a 69:31 mixture of diastereomers as determined by ^1H NMR analysis. Purification by flash chromatography (hexanes) afforded the product **15b**, as a colorless oil (0.055 g, 78%). The regioselectivity was determined from 2D gCOSY NMR spectroscopy. Major diastereomer: ^1H NMR (500 MHz, CDCl_3) δ 7.26 (m, 5H), 5.61 (m, 1H), 5.47 (tdd, $J = 10.8, 7.5, 1.5$, 1H), 4.57 (td, $J = 7.6, 3.4$, 1H), 3.13 (dd, $J = 13.9, 3.4$, 1H), 2.73 (m, 1H), 1.90 (m, 1H), 1.69 (m, 5H), 1.09 (s, 9H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.2, 134.1, 133.7, 128.3, 125.8, 125.7, 77.9, 28.6, 28.4, 24.4, 22.1, 21.4, 21.3, 20.2, 17.5. Selected data for minor diastereomer: ^1H NMR (500 MHz, CDCl_3) δ 4.12 (ddd, $J = 13.7, 9.5, 3.7$, 1H), 1.40 (m, 1H), 1.07 (s, 9H), 1.03 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.3, 128.2, 126.0, 78.7, 28.08, 28.03, 27.6, 17.6; IR (thin film) 3026, 2856, 1472, 1003, 822 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{21}\text{H}_{34}\text{OSi}$ (M)⁺ 330.2379, found 330.2362. Anal. Calcd for $\text{C}_{21}\text{H}_{34}\text{OSi}$: C, 76.30; H, 10.37. Found C, 75.94; H, 10.40.

Coupling (COSY cross peaks) observed between (1) H_a and H_b and (2) H_b and H_c

Note: no coupling observed between H_a and H_c

Oxasilacyclopentane (15c). The procedure for **15b** was followed using 0.060 g of cyclohexene silacyclopropane **1** (0.267 mmol), 0.042 mL of allylbenzene (0.321 mmol), 0.003 g of AgOCOCF₃ (0.01 mmol), 0.051 mL of freshly distilled furfural (0.534 mmol), and 0.017 g of ZnI₂ (0.0534 mmol). After 5 h, the reaction mixture was passed through silanized silica gel and concentrated *in vacuo* to afford **15c** as a 64:36 mixture of diastereomers as determined by ¹H NMR analysis. Purification using flash chromatography (hexanes) afforded the product **15c** (0.078 g, 80%). The regioselectivity was determined from 2D gCOSY NMR spectroscopy. IR (thin film) 2932, 2857, 1474, 1009, 823 cm⁻¹; HRMS (EI) *m/z* calcd for C₂₂H₃₃O₂Si (M + H)⁺ 357.2250, found 357.2253. Major diastereomer: ¹H NMR (500 MHz, CDCl₃) δ 7.26 (m, 6H), 6.29 (dd, *J* = 3.2, 1.8, 1H), 6.23 (dd, *J* = 4.5, 1.8, 1H), 4.74 (dd, *J* = 11.4, 4.4, 1H), 3.18 (m, 1H), 2.80 (m, 1H), 2.55 (m, 1H), 1.88 (m, 1H), 1.72 (m, 1H), 1.19 (s, 9H), 1.13 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 156.2, 143.1, 141.9, 128.4, 128.2, 125.9, 109.9, 105.9, 72.8, 38.2, 36.4, 27.92, 27.90, 27.5, 21.5, 21.4. Selected data for minor diastereomer: ¹H NMR (500 MHz, CDCl₃) δ 6.23 (br s, 1H), 6.00 (d, *J* = 3.2, 1H), 5.22 (dd, *J* = 7.7, 2.2, 1H), 2.21 (ddd, *J* = 10.9, 8.0, 2.4, 1H), 1.18 (s, 9H), 0.96 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 156.8, 143.0, 141.8, 128.4, 128.2, 109.7, 105.5, 71.6, 36.4, 35.5, 28.3, 28.2, 24.9, 22.1, 20.3.

Coupling (COSY cross peaks) observed between (1) H_a and H_b and (2) H_b and H_c
 Note: no coupling observed between H_a and H_c

Oxasilacyclopentane (15d). The procedure for **15b** was followed using 0.020 g of cyclohexene silacyclopropane **1** (0.089 mmol), 0.014 mL of allylbenzene (0.106 mmol), 0.001 g of AgOCOCF₃ (0.004 mmol), 0.019 mL of freshly distilled 3-pentanone (0.178 mmol), and 0.006 g of ZnI₂ (0.017 mmol). Purification using flash chromatography (hexanes) afforded the product **15d** (0.020 g, 66%): ¹H NMR (500 MHz, CDCl₃) δ 7.24 (m, 5H), 3.14 (dd, *J* = 13.9, 3.7, 1H), 2.74 (dd, *J* = 13.9, 11.5, 1H), 1.76 (m, 3H), 1.47 (m, 3H), 1.34 (m, 1H), 1.14 (s, 9H), 1.08 (s, 9H), 0.80 (q, *J* = 7.6, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 143.5, 128.3, 128.2, 125.7, 82.9, 42.6, 36.6, 32.4, 29.5, 28.7, 28.6, 25.3, 21.8, 20.5, 9.0, 8.3; IR (thin film) 2933, 2856, 1474, 989, 703 cm⁻¹; HRMS (EI) *m/z* calcd for C₂₂H₃₇OSi (M – H)⁺ 345.2614, found 345.2618.

Oxasilacyclopentane (15e). The procedure for **15b** was followed using 0.020 g of cyclohexene silacyclopentane **1** (0.089 mmol), 0.014 mL of allylbenzene (0.106 mmol), 0.001 g of AgOCOCF₃ (0.004 mmol), 0.021 mL of freshly distilled acetophenone (0.178 mmol), and 0.006 g of ZnI₂ (0.018 mmol). After 5 h, the reaction mixture was passed through silanized silica gel and concentrated *in vacuo* to afford **15e** as a 53:47 mixture of diastereomers as determined by ¹H NMR analysis. Purification using flash chromatography (hexanes) afforded the product **15e** (0.033 g, 96%): IR (thin film) 3086, 2931, 1602, 1471, 953 cm⁻¹; HRMS (CI/isobutane) *m/z* calcd for C₂₄H₃₃OSi (M – CH₃)⁺ 365.2301, found 365.2301. Major diastereomer: ¹H NMR (500 MHz, CDCl₃) δ 7.44 (m, 1H), 7.26 (m, 9H), 3.12 (dd, *J* = 13.9, 4.1, 1H), 2.82 (dd, *J* = 13.9, 11.7, 1H), 2.63 (dd, *J* = 13.4, 6.9, 1H), 1.89 (m, 2H), 1.54 (s, 3H), 1.22 (s, 9H), 0.81 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 151.0, 143.2, 128.4, 128.3, 127.8, 126.3, 125.8, 125.5, 81.4, 45.2, 36.4, 34.3, 28.8, 28.6, 25.9, 25.7, 20.4. Minor diastereomer: ¹H NMR (500 MHz, CDCl₃) δ 7.44 (m, 1H), 7.26 (m, 9H), 3.17 (dd, *J* = 13.6, 2.9, 1H), 2.74 (m, 1H), 2.33 (m, 1H), 1.84 (m, 1H), 1.70 (m, 1H), 1.41 (s, 3H), 1.20 (s, 9H), 1.10 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 147.9, 143.0, 128.4, 128.2, 127.7, 127.6, 125.9, 124.3, 81.6, 42.2, 36.2, 32.3, 26.7, 28.3, 25.7, 22.0, 21.9.

Oxasilacyclopentane (16). To a suspension of silver triflate (0.0002 g, 7 x 10⁻⁴ mmol) in CH₂Cl₂ (4 mL), inside the glove box, was added 1-hexene (0.020 ml, 0.161 mmol). A solution of **1** (0.016 g, 0.071 mmol) in CH₂Cl₂ (1 mL) was then added and the reaction mixture was stirred at room temperature for two hours. The reaction mixture was then filtered through an HPLC filter, and the filtrate was cooled to –20 °C. Butyraldehyde was then added (0.02 ml, 0.22 mmol) followed by zinc bromide (0.005 g, 0.022 mmol), and the mixture was left at –20 °C for 6 h, and then rapidly warmed to room temperature. The mixture was stirred for an additional 4 h and then taken outside of the glove box. The mixture was diluted with CH₂Cl₂ (5 mL) and washed with brine (5 mL). The water layer was extracted with CH₂Cl₂ (5 mL). The combined organic phases were filtered through a cotton plug and concentrated to afford the product as a 39:61 mixture of diastereomers as determined by GC analysis. Purification by flash chromatography (pentane) afforded the product as a colorless oil (0.017 g, 79%). Major diastereomer: ¹H NMR (500 MHz, CDCl₃) δ 4.11 (qd, *J* = 6.9, 2.1, 1H), 1.85 (ddd, *J* = 12.8, 8.5, 2.4, 1H), 1.67 (ddd, *J* = 12.8, 11.8, 7.4, 1H), 1.67 (m, 1H), 1.48 (m, 2H), 1.72 (m, 8H), 1.04 (s, 9H), 1.03 (s, 9H), 0.91 (t, *J* = 7.2, 3H), 0.90 (t, *J* = 7.1, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 76.7, 40.5, 37.6, 33.6, 30.2, 28.6, 28.4, 22.8, 22.1, 21.9, 19.9, 19.5, 14.2, 14.1; IR (thin film) 2958, 2929, 2857, 1468, 1014, 822 cm⁻¹; HRMS (CI/isobutene) *m/z* calcd

for $C_{18}H_{37}OSi$ ($M - H$)⁺ 297.2613, found 297.2616. Minor diastereomer: ¹H NMR (400 MHz, CDCl₃) δ 3.76 (m, 1H), 2.13 (ddd, $J = 12.1, 7.2, 4.1$, 1H), 1.67 (m, 2H), 1.40 (m, 8H), 1.14 (m, 2H), 1.03 (s, 9H), 1.02 (s, 9H), 0.92 (t, $J = 7.2$, 3H), 0.90 (t, $J = 7.0$, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 77.6, 40.1, 39.8, 33.6, 30.1, 28.2, 28.1, 25.0, 22.7, 21.3, 21.1, 19.0, 14.3, 14.1; IR (thin film) 2930, 2857, 1470, 1386, 1384, 1014 cm⁻¹; HRMS (CI/isobutene) m/z calcd for $C_{18}H_{37}OSi$ ($M - H$)⁺ 297.2613, found 297.2618. Anal. Calcd for $C_{18}H_{38}OSi$: C, 72.41; H, 12.83. Found C, 72.21; H, 12.97.

Oxasilacyclopentane (17a). To a cooled (−20 °C) suspension of AgOC(O)CF₃ (0.0002 g, 9 × 10⁻⁴ mmol) in CH₂Cl₂ (4 mL), inside the glove box, was added 1-hexene (0.020 mL, 0.160 mmol). A solution of cyclohexene silacyclopropane **1** (0.025 g, 0.111 mmol) in CH₂Cl₂ (2 mL) was then added and the reaction mixture was stirred for 2 h. Cinnamaldehyde (0.030 mL, 0.229 mmol) was then added followed by CuI (0.006 g, 0.035 mmol). The reaction mixture was left at −20 °C for 6 h, and then rapidly warmed up to room temperature. The mixture was then stirred for an additional 4 h and then was taken outside of the glove box. The mixture was then diluted with CH₂Cl₂ (5 mL) and washed with brine (5 mL). The water layer was then extracted with CH₂Cl₂ (5 mL). The combined organic extracts were filtered through a cotton plug and concentrated to afford the product as a 96:4 mixture of regioisomers and an 82:18 mixture of diastereomers (as determined by GC analysis). Purification by flash chromatography (pentane:EtOAc = 99:1) afforded the product as a colorless oil (0.034 g, 85%): ¹H NMR (400 MHz, CDCl₃) δ 7.41 (m, 2H), 7.32 (m, 2H), 7.22 (m, 1H), 6.61 (d, $J = 15.8$, 1H), 6.19, (dd, $J = 15.8, 7.2$, 1H), 3.97 (dd, $J = 9.7, 7.2$, 1H), 1.69 (m, 1H), 1.58 (m, 1H), 1.46 (m, 2H), 1.29 (m, 4H), 1.07 (s, 9H), 1.06 (s, 9H), 0.89 (t, $J = 7.2$, 3H), 0.47 (dd, $J = 14.7, 11.8$, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 137.1, 131.8, 130.8, 128.4, 127.3, 126.5, 85.2, 45.4, 33.8, 30.2, 27.7, 27.6, 22.8, 20.6, 19.9, 14.1, 13.0; IR (thin film) 3082, 3027, 2928, 1473, 1364, 991 cm⁻¹; HRMS (CI) m/z calcd for $C_{23}H_{38}OSi$ (M)⁺ 358.2692, found 358.2690.

Oxasilacyclopentane (17b). The procedure for **17a** was followed using 0.018 g of cyclohexene silacyclopropane **1** (0.080 mmol), 0.020 mL of 1-hexene (0.161 mmol), 0.0001 g of AgOC(O)CF₃ (4 × 10⁻⁴ mmol), 0.020 mL of cinnamaldehyde (0.153 mmol), and 0.005 g of ZnI₂ (0.015 mmol) to give product **17b** as a 73:27 mixture of diastereomers. Purification by flash chromatography (pentane:EtOAc = 99:1) yielded the product as a colorless oil (0.027 g, 92%): IR (thin film) 3060, 3026, 2857, 1473, 1364, 963 cm⁻¹; HRMS (CI/isobutane) m/z calcd for $C_{23}H_{38}OSi$ (M)⁺ 358.2692, found 358.2688. Selected data for major diastereomer: ¹H NMR (400 MHz, CDCl₃) δ 7.32 (m, 5H), 6.59 (d, $J = 15.8$, 1H), 6.28 (dd, $J = 15.8, 6.6$, 1H), 4.84 (td, $J = 6.6, 1.9$, 1H), 2.12 (ddd, $J = 13.1, 8.4, 3.0$, 1H), 2.03 (ddd, $J = 13.1, 11.3, 7.6$, 1H), 1.76 (m, 2H), 1.59 (m,

2H), 1.14 (s, 9H), 1.12 (s, 9H), 0.92, (t, $J = 7.0$, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.1, 133.1, 129.2, 128.5, 127.3, 126.4, 78.4, 40.6, 38.4, 33.6, 30.1, 28.7, 28.6, 22.8, 22.4, 20.1, 14.1. Selected data for minor diastereomer: ^1H NMR (400 MHz, CDCl_3) δ 7.32 (m, 5H), 6.66 (d, $J = 15.8$, 1H), 6.29 (dd, $J = 15.8$, 6.2, 1H), 4.46 (m, 1H), 2.27 (m, 1H), 1.13 (s, 9H), 1.11 (s, 9H), 0.95 (t, $J = 6.9$, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 132.4, 129.0, 128.4, 127.2, 126.4, 77.4, 33.4, 29.9, 28.2, 25.1, 22.7, 22.2, 21.4, 21.1.

Acetate (18). To a cooled ($-20\text{ }^\circ\text{C}$) solution of **3** (0.038 g, 0.192 mmol) in CH_2Cl_2 (4 mL), inside the glove box, was added a cold ($-20\text{ }^\circ\text{C}$) solution of *N*-benzyl-*N*-methylformamide (0.051 g, 0.342 mmol) followed by CuI (0.014 g, 0.074 mmol) and the mixture was left at $-20\text{ }^\circ\text{C}$ for six hours. The mixture was then rapidly warmed to room temperature and stirred for an additional 2 h after which it was taken outside the glove box. The reagents were then quenched with 2:1 mixture of MeOH: Et_3N (4 mL) and the mixture was concentrated. The residue was diluted with hexanes: Et_3N = 95:5 (15 mL) and washed with water once. Water layer was extracted with hexanes: Et_3N = 95:5 mixture (2×10 mL). The combined organic extracts were filtered through a cotton plug and concentrated. The residue was dissolved in 5 mL of THF and cooled to $0\text{ }^\circ\text{C}$. The solution of CuSO_4 (2.50 mL of 0.1 M solution, 0.25 mmol) was added dropwise and the mixture was allowed to reach room temperature overnight. The reaction mixture was then diluted with MTBE (15 mL) and washed with water once (10 mL). The water layer was extracted with MTBE (3×10 mL). The combined organic extracts were concentrated *in vacuo* and the resultant oil was redissolved in CH_2Cl_2 , filtered through cotton plug, and concentrated. The resulting mixture of **s-3** and **s-4** was dissolved in CH_2Cl_2 (10 mL), Et_3N (0.57 mL, 4.14 mmol) was added, followed by acetic anhydride (0.18 mL, 1.91 mmol), and a few crystals of DMAP. The reaction mixture was left stirring at ambient temperature overnight and then concentrated *in vacuo*. Purification by flash chromatography (pentane: EtOAc = 100:0 – 98:2) afforded **18** as a colorless oil (0.049 g, 90% over three steps). The characterization data match the previously reported spectra of this compound.⁴

Oxasilacyclopentane hemiacetal (19). To a cooled ($-20\text{ }^\circ\text{C}$) solution of **4** (0.053 g, 0.267 mmol) in CH_2Cl_2 (3 mL), inside the glove box, was added a cold ($-20\text{ }^\circ\text{C}$) solution of *N*-benzyl-*N*-methylformamide (0.056 g, 0.375 mmol) followed by CuI (0.016 g, 0.084 mmol) and the mixture was left at $-20\text{ }^\circ\text{C}$ for six hours. The mixture was then rapidly warmed to room temperature and stirred for an additional 2 h and then taken outside the glove box. The reagents were quenched with 2:1 mixture of MeOH: Et_3N (4 mL) and the mixture was concentrated. The residue was diluted with hexanes: Et_3N = 95:5 (15 mL)

and washed with water once. Water layer was extracted with hexanes:Et₃N = 95:5 mixture (2 x 10 mL). The combined organic extracts were filtered through a cotton plug and concentrated. The residue was dissolved in 5 mL of THF and cooled to 0 °C. The solution of CuSO₄ (2.50 mL of 0.1 M solution, 0.25 mmol) was added dropwise and the mixture was allowed to reach room temperature overnight. The reaction mixture was then diluted with MTBE (15 mL) and washed with water once (10 mL). The water layer was extracted with MTBE (3 x 10 mL). The combined organic extracts were concentrated *in vacuo* and the resultant oil was redissolved in CH₂Cl₂, filtered through cotton plug, and concentrated. Purification by flash chromatography (pentane:EtOAc = 95:5 – 90:10) yielded the resultant hemiacetal as a 79:21 mixture of epimers, as determined by ¹H NMR spectroscopy (0.059 g, 91%): IR (thin film) 2929, 1123, 1050, 1019, 991, 903 cm⁻¹; HRMS (CI/isobutene) *m/z* calcd for C₁₃H₂₈O₂Si (M)⁺ 244.1858, found 244.1860. Anal. Calcd for C₁₃H₂₈O₂Si: C, 63.87; H, 11.55. Found C, 63.93; H, 11.57. Major epimer: ¹H NMR (500 MHz, CDCl₃) δ 4.79 (dd, *J* = 7.5, 5.1, 1H), 3.83 (d, *J* = 5.1, 1H), 1.48 (dq, *J* = 3.6, 7.5, 6.5, 1H), 1.12 (d, *J* = 7.5, 3H), 1.01 (s, 9H), 0.99 (d, *J* = 6.5, 3H), 0.95 (s, 9H), 0.88 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 102.9, 48.1, 27.83, 28.81, 23.8, 21.0, 20.7, 15.5, 12.8; Selected data for minor epimer: ¹H NMR (500 MHz, CDCl₃) δ 5.34 (m, 1H), 3.03 (d, *J* = 2.5, 1H), 1.78 (m, 1H), 1.00 (s, 9H), 0.98 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 98.6, 45.0, 28.5, 21.5, 20.1, 19.8, 13.6, 12.4.

Hemiacetal (21a) and aldehyde (21b). To a suspension of AgOC(O)CF₃ (0.0002 g, 8 x 10⁻⁴ mmol) in toluene (2 mL), inside the glove box, was added **5** (0.066 g, 0.242 mmol). A solution of **1** (0.044 g, 0.196 mmol) in toluene (1 mL) was then added and the reaction mixture was stirred for 5 h. The reaction mixture was then filtered through an HPLC filter and cooled to -20 °C. A cooled (-20 °C) solution of *N*-benzyl-*N*-methyl formamide (0.035 g, 0.23 mmol) was then added followed by CuI (0.009 mg, 0.047 mmol), and the mixture was left at -20 °C for 4 h. The mixture was then rapidly warmed to room temperature and left stirring overnight. The reaction mixture was then taken outside of the glove box. The reagents were quenched with a 2:1 mixture of MeOH:Et₃N (1 mL) and the mixture was concentrated. The residue was diluted with hexanes:Et₃N = 95:5 (10 mL) and washed with water (5 mL). The water layer was extracted with hexanes:Et₃N = 95:5 mixture (2 x 10 mL). The combined organic phases were filtered through a cotton plug and concentrated. The residue was dissolved in 10 mL of THF and cooled to 0 °C. A solution of CuSO₄ (1.50 mL of 0.1 M solution, 0.15 mmol) was added dropwise and the mixture was allowed to reach room temperature overnight. The reaction mixture was then diluted with MTBE (15 mL) and washed with water (10 mL). The water layer was extracted with MTBE (3 x 10 mL). The combined organic extracts were concentrated *in vacuo* and the resultant oil was redissolved in CH₂Cl₂, filtered through cotton plug, and concentrated. Purification by flash chromatography (pentane:EtOAc = 100:0 – 96:4) yielded the products **21a** (d.r. = 9:91) and **21b** as a 83:17 mixture of compounds. The spectral data for these compounds match the already reported values.⁵

IV. Construction of 1,3-diols from oxasilacyclopentanes

Diol (21). To a cooled ($-78\text{ }^{\circ}\text{C}$) solution of **18** (1.500 g, 5.236 mmol) in CH_2Cl_2 (58 mL) was added SnBr_4 (5.20 mL of a 1.0 M solution in CH_2Cl_2 , 0.05 mmol), followed by (*Z*)-1-ethyl-1-trimethylsilyloxypropene (4.930 g, 31.141 mmol). After stirring for 15 min, the reaction mixture was poured into 150 mL of saturated aqueous NaHCO_3 and diluted with 100 mL of CH_2Cl_2 , and the layers were separated. The aqueous layer was extracted with $3 \times 50\text{ mL}$ of CH_2Cl_2 . The combined organic extracts were washed with brine, filtered through a cotton plug, and concentrated *in vacuo*. Purification by flash chromatography (hexanes:EtOAc = 99:1) afforded **20** as a colorless oil (1.555 g, 95%), as a 90:9:1 mixture of diastereomers: ^1H NMR (400 MHz, CDCl_3) δ 3.87 (dd, $J = 10.4, 2.8, 1\text{H}$), 2.57 (q, $J = 7.2, 2\text{H}$), 2.50 (dq, $J = 7.0, 2.8, 1\text{H}$), 2.03–1.97, (m, 1H), 1.42 (quintet, $J = 8.0, 1\text{H}$), 1.08 (d, $J = 7.0, 3\text{H}$), 1.10, (d, $J = 8.0, 3\text{H}$), 1.06 (t, $J = 7.2, 3\text{H}$), 1.05 (s, 9H), 0.99 (s, 9H), 0.89 (d, $J = 7.2, 3\text{H}$); ^{13}C NMR (125 MHz, CDCl_3) δ 214.0, 81.1, 49.3, 38.6, 33.2, 28.6, 28.1, 22.1, 20.6, 19.8, 12.4, 10.8, 8.4, 7.9; IR (thin film) 2967, 2861, 1710, 1468, 1384 cm^{-1} ; HRMS (CI/isobutane) m/z calcd for $\text{C}_{18}\text{H}_{37}\text{O}_2\text{Si}$ ($\text{M}+\text{H}$) $^+$ 313.2563, found 313.2568. Anal. Calcd for $\text{C}_{18}\text{H}_{36}\text{O}_2\text{Si}$: C, 69.17; H, 11.61. Found C, 69.42; H, 11.70. The stereochemistry of the major isomer has been reported⁶

To a cooled ($0\text{ }^{\circ}\text{C}$) suspension of triphenylmethylphosphonium bromide (0.058 g, 0.162 mmol) in THF (0.38 mL) was added *n*-BuLi (0.064 mL of 2.2 M solution in hexanes). After 15 minutes, the yellow mixture was cooled to $-78\text{ }^{\circ}\text{C}$ and ketone **20** (0.022 g, 0.070 mmol) was added as a solution in THF (0.90 mL). The solution was allowed to warm to room temperature and then heated to reflux for 6 h. The mixture was cooled to room temperature, quenched with 0.10 mL of methanol, and suspended in 20 mL of pentane. The resulting suspension was filtered through silica gel and concentrated *in vacuo*. Purification by flash chromatography (hexanes) yielded the product **s-5** as a colorless oil (0.016 g, 73%): ^1H NMR (500 MHz, CDCl_3) δ 4.93 (bs, 1H), 4.74 (bs, 1H), 3.54 (dd, $J = 10.1, 2.3, 1\text{H}$), 2.23 (dq, $J = 6.9, 2.2, 1\text{H}$), 2.12 (m, 2H), 1.97 (dq, $J = 10.1, 8.2, 7.0, 1\text{H}$), 1.40 (quintet, $J = 8.2, 1\text{H}$), 1.06 (s, 9H and m, 3H), 1.04 (t, $J = 7.4, 3\text{H}$), 1.02 (d, $J = 6.9, 3\text{H}$), 1.00 (s, 9H), 0.88 (d, $J = 7.0, 3\text{H}$); ^{13}C NMR (125 MHz, CDCl_3) δ 156.0, 107.3, 83.8, 42.3, 39.1, 29.9, 28.9, 28.4, 27.3, 22.3, 20.8, 20.2, 13.3, 12.8, 11.2 IR (thin film): 3083, 2964, 1468, 1386 cm^{-1} ; HRMS (CI/isobutane) m/z calcd for $\text{C}_{19}\text{H}_{39}\text{OSi}$ ($\text{M}+\text{H}$) $^+$ 311.2770, found 311.2770. Anal. Calcd for $\text{C}_{19}\text{H}_{38}\text{OSi}$: C, 73.47; H, 12.33. Found C, 73.33; H 12.20.

To a cooled ($0\text{ }^{\circ}\text{C}$) suspension of KH (0.017 g, 0.424 mmol) in 0.35 mL of NMP was added *tert*-butylhydroperoxide (0.055 mL of 70% aqueous solution, 0.427 mmol) dropwise. After the solution was warmed to $25\text{ }^{\circ}\text{C}$, the solution of oxasilacyclopentane **s-5** (0.044 g, 0.143 mmol) in 0.80 mL of NMP was added. After stirring for 5 min, CsF (0.221 g, 1.454 mmol) was added, followed by TBAF (0.010 mL of 1.0 M solution in THF, 0.010 mmol). The reaction mixture was heated at $40\text{ }^{\circ}\text{C}$ for 6 h. After the mixture was cooled to $25\text{ }^{\circ}\text{C}$, a solution of $\text{Na}_2\text{S}_2\text{O}_3$ (3.0 mL of 1.3 M solution, 3.9 mmol) was

added and the mixture was stirred for 1 h. The mixture was then washed with 4×10 mL of MTBE. The combined organic extracts were washed with 5×10 mL water, dried over Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography (hexanes:EtOAc = 91:9 – 84:16) afforded the product **21** as colorless oil (0.024 g, 90%): ^1H NMR (500 MHz, CDCl_3) δ 4.94 (m, 1H), 4.84 (bs, 1H), 4.06 (d quintet, $J = 6.6, 2.3$, 1H), 3.56 (ddd, $J = 7.8, 4.4, 2.3$, 1H), 3.05 (d, $J = 6.7$, 1H), 2.37 (dq, $J = 6.9, 4.4$, 1H), 2.27 (d, $J = 2.3$, 1H), 2.16-1.94 (m, 2H), 1.80 (d quintet, $J = 7.2, 2.3$, 1H), 1.18 (d, $J = 6.6$, 3H), 1.06 (t, $J = 7.4$, 3H), 1.05 (d, $J = 6.9$, 3H), 0.88 (d, $J = 7.1$, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 153.9, 109.4, 74.5, 69.8, 41.9, 39.4, 28.0, 19.0, 12.4, 12.3, 12.0; IR (thin film) 3355, 3083, 2969, 1642, 1459, 1112 cm^{-1} ; HRMS (CI/isobutane) m/z calcd for $\text{C}_{11}\text{H}_{21}\text{O}_2$ (M-H) $^+$ 185.1541, found 185.1543. Anal. Calcd for $\text{C}_{11}\text{H}_{22}\text{O}_2$: C, 70.92; H, 11.90. Found C, 70.68; H, 12.08.

IV. References

- (1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.
- (2) Cirakovic, J.; Driver, T. G.; Woerpel, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 9370-9371.
- (3) Boudjouk, P.; Samaraweera, U.; Sooriyakumaran, R.; Chrusciel, J.; Anderson, K. R. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1355-1356.
- (4) Nguyen, P. T.; Palmer, W. S.; Woerpel, K. A. *J. Org. Chem.* **1999**, *64*, 1843-1848.
- (5) Driver, T. G.; Franz, A. K.; Woerpel, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 6524-6525.
- (6) Bear, T. J.; Shaw, J. T.; Woerpel, K. A. *J. Org. Chem.* **2002**, *67*, 2056-2064.

jc-VI-68-3-1
¹H spectrum

jc-VI-68-3-1
13C spectrum with 1H decoupling

jc-VI-71-2-1
1H spectrum

jc-VI-71-2-1
¹³C spectrum with ¹H decoupling

jc-VI-123-1
1H spectrum

jc-VI-72-2-1
13C spectrum with 1H decoupling

jc-VI-137
1H spectrum

jc-VI-137
1H spectrum

jc-VI-137

jC-VI-80-1
1H spectrum

ic-VI-80-2
¹³C spectrum with ¹H decoupling

jc-VI-90-1
1H spectrum

jc-VI-90-1
¹³C spectrum with ¹H decoupling

n-bu silirane
1H spectrum

JC-VI-77-1
¹³C spectrum with ¹H decoupling

JC-V-187-2-2

JC-V-187-2-2 (exp 3)

¹³C spectrum with ¹H decoupling

TD-VII-138F1
1H spectrum

10-VII-138F1
13C spectrum with 1H decoupling

1D-VII-163F1
1H spectrum

¹³C spectrum with ¹H decoupling

TD-VII-156F1
1H spectrum

TD-VII-156f1
¹³C spectrum with ¹H decoupling

TD-VII-150F1
1H spectrum

¹³C spectrum with ¹H decoupling

jc-V-193-2-2
1H spectrum

jc-V-193-2-2
¹³C spectrum with ¹H decoupling

Current Data Parameters
 USER jc-V-193-2-2
 NAME jc-V-193-2-2
 EXPNO 2
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20051005
 Time_ 14.00
 INSTRUM omegasp500
 PROBHD 5 mm broadband
 PULPROG zgpg30
 PROCES 200536
 FIDRES 0.000133
 SFO1 500.136113 MHz
 NS 1500
 DS 2
 SWH 30303.361 Hz
 FIDRES 0.452388 Hz
 AQ 1.0013040 sec
 RG 6502
 DD 19.300 usec
 DE 1.000000 usec
 TE 300.0 K
 D1 0.25000000 sec
 D11 0.03000000 sec
 ----- CHANNEL f1 -----
 NU1 13C
 P1 29.00 usec
 PL1 -8.00 dB
 SFO1 125.760406 MHz
 ----- CHANNEL f2 -----
 CPDPRG2 waltz16
 NU2 1H
 P2 120.00 usec
 PL2 0.00 dB
 PL12 120.00 dB
 PL12 14.40 dB
 SFO2 500.2536013 MHz
 F2 - Processing parameters
 SI 65536
 SF 125.760406 MHz
 DS 2
 SW 30303.361 Hz
 LB 3.00 Hz
 GB 0
 PC 2.00
 10 NMR data parameters
 CX 22.80 cm
 FIP 230.005 ppm
 F1 125.760406 MHz
 F2 500.253601 MHz
 F3 -1372.96 Hz
 PPMCH 10.50607 ppm/cm
 HZCH 1329.08032 Hz/cm

jc-V-193-2-1
 13C spectrum with 1H decoupling

jc-VI-133-2-1
1H spectrum

jc-VI-133-2-1
¹³C spectrum with ¹H decoupling

File C:\HPCHEM\1\DATA\JELENA\DSII33.D

Sample Name: jc-VI-22-1

=====

Injection Date : 1/16/2003 10:37:27 AM
 Sample Name : jc-VI-22-1
 Acq. Operator : jelena
 Location : Vial 18
 Inj : 1
 Inj Volume : 1 µl

Acq. Method : C:\HPCHEM\1\METHODS\JELENA.M
 Last changed : 10/22/2002 8:52:13 AM by jelena
 Analysis Method : C:\HPCHEM\1\METHODS\JELENA.M
 Last changed : 1/16/2003 10:57:13 AM by jelena
 (modified after loading)

jc-v-5-4-1
1H spectrum

jc-V-5-4-1
13C spectrum with 1H decoupling

Data File C:\HPCHEM\1\DATA\JELENA\JCVI147.D

Sample Name: jc-VI-147-1

```

=====
Injection Date   : 8/22/2003 10:04:04 AM      Seq. Line :    2
Sample Name     : jc-VI-147-1                Location  : Vial 25
Acq. Operator   : jelena                     Inj       :    1
                                           Inj Volume: 1 µl

Sequence File   : C:\HPCHEM\1\SEQUENCE\SBB_GC.S
Method          : C:\HPCHEM\1\METHODS\JELENA.M
Last changed    : 2/12/2003 6:26:09 PM by jelena
=====

```

```

=====
Area Percent Report
=====

```

```

Sorted By      : Signal
Calib. Data Modified : Thursday, May 16, 2002 3:24:15 PM
Multiplier     : 1.0000
Dilution       : 1.0000

```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
1	0.790		0.0000	0.00000	0.00000	
2	0.855		0.0000	0.00000	0.00000	
3	1.405	VV	0.0127	226.08527	32.82365 ?	
4	6.940	VP	0.0276	9.34816	1.35719 ?	
5	10.014	VV	0.0255	333.32144	48.39247 ?	
6	10.122	VB	0.0263	120.03291	17.42669 ?	

Totals : 688.78778

Results obtained with enhanced integrator!
2 Warnings or Errors :

Warning : Calibration warnings (see calibration table listing)
Warning : Calibrated compound(s) not found

jc-vl-38-2-1
1H spectrum

jc-VI-38-2-1
¹³C spectrum with ¹H decoupling

jc-I-31-p, 400 MHz, CDCl₃, Proton

jc-I-158-2, CDCl₃, 500 MHz, ethyl ketone
¹³C spectrum with ¹H decoupling

5s

jc-I-181-2b, 125 MHz, 6N, Wittig product, CDCl₃,
 13C spectrum with 1H decoupling

CC(C)(O)C(C)(O)C(C)(O)C(C)C

jc-II-24-22, 125 MHz, CDCl₃, new diol,
13C spectrum with 1H decoupling

21