Silylene Transfer to Carbonyl Compounds and Subsequent Ireland-Claisen Rearrangements to Control Formation of Quaternary Carbon Stereocenters

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Supporting Information

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Experimental Section

General. Melting points were obtained using a Büchi 510 melting point apparatus and are reported uncorrected. Analytical gas chromatography (GC) was performed using an Agilent 6850 series chromatograph, equipped with an Agilent 6850 auto sampler and a flame ionization detector. A fused silica capillary column (30 m x 0.32 mm x 0.25 μ m) wall-coated with HP-1 (J & W Scientific) was used with helium as the carrier gas. 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 reagents silica gel (SiO₂) 60 (230–400) mesh or on Aldrich DavaSil[®] silica gel (SiO₂) as indicated. ¹H NMR and ¹³C NMR spectra were recorded at 25 °C at 400 and 100, and 500 and 125 MHz, respectively, using Bruker DRX 400 or DRX 500 spectrometers, as indicated. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet), coupling constants (Hz), and integration. The ²⁹Si NMR chemical shifts are reported in ppm from tetramethylsilane on the δ scale, using tetramethylsilane as an external standard. 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 Microlabs, Atlanta, GA or Desert Analytics, Tucson, AZ. Silacyclopropanes and oxasilacyclopentenes (where indicated) were stored and manipulated in an Innovative Technologies nitrogen-atmosphere dry box. All reactions were performed under an atmosphere of nitrogen or Argon in glassware that had been flame-dried under a stream of nitrogen or under vacuum. Solvents were distilled or filtered before use. Cyclohexenesilacyclopropane (**2**) was constructed by known methods.^{1,2}

I. Silver-catalyzed Silylene Transfer to Esters and Ketones

Isobutyric Acid But-3-enyl Ester (1).³

To a cooled solution (0 °C) of 4-(dimethylamino)pyridine (0.0190 g, 0.155 mmol) in 4 mL of pyridine was added 3-buten-1-ol (0.735 mL, 8.54 mmol). Isobutyryl chloride (0.980 mL, 9.39 mmol) was added dropwise to the stirred solution. After 6.5 h, the white opaque mixture was poured into 50 mL of H₂O and the aqueous layer was extracted with 2 × 50 mL of Et₂O. The combined organic layers were washed with 2 × 50 mL of saturated NH₄Cl, 2 × 50 mL of H₂O, and 50 mL of brine. The resulting organic phase was dried (MgSO₄), filtered, and concentrated *in vacuo*. Purification by flash chromatography (20:1 pentane:Et₂O) afforded the product as a clear oil (0.885 g, 73%): ¹H NMR (CDCl₃, 500 MHz) δ 5.80 (tdd, *J* = 6.8, 10.3, 17.1, 1H), 5.12 (qd, *J* = 1.6, 17.2, 1H), 5.08 (qd, *J* = 1.2, 10.2, 1H), 4.13 (t, *J* = 6.7, 2H), 2.54 (septet, *J* = 7.0, 1H), 2.40 (td, *J* = 1.4, 6.7, 1H), 2.37 (td, *J* = 1.4, 6.7, 1H), 1.17 (d, *J* = 7.0, 6H); ¹³C NMR (CDCl₃, 125 MHz) δ 177.3, 134.3, 117.3, 63.4, 34.2, 33.3, 19.2; IR (thin film) 3082, 2976, 1737, 1193, 1158 cm⁻¹; HRMS (EI) *m/z* calcd for C₈H₁₄O₂ (M⁺) 142.0994, found 142.0992.

Vinyl Silanol (3). To a solution of AgOCOCF₃ (0.001 g, 0.005 mmol) in 0.35 mL of toluene was added isobutyrate **1** (0.143 g, 1.00 mmol) in 2.0 mL of toluene followed by cyclohexene silacyclopropane **2** (0.240 g, 1.07 mmol) in 2.0 mL of toluene. After 1.5 h, the mixture was poured into 30 mL of NaHCO₃ (saturated, aq) and the aqueous layer was extracted with 3 × 20 mL of CH₂Cl₂. The combined organic layers were washed with 30 mL of brine, dried (NaSO₄), filtered, and concentrated *in vacuo*. Flash chromatography (3:97 Et₂O: pentane) afforded the product (0.128 g, 45%): ¹H NMR (CDCl₃, 500 MHz) δ 5.75-5.84 (tdd, *J* = 7.0, 10.1, 17.2, 1H), 5.06 (d, *J* = 17.3, 1H), 5.02 (d, *J* = 10.2, 1H), 3.47 (t, *J* = 6.5, 2H), 2.30 (m, 2H), 1.68 (s, 3H), 1.66 (s, 3H), 0.96 (s, 18H); ¹³C NMR (CDCl₃, 125 MHz) δ 151.8, 136.2, 135.5, 117.6, 70.5, 35.0, 28.5, 22.2, 21.2, 18.5; IR (thin film) 3520, 2933, 2858, 1473, 1095, 823 cm⁻¹; HRMS (CI) *m/z* calcd for C₁₆H₃₃O₂Si (M+H)⁺ 285.2251, found 285.2249. Anal. Calcd for C₁₆H₃₂O₂Si: C, 67.54; H, 11.34. Found: C, 67.58; H, 11.60.

Oxasilacyclopentene (7a).**Representative procedure for silver-catalyzed silylene transfer to α,β-unsaturated esters:**

To a solution of AgOCOCF₃ (0.003 g, 0.01 mmol) in 0.4 mL of a 0.0436 M solution of PhSi(CH₃)₃ in C₆D₆ (contained in an NMR tube) was added benzyl acrylate (0.039 g, 0.27 mmol). Cyclohexene silacyclopropane **2** (0.055 g, 0.24 mmol) was added to the reaction mixture in 0.4 mL of a 0.0436 M solution of PhSi(CH₃)₃ in C₆D₆. After 20 min, ¹H NMR spectroscopy showed the disappearance of the starting silacyclopropane *t*-Bu peaks (δ 1.20 and 1.02 ppm), and the growth of peaks associated with the products: cyclohexene (δ 5.68 ppm) and the *t*-Bu peak of **7a** (δ 1.02 ppm). The yield was found to be 98% through comparison of the area of the PhSi(CH₃)₃ peak (δ 0.19 ppm) and the area of the *t*-Bu peak in the product: ¹H NMR (C₆D₆, 500 MHz) δ 7.10 (m, 5H), 4.74 (s, 2H), 4.00 (t, *J* = 2.9, 1H), 1.42 (d, *J* = 3.0, 2H), 1.02 (s, 18H); ¹³C NMR (C₆D₆, 125 MHz) δ 163.7, 137.8, 132.0, 128.9, 128.0, 70.2, 70.0, 27.2, 20.7, 7.9; ²⁹Si NMR (C₆D₆, 99.3 MHz) δ 35.7.

Procedure for isolation of oxasilacyclopentene (7a):

This procedure was conducted in a drybox. To a solution of AgOCOCF₃ (0.001 g, 0.005 mmol) in 5.0 mL of CH₂Cl₂ was added benzyl acrylate (0.348 g, 2.35 mmol) followed by cyclohexene silacyclopropane **2** (0.501 g,

2.23 mmol) in 5.0 mL of CH_2Cl_2 . After 3 h, the solution was filtered through Celite 545, rinsed with CH_2Cl_2 , and concentrated *in vacuo*. The residue was dissolved in 5 mL of hexanes and extracted with 3×3 mL of MeCN. The MeCN layers were combined and concentrated to an oily solid (0.515 g, 76%): ^1H NMR (C_6D_6 , 400 MHz) δ 7.23 (d, $J = 7.5$, 2H), 7.06 (m, 3H), 4.75 (s, 2H), 4.01 (t, $J = 3.1$, 1H), 1.43 (d, $J = 3.1$, 2H), 1.03 (s, 18H); ^{13}C NMR (C_6D_6 , 100 MHz) δ 163.7, 137.8, 128.9, 128.7, 128.0, 70.3, 70.0, 27.2, 20.7, 7.9; IR (thin film) 2933, 2859, 1636, 1140, 824 cm^{-1} ; HRMS (CI) m/z calcd for $\text{C}_{18}\text{H}_{28}\text{O}_2\text{Si}$ (M) $^+$ 304.1859, found 304.1859. Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{O}_2\text{Si}$: C, 71.00; H, 9.27. Found: C, 70.67; H, 9.11.

Oxasilacyclopentene (7b).

The representative procedure for silver-catalyzed silylene transfer to α,β -unsaturated esters was followed using AgOCOCF_3 (0.0004 g, 0.0016 mmol), benzyl methacrylate (0.0273 mL, 0.161 mmol), and **2** (0.0397 g, 0.177 mmol). The yield (NMR) was found to be 93% after 40 min: ^1H NMR (C_6D_6 , 500 MHz) δ 7.33 (d, $J = 8.1$, 2H), 7.16 (m, 3H), 4.98 (s, 2H), 1.84 (s, 2H), 1.05 (s, 3H), 1.00 (s, 18H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 155.5, 138.8, 128.8, 128.3, 128.2, 83.7, 70.2, 27.2, 20.5, 15.2, 14.1; ^{29}Si NMR (C_6D_6 , 99.3 MHz) δ 30.6.

Oxasilacyclopentene (7c).

The representative procedure for silver-catalyzed silylene transfer to α,β -unsaturated esters was followed using AgOCOCF_3 (0.0004 g, 0.0016 mmol), benzyl tiglate (0.0297 mL, 0.161 mmol), and **2** (0.0397 g, 0.177 mmol). The yield (NMR) was found to be 99% after 50 min: ^1H NMR (C_6D_6 , 500 MHz) δ 7.32 (m, 2H), 7.14 (m, 3H), 4.97 (s, 2H), 1.34 (d, $J = 6.9$, 1H), 1.18 (d, $J = 6.2$, 3H), 1.07 (s, 9H), 1.03 (s, 3H), 0.98 (s, 9H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 154.6, 134.0, 128.8, 128.3, 128.2, 88.9, 70.1, 28.4, 27.6, 22.5, 22.1, 20.9, 14.6, 10.9; ^{29}Si NMR (C_6D_6 , 99.3 MHz) δ 27.7.

Oxasilacyclopentene (7d).

The representative procedure for silver-catalyzed silylene transfer to α,β -unsaturated esters was followed using AgOCOCF_3 (0.0004 g, 0.0016 mmol), ethyl *trans*-crotonate (0.0210 mL, 0.172 mmol), and **2** (0.0385 g, 0.172 mmol). The yield (NMR) was found to be 98% after 75 min: ^1H NMR (C_6D_6 , 500 MHz) δ 3.79 (d, $J = 2.7$, 1H), 3.61 (q, $J = 7.0$, 2H), 2.16 (dq, $J = 2.7, 7.5$, 1H), 1.30 (d, $J = 7.6$, 3H), 1.13 (s, 9H), 1.05 (s, 9H), 0.99 (t, $J = 7.1$, 3H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 162.6, 77.4, 63.9, 28.3, 27.6, 25.8, 23.3, 19.0, 18.0, 15.0; ^{29}Si NMR (C_6D_6 , 99.3 MHz) δ 30.4.

Oxasilacyclopentene (7e).

To a flask containing AgOCOCF_3 (0.001 g, 0.005 mmol) was added isopropylidene phenyl ketone⁴ (0.038 g, 0.26 mmol) in 0.5 mL of toluene followed by cyclohexene silacyclopropane **2** (0.056 g, 0.25 mmol) in 0.5 mL of toluene. After 18 h, the brown solution was diluted with 1.0 mL of pentane and concentrated *in vacuo*. Column chromatography (1:99 Et_3N :pentane) afforded the product as an oil (0.051 g, 71%): ^1H NMR (CDCl_3 , 500 MHz) δ 7.51 (d, $J = 7.1$, 2H), 7.36 (t, $J = 7.4$, 2H), 7.27 (t, $J = 7.4$, 1H), 1.90 (s, 3H), 1.57 (s, 2H), 1.09 (s, 18H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 150.7, 136.1, 128.0, 127.9, 127.3, 109.8, 27.2, 20.3, 18.3, 17.7; IR (thin film) 2931, 2857, 1470, 1138, 825 cm^{-1} ; HRMS (CI) m/z calcd for $\text{C}_{18}\text{H}_{28}\text{OSi}$ (M)⁺ 288.1909, found 288.1891.

Oxasilacyclopentene (7f).

To a flask containing AgOCOCF_3 (0.001 g, 0.005 mmol) was added *trans*-4-phenyl-3-buten-2-one (0.149 g, 1.02 mmol) in 2.0 mL of CH_2Cl_2 followed by cyclohexene silacyclopropane **2** (0.236 g, 1.05 mmol) in 2.0 mL of CH_2Cl_2 . After 1.5 h, the solution was concentrated *in vacuo* and chromatographed (1:99 Et_3N :pentane) to afford the product as a colorless oil (0.149 g, 52%): ^1H NMR (CDCl_3 , 500 MHz) δ 7.21 (m, 4H), 7.08 (t, $J = 7.2$, 1H), 4.89 (m, 1H), 3.53 (m, 1H), 1.94 (dd, $J = 1.0, 2.4$, 3H), 1.15 (s, 9H), 0.75 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 157.7, 143.3, 128.2, 127.7, 124.7, 102.8, 34.2, 27.7, 27.5, 22.2, 21.2, 18.3; ^{29}Si NMR (CDCl_3 , 99.3 MHz) δ 30.7; IR (thin film): 2859, 1652, 1094, 919, 822 cm^{-1} .

Silanol (9).

To a solution of AgOCOCF_3 (0.002 g, 0.007 mmol) in 1.0 mL of toluene was added ethyl tiglate (0.061 g, 0.47 mmol) followed by cyclohexene silacyclopropane **2** (0.10 g, 0.45 mmol) in 1.0 mL of toluene. After 2 h, the mixture was poured into 30 mL of NaHCO_3 (saturated, aq) and the aqueous layer was extracted with 2×30 mL of Et_2O . The combined organic layers were washed with 30 mL of brine, dried (MgSO_4), filtered, and concentrated *in vacuo*. Column chromatography (95:5 hexanes: EtOAc) afforded the product as a clear oil (0.091 g, 70%): ^1H NMR (CDCl_3 , 500 MHz) δ 4.13 (q, $J = 7.1$, 2H), 2.68 (qd, $J = 7.0, 16.6$, 1H), 1.54 (qd, $J = 7.8, 17.3$, 1H), 1.27 (t, $J = 7.1$, 3H), 1.21 (d, $J = 7.0$, 3H), 1.15 (d, $J = 7.8$, 3H), 1.08 (s, 9H), 1.05 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 179.3, 60.6, 41.8, 28.9, 28.3, 22.1, 21.2, 21.1, 17.0, 14.3, 13.2; IR (thin film) 3507, 2934, 2861, 1732, 829 cm^{-1} ; HRMS (CI) m/z calcd for $\text{C}_{14}\text{H}_{29}\text{O}_3\text{Si}$ ($\text{M} - \text{CH}_3$)⁺ 273.1886, found 273.1885. Anal. Calcd for $\text{C}_{15}\text{H}_{32}\text{O}_3\text{Si}$: C, 62.45; H, 11.18. Found: C, 62.34; H, 11.20.

II. Ireland-Claisen Rearrangements and Utility of Products

Oxasilacyclopentane (**12**).

To an NMR tube containing AgOCOCF_3 (0.0002 g, 0.001 mmol) was added allyl methacrylate (0.022 mL, 0.16 mmol) followed by cyclohexene silacyclop propane **2** (0.148 g, 0.322 mmol) in 0.7 mL of a 0.153 M solution of $\text{PhSi}(\text{CH}_3)_3$ in C_6D_6 . After 20 min, the yield of **11** was found to be 45% and the yield of **12** was found to be 14%. The peaks associated with **11** slowly decreased as peaks associated with **12** increased. After 23 h, complete conversion of **11** to **12** was observed and the solution was filtered through Celite, rinsed with CH_2Cl_2 , and concentrated *in vacuo*. Column chromatography (100% hexanes to 97:3 hexanes:EtOAc) afforded the product as an oil (0.031 g, 72%): ^1H NMR (CDCl_3 , 500 MHz) δ 5.84 (tdd, $J = 7.3, 10.2, 17.3$, 1H), 5.15 (m, 2H), 2.47 (dd, $J = 7.2, 13.8$, 1H), 2.31 (dd, $J = 7.5, 13.8$, 1H), 1.33 (s, 3H), 1.20 (d, $J = 16.1$, 1H), 1.09 (s, 9H), 1.08 (s, 9H), 0.81 (d, $J = 16.1$, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 181.6, 133.6, 119.1, 45.2, 45.0, 27.33, 27.30, 27.0, 19.73, 19.71, 14.8; IR (thin film) 2934, 2862, 1746, 1473, 1135 cm^{-1} ; HRMS (ES) m/z calcd for $\text{C}_{15}\text{H}_{28}\text{O}_2\text{Si}$ ($\text{M} + \text{Na}$) $^+$ 291.1756, found 291.1746. Anal. Calcd for $\text{C}_{15}\text{H}_{28}\text{O}_2\text{Si}$: C, 67.11; H, 10.51. Found: C, 67.54; H, 10.94.

Silalactone (**15a**).

To a flask containing cinnamyl tiglate **13a** (0.213 g, 0.986 mmol) was added AgOCOCF_3 (0.002 g, 0.009 mmol) in 2.0 mL of benzene followed by cyclohexene silacyclop propane **2** (0.449 g, 2.00 mmol) in 2.35 mL of benzene. After 15 h, the mixture was filtered through Celite, rinsed with CHCl_3 , and concentrated *in vacuo*. Analysis of the unpurified reaction mixture by gas chromatography revealed a 97:3 ratio of stereoisomers. Column chromatography (100% hexanes to 95:5 hexanes:EtOAc) and recrystallization from hexanes afforded the product as colorless crystals (0.339 g, 96%): mp 122–125 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 500 MHz) δ 7.33 (d, $J = 7.2$, 2H), 7.25 (dd, $J = 7.5, 7.9$, 2H), 7.16 (t, $J = 7.3$, 1H), 6.33 (m, 1H), 5.19 (m, 2H), 4.00 (d, $J = 10.8$, 1H), 2.02 (q, $J = 7.8$, 1H), 1.34 (s, 3H), 1.24 (d, $J = 7.8$, 3H), 1.11 (s, 9H), 0.60 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 180.8, 141.1, 136.2, 129.8, 128.5, 127.0, 118.6, 58.6, 52.4, 28.4, 27.2, 22.6, 21.1, 20.3, 18.3, 11.7; IR (thin film) 2938, 2861, 1736, 1474, 914 cm^{-1} ; HRMS (ES) m/z calcd for $\text{C}_{22}\text{H}_{34}\text{O}_2\text{Si}$ ($\text{M} + \text{H}$) $^+$ 359.2406, found 359.2392. Anal. Calcd for $\text{C}_{22}\text{H}_{34}\text{O}_2\text{Si}$: C, 73.69; H, 9.56. Found: C, 73.41; H, 9.62.

Diol **16** was constructed in three steps from ester **13b** (Scheme S-1). Silylene transfer to the ester provided silalactone **15b** and reduction of **15b** afforded intermediate **A**. Oxidation of **A** afforded diol **16**. Experimentals for these transformations follow:

Scheme S-1

Crotyl Tiglate (13b).

To a solution of tiglic acid (3.90 g, 30.8 mmol) in CH_2Cl_2 (66.7 mL) was added 4-(dimethylamino)pyridine (0.122 g, 1.00 mmol) and crotyl alcohol (1.69 mL, 20.0 mmol), followed by *N,N'*-dicyclohexylcarbodiimide (6.19 g, 30.0 mmol). After 14 h, the precipitated urea was filtered off and the filtrate was rinsed with CH_2Cl_2 and concentrated *in vacuo*. Column chromatography (100% pentane to 97:3 pentane:Et₂O) afforded the product as a colorless oil (2.19 g, 71%): ¹H NMR (CDCl_3 , 500 MHz) δ 6.86 (qd, J = 1.4, 7.1, 1H), 5.79 (m, 1H), 5.62 (m, 1H), 4.56 (d, J = 6.4, 2H), 1.84 (s, 3H), 1.78 (dd, J = 1.0, 7.1, 3H), 1.72 (dd, J = 1.1, 6.5, 3H); ¹³C NMR (CDCl_3 , 125 MHz) δ 167.9, 137.1, 130.7, 128.7, 125.5, 65.1, 17.8, 14.3, 12.0; IR (thin film) 2921, 1708, 1653, 1251 cm^{-1} .

Silalactone (15b).

To a flask containing AgOCOCF_3 (0.002 g, 0.010 mmol) was added crotyl tiglate **13b** (0.155 g, 1.00 mmol) in 2.35 mL of toluene followed by cyclohexene silacyclopropane **2** (0.449 g, 2.00 mmol) in 2.0 mL of toluene. After 23 h, the solution was filtered over silica gel, which was rinsed with CH_2Cl_2 , and the filtrate was concentrated *in vacuo*. Analysis of the unpurified reaction mixture by gas chromatography revealed the product to be a single stereoisomer. Column chromatography (100% hexanes to 97:3 hexanes: Et₂O) afforded **15b** as colorless crystals (0.283 g, 95%): mp 74-76 °C; ¹H NMR (CDCl_3 , 400 MHz) δ 5.76 (ddd, J = 9.0, 10.6, 17.0, 1H), 5.09 (m, 2H), 2.62 (m, 1H), 1.82 (q, J = 7.8, 1H), 1.29 (s, 3H), 1.15 (m, 12H), 1.11 (s, 9H), 1.05 (d, J = 6.8, 3H); ¹³C NMR (CDCl_3 , 125 MHz) δ 181.3, 139.4, 116.6, 51.1, 48.2, 28.5, 28.3, 21.7, 21.2, 18.1, 17.2, 11.8; IR (thin film) 2939, 2862, 1745, 913, 822 cm^{-1} ; HRMS (ES) m/z calcd for $\text{C}_{17}\text{H}_{32}\text{O}_2\text{Si}$ ($M + H$)⁺ 297.2250, found 297.2254. Anal. Calcd for $\text{C}_{17}\text{H}_{32}\text{O}_2\text{Si}$: C, 68.86; H, 10.88. Found: C, 68.84; H, 11.01.

Oxasilacyclopentane (A).

To a cooled (0 °C) solution of silalactone **15b** (0.134 g, 0.453 mmol) in 2.5 mL of THF was added LiAlH_4 (0.061 g, 1.6 mmol). The cold bath was removed, a reflux condenser was affixed to the flask, and the solution

was heated to 90 °C. After 22 h, 0.060 mL of water was added, followed by 0.060 mL of NaOH (15% aq solution) and then an additional 0.180 mL of water. NaSO₄ was added to the solution, and the solution was filtered. The filter cake was rinsed with Et₂O and the filtrate was concentrated *in vacuo*. Column chromatography (97:3 hexanes:EtOAc) afforded product **A** as a colorless oil (0.12 g, 94%): ¹H NMR (CDCl₃, 500 MHz) δ 5.75 (m, 1H), 4.99 (m, 2H), 3.70 (d, *J* = 9.8, 1H), 3.61 (d, *J* = 9.8, 1H), 2.19 (m, 1H), 1.52 (q, *J* = 7.8, 1H), 1.12 (d, *J* = 7.8, 1H), 1.10 (s, 9H), 1.034 (d, *J* = 7.2, 3H), 1.027 (s, 9H); ¹³C NMR (CDCl₃, 125 MHz) δ 141.4, 114.6, 76.8, 47.5, 45.0, 28.9, 28.4, 24.5, 22.4, 21.1, 18.8, 15.9, 10.8; IR (thin film) 2934, 2859, 1472, 1031, 822 cm⁻¹; HRMS (ES) *m/z* calcd for C₁₇H₃₄OSi (M + H)⁺ 283.2457, found 283.2458. Anal. Calcd for C₁₇H₃₄O₂Si: C, 72.27; H, 12.13. Found: C, 72.18; H, 12.31.

Diol (16).

To a cooled (0 °C) solution of KH (0.048 g, 1.2 mmol) in 0.67 mL of 1-methyl-2-pyrrolidinone (NMP) was added cumene hydroperoxide (0.100 mL, 88.0% solution, 0.600 mmol). After 5 min, the cold bath was removed and substrate **A** (0.056 g, 0.20 mmol) was added in 0.67 mL of NMP and rinsed with 0.67 mL of THF. After 10 min, CsF (0.181 g, 1.20 mmol) was added. The solution was stirred at 22 °C for 6.5 h and then diluted with 5 mL of Na₂S₂O₃ (saturated, aq). This mixture was poured into 10 mL of water and extracted with 3 × 10 mL of CH₂Cl₂. The combined organic layers were washed with 4 × 5 mL of water, 10 mL of brine, dried (Na₂SO₄), filtered, and concentrated *in vacuo*. Column chromatography (80:20 to 70:30 pentane:Et₂O) afforded **16** as a colorless oil (0.029 g, 93%): ¹H NMR (CDCl₃, 500 MHz) δ 5.87 (ddd, *J* = 9.0, 10.2, 17.1, 1H), 5.10 (ddd, *J* = 0.9, 2.0, 17.1, 1H), 5.05 (dd, *J* = 2.0, 10.2, 1H), 3.93 (q, *J* = 6.2, 1H), 3.71 (d, *J* = 11.2, 1H), 3.60 (d, *J* = 11.2, 1H), 2.80 (p, *J* = 6.9, 1H), 2.74 (br s, 1H), 2.59 (br s, 1H), 1.26 (d, *J* = 6.4, 3H), 1.03 (d, *J* = 6.9, 3H), 0.63 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 141.2, 115.2, 72.7, 66.6, 42.8, 39.2, 18.3, 14.26, 14.24; IR (thin film) 3361, 2973, 2926, 1038, 915 cm⁻¹; HRMS (ES) *m/z* calcd for C₉H₁₈O₂ (M + Na)⁺ 181.1205, found 181.1200.

III. Aldol Reactions of Intermediate Oxasilacyclopentenones

Oxasilacyclopentane (17) and Silanol (18).

To a stirred solution of AgOCOCF₃ (0.002 g, 0.01 mmol) in 5.0 mL of CH₂Cl₂ was added benzyl acrylate (0.236 g, 1.46 mmol) and a solution of cyclohexene silacyclopropane **2** (0.336 g, 1.50 mmol) in 1.0 mL of CH₂Cl₂. After 1.5 h, the solution was cooled to -78 °C and benzaldehyde (0.153 mL, 1.500 mmol) was added, followed by SnCl₄ (0.150 mL of a 1.0 M solution in CH₂Cl₂). The solution was stirred for 3 h at -78 °C, then it was diluted with 30 mL of NaHCO₃ (saturated, aq) and the aqueous layer was extracted with 3 × 30 mL of CH₂Cl₂. The combined organic layers were washed with 20 mL of brine, dried (Na₂SO₄), filtered, and concentrated *in vacuo*. Analysis of the unpurified reaction mixture by gas chromatography revealed a 90:10 ratio of diastereomers. Column chromatography (10:90 EtOAc:hexanes) afforded oxasilacyclopentane **17** (0.291 g, 48%) as a mixture of diastereomers (89:11) and silanol **18** (0.626 g, 20%) as a single diastereomer.

Oxasilacyclopentane *syn*-17. ^1H NMR (CDCl_3 , 500 MHz) δ 7.32 (m, 10H), 5.48 (d, $J = 8.7$, 1H), 4.72 (d, $J = 12.1$, 1H), 4.29 (d, $J = 12.1$, 1H), 3.63 (ddd, $J = 7.1$, 8.7, 10.1, 1H), 1.56 (dd, $J = 15.0$, 7.0, 1H), 1.25 (dd, $J = 15.0$, 10.0, 1H), 1.20 (s, 9H), 1.13 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 173.9, 141.6, 135.5, 128.6, 128.5, 128.2, 128.1, 127.6, 126.9, 81.7, 66.5, 48.5, 28.5, 28.0, 21.6, 20.2, 8.8; IR (thin film) 2932, 2858, 1736, 1169, 1023, 824 cm^{-1} ; HRMS (CI) m/z calcd for $\text{C}_{25}\text{H}_{33}\text{O}_3\text{Si}$ ($\text{M} - \text{H}$) $^+$ 409.2199, found 409.2208. Anal. Calcd for $\text{C}_{25}\text{H}_{34}\text{O}_3\text{Si}$: C, 73.13; H, 8.35. Found: C, 72.91; H, 8.49.

Silanol 18. ^1H NMR (CDCl_3 , 500 MHz) δ 7.34 (m, 10H), 5.14 (s, 2H), 4.84 (d, $J = 7.3$, 1H), 3.04 (ddd, $J = 3.6$, 7.4, 10.9 1H), 2.81 (br s, 1H), 2.23 (br s, 1H), 0.99 (dd, $J = 10.9$, 15.3, 1H), 0.91 (s, 9H), 0.82 (s, 9H), 0.71 (dd, $J = 3.6$, 15.3, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 176.2, 141.8, 135.5, 128.8, 128.61, 128.58, 128.5, 128.2, 126.8, 67.0, 49.3, 27.5, 27.4, 20.7, 20.5, 9.7; IR (thin film) 3401, 2861, 1708, 1461, 1161, 820 cm^{-1} ; HRMS (CI) m/z calcd for $\text{C}_{21}\text{H}_{25}\text{O}_3\text{Si}$ ($\text{M} - \text{H}_2\text{O} - t\text{-Bu}$) $^+$ 353.1573, found 353.1581. Anal. Calcd for $\text{C}_{25}\text{H}_{36}\text{O}_4\text{Si}$: C, 70.05; H, 8.47. Found: C, 70.37; H, 8.65.

IV. Stereochemical Assignment of Aldol Products

nOe experiments:

Oxasilacyclopentene (17):

H_a irradiated: 11.7% nOe observed to **H_b**, 5.73% nOe observed to **H_c**, no nOe to **H_d**

H_b irradiated: 12.2% nOe observed to **H_a**, 5.92% nOe observed to **H_c**, no nOe to **H_d**

H_c irradiated: 2.9% nOe observed to **H_a**, 1.8% nOe observed to **H_b**

The stereochemistry of the open aldol product (**18**) is the same as the major diastereomer of the closed aldol product (**17**). Analysis by gas chromatography (GC) showed the same retention times for **18** and *syn*-**17**. High temperatures of the GC most likely caused silanol **18** to cyclize to the closed product (**17**).

To further prove that **18** and the major isomer of **17** contain the same stereochemistry, the following experiments were undertaken. Under slightly modified aldol reaction conditions, a 90:10 ratio of diastereomers was achieved. Treatment of a similar reaction mixture with $\text{BF}_3 \cdot \text{OEt}_2$ provided the open aldol product with fluorine incorporation as an 89:11 ratio of diastereomers. Treatment of the isolated compounds **17** and **18** with

$\text{BF}_3\cdot\text{OEt}_2$ afforded the same major product (**19**). Compounds *syn*-**17**, **18**, and **19** all have the same retention times by GC.

Oxasilacyclopentane (**17**) and Silanol (**18**).

To a solution of oxasilacyclopentene **7a** (0.0614 g, 0.202 mmol) in 1.0 mL of CH_2Cl_2 was added benzaldehyde (0.022 mL, 0.21 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (0.044 g, 0.21 mmol). The solution was cooled to -78°C and SnCl_4 (0.212 mL of a 1.0 M solution in CH_2Cl_2) was added dropwise. After 8 h, the mixture was poured into 20 mL of NaHCO_3 (saturated, aq) and the aqueous layer was extracted with 3×15 mL of CH_2Cl_2 . The combined organic layers were washed with 20 mL of brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Analysis of the unpurified reaction mixture by gas chromatography revealed a 90:10 ratio of diastereomers (*syn*-**17** and *syn*-**18** to *anti*-**17**). Column chromatography (5:95 to 15:85 EtOAc:hexanes) afforded oxasilacyclopentane **17** (0.0313 g, 38%) as a mixture of diastereomers and silanol **18** (0.0154 g, 18%) as a single diastereomer.

Fluorosilane (**19**).

To a solution of oxasilacyclopentene **7a** (0.0564 g, 0.185 mmol) in 0.5 mL of CH_2Cl_2 was added benzaldehyde (0.020 mL, 0.195 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (0.0400 g, 0.195 mmol). The solution was cooled to -78°C and SnCl_4 (0.195 mL of a 1.0 M solution in CH_2Cl_2) was added dropwise. After 2 h, $\text{BF}_3\cdot\text{OEt}_2$ was added to the solution. After an additional 2 h at -78°C , the mixture was poured into 20 mL of NaHCO_3 (saturated, aq) and the aqueous layer was extracted with 3×10 mL of CH_2Cl_2 . The combined organic layers were washed with 2×20 mL of H_2O , washed with 20 mL of brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Analysis of the unpurified reaction mixture by gas chromatography revealed an 89:11 ratio of diastereomers (*syn*-**19** to *anti*-**19**). Column chromatography (5:95 to 15:85 EtOAc:hexanes) afforded the product (0.0286 g, 36%): ^1H NMR (CDCl_3 , 500 MHz) δ 7.27 (m, 10H), 5.10 (d, $J = 12.3$, 1H), 5.08 (d, $J = 12.4$, 1H), 4.75 (t, $J = 6.5$, 1H), 3.05 (ddd, $J = 5.0, 6.5, 9.7$, 1H), 2.91 (d, $J = 6.6$, 1H), 1.16 (ddd, $J = 3.6, 9.7, 15.2$, 1H), 0.97 (d, $J = 1.0$, 9H), 0.91 (d, $J = 1.0$, 9H), 0.87 (m, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 175.5, 142.1, 135.8, 128.6, 128.5, 128.3, 128.2, 128.1, 126.5, 77.4, 66.7, 48.1, 27.1, 27.0, 20.6 (d, $^2J_{\text{CF}} = 12.5$), 20.4 (d, $^2J_{\text{CF}} = 12.5$), 9.7 (d, $^2J_{\text{CF}} = 12.5$); IR (thin film) 3366, 2934, 2343, 1731, 1167, 825 cm^{-1} ; HRMS (CI) m/z calcd for $\text{C}_{25}\text{H}_{35}\text{FO}_3\text{Si}$ ($\text{M} - \text{HF} - t\text{-Bu}$) $^+$ 353.1573, found 353.1578.

V. References

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VI. X-ray Crystallographic Data

A. Silalactone **15a**

X-ray Data Collection, Structure Solution and Refinement for **15a**.

A colorless crystal of approximate dimensions 0.22 x 0.37 x 0.44 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART¹ program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ program. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$ which was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵ for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (x, y, z and U_{iso}). At convergence, $wR2 = 0.0938$ and $Goof = 1.034$ for 362 variables refined against 5028 unique data. As a comparison for refinement on F , $R1 = 0.0327$ for those 4327 data with $I > 2.0\sigma(I)$.

References.

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 5. International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer Academic Publishers.
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Definitions:

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

$$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$$

Goof = S = $[\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.

15a

Table 1. Crystal data and structure refinement for **15a**.

Identification code	kaw60 (Stacie Calad)	
Empirical formula	C ₂₂ H ₃₄ O ₂ Si	
Formula weight	358.58	
Temperature	163(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	a = 10.6806(13) Å	α = 90°.
	b = 13.2710(16) Å	β = 90.257(2)°.
	c = 14.7945(18) Å	γ = 90°.
Volume	2097.0(4) Å ³	
Z	4	
Density (calculated)	1.136 Mg/m ³	
Absorption coefficient	0.124 mm ⁻¹	
F(000)	784	
Crystal size	0.44 x 0.37 x 0.22 mm ³	
Theta range for data collection	2.06 to 28.28°.	
Index ranges	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19	
Reflections collected	21777	
Independent reflections	5028 [R(int) = 0.0224]	
Completeness to theta = 28.28°	96.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9733 and 0.9475	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5028 / 0 / 362	
Goodness-of-fit on F ²	1.034	
Final R indices [I > 2σ(I); 4327 data]	R1 = 0.0327, wR2 = 0.0875	
R indices (all data)	R1 = 0.0400, wR2 = 0.0938	
Largest diff. peak and hole	0.376 and -0.218 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **15a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	3362(1)	2956(1)	1262(1)	17(1)
O(1)	2805(1)	2248(1)	2133(1)	22(1)
O(2)	1323(1)	2185(1)	3182(1)	26(1)
C(1)	1781(1)	2617(1)	2550(1)	17(1)
C(2)	1309(1)	3640(1)	2179(1)	15(1)
C(3)	2004(1)	3872(1)	1278(1)	15(1)
C(4)	2272(1)	4986(1)	1075(1)	25(1)
C(5)	1605(1)	4408(1)	2932(1)	22(1)
C(6)	-158(1)	3562(1)	2087(1)	17(1)
C(7)	-760(1)	4580(1)	1946(1)	24(1)
C(8)	-1600(1)	4970(1)	2496(1)	32(1)
C(9)	-595(1)	2808(1)	1375(1)	18(1)
C(10)	-932(1)	3101(1)	502(1)	25(1)
C(11)	-1355(1)	2407(1)	-132(1)	33(1)
C(12)	-1431(1)	1397(1)	94(1)	33(1)
C(13)	-1101(1)	1088(1)	955(1)	29(1)
C(14)	-699(1)	1786(1)	1596(1)	22(1)
C(15)	3304(1)	2177(1)	184(1)	25(1)
C(16)	4414(1)	1451(1)	61(1)	37(1)
C(17)	2099(1)	1541(1)	202(1)	35(1)
C(18)	3245(1)	2892(1)	-635(1)	32(1)
C(19)	4976(1)	3398(1)	1629(1)	24(1)
C(20)	5787(1)	2487(1)	1907(1)	37(1)
C(21)	4897(1)	4088(1)	2458(1)	35(1)
C(22)	5631(1)	3976(1)	863(1)	33(1)

Table 3. Bond lengths [Å] and angles [°] for **15a**.

Si(1)-O(1)	1.7040(8)
Si(1)-C(3)	1.8928(10)
Si(1)-C(19)	1.8976(11)
Si(1)-C(15)	1.9013(12)
O(1)-C(1)	1.3500(12)
O(2)-C(1)	1.2027(13)
C(1)-C(2)	1.5487(14)
C(2)-C(5)	1.5409(14)
C(2)-C(3)	1.5598(13)
C(2)-C(6)	1.5756(14)
C(3)-C(4)	1.5356(14)
C(6)-C(7)	1.5108(14)
C(6)-C(9)	1.5242(14)
C(7)-C(8)	1.3195(17)
C(9)-C(10)	1.3941(15)
C(9)-C(14)	1.3993(15)
C(10)-C(11)	1.3890(17)
C(11)-C(12)	1.3842(19)
C(12)-C(13)	1.3831(18)
C(13)-C(14)	1.3926(16)
C(15)-C(16)	1.5388(17)
C(15)-C(17)	1.5392(17)
C(15)-C(18)	1.5403(17)
C(19)-C(21)	1.5334(18)
C(19)-C(22)	1.5376(16)
C(19)-C(20)	1.5419(17)
O(1)-Si(1)-C(3)	94.25(4)
O(1)-Si(1)-C(19)	105.90(5)
C(3)-Si(1)-C(19)	119.55(5)
O(1)-Si(1)-C(15)	108.89(5)
C(3)-Si(1)-C(15)	109.76(5)
C(19)-Si(1)-C(15)	115.73(5)

C(1)-O(1)-Si(1)	115.64(6)
O(2)-C(1)-O(1)	121.08(9)
O(2)-C(1)-C(2)	124.10(9)
O(1)-C(1)-C(2)	114.76(8)
C(5)-C(2)-C(1)	104.98(8)
C(5)-C(2)-C(3)	112.99(8)
C(1)-C(2)-C(3)	108.67(8)
C(5)-C(2)-C(6)	107.93(8)
C(1)-C(2)-C(6)	107.13(8)
C(3)-C(2)-C(6)	114.56(8)
C(4)-C(3)-C(2)	116.55(8)
C(4)-C(3)-Si(1)	118.17(7)
C(2)-C(3)-Si(1)	104.60(6)
C(7)-C(6)-C(9)	111.32(9)
C(7)-C(6)-C(2)	112.00(8)
C(9)-C(6)-C(2)	113.91(8)
C(8)-C(7)-C(6)	123.79(12)
C(10)-C(9)-C(14)	117.86(10)
C(10)-C(9)-C(6)	122.21(9)
C(14)-C(9)-C(6)	119.90(9)
C(11)-C(10)-C(9)	121.49(11)
C(12)-C(11)-C(10)	119.89(12)
C(13)-C(12)-C(11)	119.64(11)
C(12)-C(13)-C(14)	120.48(11)
C(13)-C(14)-C(9)	120.62(10)
C(16)-C(15)-C(17)	107.64(10)
C(16)-C(15)-C(18)	108.76(10)
C(17)-C(15)-C(18)	108.64(11)
C(16)-C(15)-Si(1)	114.68(9)
C(17)-C(15)-Si(1)	107.97(8)
C(18)-C(15)-Si(1)	109.00(8)
C(21)-C(19)-C(22)	108.53(11)
C(21)-C(19)-C(20)	106.69(11)
C(22)-C(19)-C(20)	109.32(10)
C(21)-C(19)-Si(1)	111.11(8)

C(22)-C(19)-Si(1)	111.03(8)
C(20)-C(19)-Si(1)	110.05(9)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **15a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	15(1)	16(1)	18(1)	2(1)	3(1)	1(1)
O(1)	21(1)	19(1)	25(1)	7(1)	5(1)	5(1)
O(2)	24(1)	31(1)	22(1)	11(1)	3(1)	2(1)
C(1)	16(1)	20(1)	16(1)	1(1)	-2(1)	-1(1)
C(2)	15(1)	16(1)	15(1)	0(1)	0(1)	1(1)
C(3)	16(1)	16(1)	15(1)	1(1)	0(1)	-1(1)
C(4)	26(1)	17(1)	30(1)	6(1)	4(1)	0(1)
C(5)	22(1)	26(1)	19(1)	-6(1)	-1(1)	-2(1)
C(6)	15(1)	19(1)	18(1)	0(1)	1(1)	1(1)
C(7)	19(1)	21(1)	32(1)	-1(1)	-3(1)	2(1)
C(8)	23(1)	28(1)	45(1)	-10(1)	-2(1)	6(1)
C(9)	13(1)	21(1)	20(1)	0(1)	0(1)	0(1)
C(10)	26(1)	25(1)	26(1)	3(1)	-7(1)	0(1)
C(11)	37(1)	38(1)	25(1)	1(1)	-13(1)	-4(1)
C(12)	35(1)	35(1)	29(1)	-6(1)	-8(1)	-11(1)
C(13)	32(1)	24(1)	31(1)	-1(1)	-1(1)	-10(1)
C(14)	22(1)	23(1)	21(1)	3(1)	0(1)	-5(1)
C(15)	25(1)	23(1)	26(1)	-5(1)	8(1)	0(1)
C(16)	35(1)	33(1)	43(1)	-9(1)	13(1)	7(1)
C(17)	33(1)	30(1)	42(1)	-17(1)	10(1)	-8(1)
C(18)	36(1)	40(1)	21(1)	-4(1)	4(1)	0(1)
C(19)	15(1)	31(1)	26(1)	5(1)	-1(1)	0(1)
C(20)	24(1)	47(1)	42(1)	12(1)	-2(1)	10(1)
C(21)	22(1)	51(1)	32(1)	-7(1)	-6(1)	-4(1)
C(22)	21(1)	43(1)	35(1)	9(1)	0(1)	-10(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **15a**.

	x	y	z	U(eq)
H(3)	1461(12)	3612(10)	795(9)	19(3)
H(4A)	1514(15)	5383(12)	1078(10)	35(4)
H(4B)	2647(15)	5047(11)	468(11)	34(4)
H(4C)	2851(14)	5293(11)	1507(10)	32(4)
H(5A)	2507(14)	4430(11)	3066(10)	30(4)
H(5B)	1139(14)	4199(11)	3473(11)	33(4)
H(5C)	1347(13)	5095(11)	2750(10)	29(4)
H(6)	-452(12)	3319(10)	2676(9)	19(3)
H(7)	-532(14)	4950(11)	1411(11)	36(4)
H(8A)	-1958(15)	5599(13)	2374(11)	41(4)
H(8B)	-1853(15)	4590(12)	3044(11)	41(4)
H(10)	-900(14)	3808(12)	335(10)	35(4)
H(11)	-1599(16)	2639(13)	-722(12)	46(5)
H(12)	-1723(16)	923(13)	-346(12)	48(5)
H(13)	-1141(14)	376(12)	1109(10)	35(4)
H(14)	-498(13)	1571(10)	2195(9)	23(3)
H(16A)	5202(16)	1798(13)	-42(11)	42(4)
H(16B)	4513(16)	981(13)	583(12)	48(5)
H(16C)	4257(16)	1041(14)	-487(13)	52(5)
H(17A)	1327(16)	1956(12)	252(11)	40(4)
H(17B)	2026(15)	1162(13)	-351(12)	45(4)
H(17C)	2074(18)	1050(15)	712(13)	58(5)
H(18A)	3122(17)	2484(14)	-1174(13)	50(5)
H(18B)	2522(16)	3360(13)	-580(11)	43(4)
H(18C)	4020(16)	3285(13)	-720(11)	43(4)
H(20A)	5980(18)	2027(13)	1430(13)	50(5)
H(20B)	5354(17)	2074(12)	2349(12)	45(5)
H(20C)	6592(18)	2737(13)	2167(13)	52(5)
H(21A)	4401(16)	4723(13)	2324(11)	42(4)

H(21B)	4516(15)	3748(12)	2984(11)	40(4)
H(21C)	5758(17)	4282(13)	2642(12)	53(5)
H(22A)	5151(16)	4571(13)	692(12)	46(4)
H(22B)	5743(15)	3554(12)	305(12)	40(4)
H(22C)	6463(16)	4180(13)	1070(11)	45(4)

Table 6. Torsion angles [°] for **15a**.

C(3)-Si(1)-O(1)-C(1)	-6.69(8)
C(19)-Si(1)-O(1)-C(1)	115.68(8)
C(15)-Si(1)-O(1)-C(1)	-119.26(8)
Si(1)-O(1)-C(1)-O(2)	-178.84(8)
Si(1)-O(1)-C(1)-C(2)	-1.63(11)
O(2)-C(1)-C(2)-C(5)	67.30(12)
O(1)-C(1)-C(2)-C(5)	-109.82(10)
O(2)-C(1)-C(2)-C(3)	-171.56(10)
O(1)-C(1)-C(2)-C(3)	11.32(11)
O(2)-C(1)-C(2)-C(6)	-47.27(13)
O(1)-C(1)-C(2)-C(6)	135.61(9)
C(5)-C(2)-C(3)-C(4)	-30.82(12)
C(1)-C(2)-C(3)-C(4)	-146.91(9)
C(6)-C(2)-C(3)-C(4)	93.33(10)
C(5)-C(2)-C(3)-Si(1)	101.68(8)
C(1)-C(2)-C(3)-Si(1)	-14.41(9)
C(6)-C(2)-C(3)-Si(1)	-134.17(7)
O(1)-Si(1)-C(3)-C(4)	143.83(8)
C(19)-Si(1)-C(3)-C(4)	32.86(10)
C(15)-Si(1)-C(3)-C(4)	-104.35(9)
O(1)-Si(1)-C(3)-C(2)	12.26(7)
C(19)-Si(1)-C(3)-C(2)	-98.71(7)
C(15)-Si(1)-C(3)-C(2)	124.08(7)
C(5)-C(2)-C(6)-C(7)	53.76(11)
C(1)-C(2)-C(6)-C(7)	166.34(9)
C(3)-C(2)-C(6)-C(7)	-73.05(11)
C(5)-C(2)-C(6)-C(9)	-178.78(8)

C(1)-C(2)-C(6)-C(9)	-66.20(10)
C(3)-C(2)-C(6)-C(9)	54.41(11)
C(9)-C(6)-C(7)-C(8)	110.68(13)
C(2)-C(6)-C(7)-C(8)	-120.49(12)
C(7)-C(6)-C(9)-C(10)	30.50(14)
C(2)-C(6)-C(9)-C(10)	-97.30(11)
C(7)-C(6)-C(9)-C(14)	-147.89(10)
C(2)-C(6)-C(9)-C(14)	84.31(12)
C(14)-C(9)-C(10)-C(11)	-0.16(17)
C(6)-C(9)-C(10)-C(11)	-178.58(11)
C(9)-C(10)-C(11)-C(12)	-0.9(2)
C(10)-C(11)-C(12)-C(13)	0.8(2)
C(11)-C(12)-C(13)-C(14)	0.3(2)
C(12)-C(13)-C(14)-C(9)	-1.42(18)
C(10)-C(9)-C(14)-C(13)	1.32(16)
C(6)-C(9)-C(14)-C(13)	179.77(10)
O(1)-Si(1)-C(15)-C(16)	-82.03(9)
C(3)-Si(1)-C(15)-C(16)	176.07(9)
C(19)-Si(1)-C(15)-C(16)	37.07(11)
O(1)-Si(1)-C(15)-C(17)	37.95(10)
C(3)-Si(1)-C(15)-C(17)	-63.95(10)
C(19)-Si(1)-C(15)-C(17)	157.05(9)
O(1)-Si(1)-C(15)-C(18)	155.80(8)
C(3)-Si(1)-C(15)-C(18)	53.90(9)
C(19)-Si(1)-C(15)-C(18)	-85.10(9)
O(1)-Si(1)-C(19)-C(21)	-63.89(10)
C(3)-Si(1)-C(19)-C(21)	40.59(10)
C(15)-Si(1)-C(19)-C(21)	175.38(9)
O(1)-Si(1)-C(19)-C(22)	175.22(8)
C(3)-Si(1)-C(19)-C(22)	-80.30(10)
C(15)-Si(1)-C(19)-C(22)	54.49(10)
O(1)-Si(1)-C(19)-C(20)	54.05(9)
C(3)-Si(1)-C(19)-C(20)	158.53(8)
C(15)-Si(1)-C(19)-C(20)	-66.68(10)

B. Silalactone 15b. **X-ray Data Collection, Structure Solution and Refinement for 15b.**

A colorless crystal of approximate dimensions 0.26 x 0.32 x 0.41 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART¹ program package was used to determine the unit-cell parameters and for data collection (20 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ program. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/c$ which was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵ for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (x, y, z and U_{iso}). At convergence, $wR2 = 0.0980$ and $Goof = 1.069$ for 310 variables refined against 4324 data. As a comparison for refinement on F , $R1 = 0.0356$ for those 3760 data with $I > 2.0\sigma(I)$.

References.

1. SMART Software Users Guide, Version 5.1, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
 2. SAINT Software Users Guide, Version 6.0, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
 3. Sheldrick, G. M. SADABS, Version 2.05, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 2001.
 4. Sheldrick, G. M. SHELXTL Version 6.12, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 2001.
 5. International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer Academic Publishers.
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Definitions:

$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

$$R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$$

Goof = S = $[\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.

15b

Table 1. Crystal data and structure refinement for **15b**.

Identification code	kaw67 (Stacie Calad)	
Empirical formula	$C_{17} H_{32} O_2 Si$	
Formula weight	296.52	
Temperature	158(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 6.3526(8)$ Å	$\alpha = 90^\circ$.
	$b = 19.973(3)$ Å	$\beta = 93.574(2)^\circ$.
	$c = 14.0526(17)$ Å	$\gamma = 90^\circ$.
Volume	$1779.6(4)$ Å ³	
Z	4	
Density (calculated)	1.107 Mg/m ³	
Absorption coefficient	0.133 mm ⁻¹	
F(000)	656	
Crystal size	0.41 x 0.32 x 0.26 mm ³	
Theta range for data collection	1.77 to 28.31°.	
Index ranges	$-8 \leq h \leq 8, -26 \leq k \leq 26, -18 \leq l \leq 18$	
Reflections collected	21369	
Independent reflections	4324 [R(int) = 0.0268]	
Completeness to theta = 28.31°	97.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9663 and 0.9476	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4324 / 0 / 310	
Goodness-of-fit on F ²	1.069	
Final R indices [I>2sigma(I); 3760 data]	R1 = 0.0356, wR2 = 0.0905	
R indices (all data)	R1 = 0.0434, wR2 = 0.0980	
Extinction coefficient	0.0030(9)	
Largest diff. peak and hole	0.388 and -0.269 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **15b**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	2115(1)	4058(1)	2283(1)	16(1)
O(1)	-243(1)	4465(1)	2156(1)	20(1)
O(2)	-1633(1)	5489(1)	2167(1)	23(1)
C(1)	-167(2)	5127(1)	2376(1)	16(1)
C(2)	1860(2)	5336(1)	2965(1)	14(1)
C(3)	3619(2)	4808(1)	2799(1)	14(1)
C(4)	1177(2)	5335(1)	3999(1)	19(1)
C(5)	5244(2)	4692(1)	3640(1)	20(1)
C(6)	2415(2)	6071(1)	2694(1)	18(1)
C(7)	4245(2)	6343(1)	3313(1)	26(1)
C(8)	4065(3)	6774(1)	4016(1)	38(1)
C(9)	2861(2)	6162(1)	1644(1)	24(1)
C(10)	2886(2)	3867(1)	1026(1)	22(1)
C(11)	2492(4)	4498(1)	429(1)	48(1)
C(12)	1579(3)	3300(1)	534(1)	46(1)
C(13)	5222(2)	3679(1)	1024(1)	31(1)
C(14)	1747(2)	3305(1)	3089(1)	23(1)
C(15)	29(4)	2830(1)	2657(2)	52(1)
C(16)	994(2)	3522(1)	4060(1)	30(1)
C(17)	3820(2)	2918(1)	3259(1)	33(1)

Table 3. Bond lengths [Å] and angles [°] for **15b**.

Si(1)-O(1)	1.7039(9)
Si(1)-C(3)	1.8966(11)
Si(1)-C(10)	1.9007(13)
Si(1)-C(14)	1.9063(13)
O(1)-C(1)	1.3569(14)
O(2)-C(1)	1.2019(14)
C(1)-C(2)	1.5441(15)
C(2)-C(4)	1.5418(15)
C(2)-C(6)	1.5618(15)
C(2)-C(3)	1.5650(15)
C(3)-C(5)	1.5372(15)
C(6)-C(7)	1.5083(17)
C(6)-C(9)	1.5303(16)
C(7)-C(8)	1.321(2)
C(10)-C(11)	1.525(2)
C(10)-C(13)	1.5313(18)
C(10)-C(12)	1.543(2)
C(14)-C(17)	1.5333(18)
C(14)-C(16)	1.5364(19)
C(14)-C(15)	1.542(2)
O(1)-Si(1)-C(3)	94.69(4)
O(1)-Si(1)-C(10)	105.93(5)
C(3)-Si(1)-C(10)	111.19(5)
O(1)-Si(1)-C(14)	107.40(5)
C(3)-Si(1)-C(14)	118.25(5)
C(10)-Si(1)-C(14)	116.23(6)
C(1)-O(1)-Si(1)	114.98(7)
O(2)-C(1)-O(1)	120.96(10)
O(2)-C(1)-C(2)	125.14(10)
O(1)-C(1)-C(2)	113.75(9)
C(4)-C(2)-C(1)	103.28(8)
C(4)-C(2)-C(6)	108.23(9)

C(1)-C(2)-C(6)	108.53(9)
C(4)-C(2)-C(3)	112.58(9)
C(1)-C(2)-C(3)	108.47(9)
C(6)-C(2)-C(3)	115.03(9)
C(5)-C(3)-C(2)	116.03(9)
C(5)-C(3)-Si(1)	118.23(8)
C(2)-C(3)-Si(1)	104.00(7)
C(7)-C(6)-C(9)	109.30(10)
C(7)-C(6)-C(2)	112.05(9)
C(9)-C(6)-C(2)	113.84(9)
C(8)-C(7)-C(6)	124.49(14)
C(11)-C(10)-C(13)	109.15(14)
C(11)-C(10)-C(12)	107.12(14)
C(13)-C(10)-C(12)	108.23(12)
C(11)-C(10)-Si(1)	107.61(9)
C(13)-C(10)-Si(1)	110.91(8)
C(12)-C(10)-Si(1)	113.67(10)
C(17)-C(14)-C(16)	108.38(11)
C(17)-C(14)-C(15)	109.35(14)
C(16)-C(14)-C(15)	105.71(13)
C(17)-C(14)-Si(1)	110.79(9)
C(16)-C(14)-Si(1)	111.23(8)
C(15)-C(14)-Si(1)	111.22(10)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **15b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	16(1)	16(1)	16(1)	-1(1)	-1(1)	1(1)
O(1)	15(1)	20(1)	24(1)	-4(1)	-3(1)	1(1)
O(2)	16(1)	26(1)	26(1)	1(1)	0(1)	5(1)
C(1)	15(1)	20(1)	14(1)	1(1)	3(1)	0(1)
C(2)	14(1)	16(1)	13(1)	0(1)	2(1)	0(1)
C(3)	13(1)	17(1)	14(1)	1(1)	1(1)	1(1)
C(4)	22(1)	22(1)	14(1)	-1(1)	4(1)	1(1)
C(5)	16(1)	23(1)	20(1)	1(1)	-4(1)	1(1)
C(6)	20(1)	16(1)	18(1)	1(1)	3(1)	1(1)
C(7)	27(1)	19(1)	32(1)	5(1)	-3(1)	-5(1)
C(8)	54(1)	26(1)	32(1)	0(1)	-9(1)	-12(1)
C(9)	31(1)	21(1)	21(1)	6(1)	7(1)	2(1)
C(10)	24(1)	25(1)	18(1)	-6(1)	-2(1)	6(1)
C(11)	86(1)	43(1)	17(1)	3(1)	6(1)	28(1)
C(12)	34(1)	67(1)	37(1)	-31(1)	2(1)	-9(1)
C(13)	23(1)	45(1)	25(1)	0(1)	5(1)	5(1)
C(14)	25(1)	17(1)	27(1)	2(1)	0(1)	-2(1)
C(15)	64(1)	35(1)	54(1)	7(1)	-13(1)	-28(1)
C(16)	30(1)	25(1)	35(1)	9(1)	14(1)	3(1)
C(17)	39(1)	27(1)	35(1)	10(1)	13(1)	14(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **15b**.

	x	y	z	U(eq)
H(3)	4400(20)	4973(7)	2269(10)	19(3)
H(4A)	680(20)	4878(8)	4183(11)	23(4)
H(4B)	40(30)	5664(8)	4057(12)	30(4)
H(4C)	2370(30)	5462(8)	4432(12)	27(4)
H(5A)	4680(20)	4490(8)	4198(11)	25(4)
H(5B)	6340(20)	4390(8)	3443(11)	25(4)
H(5C)	5910(30)	5102(9)	3866(12)	30(4)
H(6)	1180(20)	6340(8)	2832(11)	23(4)
H(7)	5610(30)	6204(8)	3151(12)	30(4)
H(8A)	5290(30)	6922(10)	4369(15)	50(5)
H(8B)	2690(30)	6943(10)	4162(14)	47(5)
H(9A)	1650(30)	5984(8)	1243(13)	34(4)
H(9B)	2970(30)	6644(9)	1523(12)	33(4)
H(9C)	4120(30)	5951(9)	1501(13)	36(5)
H(11A)	3400(30)	4812(10)	630(13)	36(5)
H(11B)	2870(30)	4420(10)	-239(15)	50(5)
H(11C)	930(40)	4660(13)	415(18)	78(8)
H(12A)	80(30)	3381(10)	551(15)	57(6)
H(12B)	1930(30)	3322(11)	-139(16)	61(6)
H(12C)	2000(50)	2800(15)	860(20)	102(10)
H(13A)	5630(30)	3622(9)	362(13)	39(5)
H(13B)	5500(30)	3254(10)	1361(14)	44(5)
H(13C)	6150(30)	4026(10)	1331(15)	50(6)
H(15A)	620(30)	2633(11)	2139(17)	60(7)
H(15B)	-200(30)	2462(11)	3131(15)	53(6)
H(15C)	-1300(40)	3042(13)	2487(17)	70(7)
H(16A)	2040(30)	3806(9)	4424(13)	36(4)
H(16B)	-350(30)	3758(9)	4002(13)	42(5)
H(16C)	770(30)	3116(9)	4463(13)	40(5)

H(17A)	4960(30)	3207(10)	3542(13)	41(5)
H(17B)	3580(30)	2534(9)	3677(13)	40(5)
H(17C)	4270(30)	2732(11)	2649(16)	59(6)

Table 6. Torsion angles [°] for **15b**.

C(3)-Si(1)-O(1)-C(1)	4.61(8)
C(10)-Si(1)-O(1)-C(1)	-109.00(8)
C(14)-Si(1)-O(1)-C(1)	126.16(8)
Si(1)-O(1)-C(1)-O(2)	167.45(9)
Si(1)-O(1)-C(1)-C(2)	-16.69(11)
O(2)-C(1)-C(2)-C(4)	78.45(13)
O(1)-C(1)-C(2)-C(4)	-97.21(10)
O(2)-C(1)-C(2)-C(6)	-36.27(14)
O(1)-C(1)-C(2)-C(6)	148.07(9)
O(2)-C(1)-C(2)-C(3)	-161.89(10)
O(1)-C(1)-C(2)-C(3)	22.45(12)
C(4)-C(2)-C(3)-C(5)	-35.15(13)
C(1)-C(2)-C(3)-C(5)	-148.81(9)
C(6)-C(2)-C(3)-C(5)	89.47(12)
C(4)-C(2)-C(3)-Si(1)	96.49(9)
C(1)-C(2)-C(3)-Si(1)	-17.18(9)
C(6)-C(2)-C(3)-Si(1)	-138.89(8)
O(1)-Si(1)-C(3)-C(5)	138.46(9)
C(10)-Si(1)-C(3)-C(5)	-112.44(9)
C(14)-Si(1)-C(3)-C(5)	25.83(10)
O(1)-Si(1)-C(3)-C(2)	8.12(7)
C(10)-Si(1)-C(3)-C(2)	117.22(7)
C(14)-Si(1)-C(3)-C(2)	-104.50(8)
C(4)-C(2)-C(6)-C(7)	62.43(12)
C(1)-C(2)-C(6)-C(7)	173.87(10)
C(3)-C(2)-C(6)-C(7)	-64.44(13)
C(4)-C(2)-C(6)-C(9)	-172.90(10)
C(1)-C(2)-C(6)-C(9)	-61.46(12)
C(3)-C(2)-C(6)-C(9)	60.23(13)
C(9)-C(6)-C(7)-C(8)	128.74(14)
C(2)-C(6)-C(7)-C(8)	-104.11(15)
O(1)-Si(1)-C(10)-C(11)	45.04(13)
C(3)-Si(1)-C(10)-C(11)	-56.61(13)

C(14)-Si(1)-C(10)-C(11)	164.20(12)
O(1)-Si(1)-C(10)-C(13)	164.36(9)
C(3)-Si(1)-C(10)-C(13)	62.72(11)
C(14)-Si(1)-C(10)-C(13)	-76.47(11)
O(1)-Si(1)-C(10)-C(12)	-73.41(12)
C(3)-Si(1)-C(10)-C(12)	-175.06(11)
C(14)-Si(1)-C(10)-C(12)	45.76(13)
O(1)-Si(1)-C(14)-C(17)	-178.68(9)
C(3)-Si(1)-C(14)-C(17)	-73.28(11)
C(10)-Si(1)-C(14)-C(17)	62.95(11)
O(1)-Si(1)-C(14)-C(16)	-58.07(10)
C(3)-Si(1)-C(14)-C(16)	47.33(11)
C(10)-Si(1)-C(14)-C(16)	-176.44(9)
O(1)-Si(1)-C(14)-C(15)	59.47(14)
C(3)-Si(1)-C(14)-C(15)	164.87(12)
C(10)-Si(1)-C(14)-C(15)	-58.90(14)

VII. Selected Spectra

MeCN layers after extraction from hexanes
1H spectrum

Current Data Parameters
 USER: sc-11-091
 NAME: 7a
 EXPNO: 1
 PROCNO: 1
 F2 - Acquisition Parameters
 Date_: 2003104
 Time: 11:13:10
 INSTRUM: spect
 PULPROG: zgpg30
 PC: 10.000
 TO: 10.000
 TD: 65536
 SFO: 400.125970 MHz
 SI: 32768
 SF: 400.125970 MHz
 SC: 10.000
 SS: 0.30 Hz
 SB: 0
 GB: 0
 PC: 2.00
 ID: 10.000
 CHAN: 1
 NUC1: 13C
 P1: 12.00 usec
 PL1: 0.00 dB
 SFO1: 400.125970 MHz
 F2 - Processing parameters
 SI: 65536
 SF: 400.125970 MHz
 SC: 10.000
 SS: 0.30 Hz
 SB: 0
 GB: 0
 PC: 2.00
 ID: 10.000
 CHAN: 1
 NUC1: 13C
 P1: 12.00 usec
 PL1: 0.00 dB
 SFO1: 400.125970 MHz
 F2 - Processing parameters
 SI: 65536
 SF: 400.125970 MHz
 SC: 10.000
 SS: 0.30 Hz
 SB: 0
 GB: 0
 PC: 2.00
 ID: 10.000
 CHAN: 1
 NUC1: 13C
 P1: 12.00 usec
 PL1: 0.00 dB
 SFO1: 400.125970 MHz

Current Data Parameters
 User: Standard
 Name: 7e
 ExpNo: 1
 PROCNO: 1
 F2 - Acquisition Parameters
 Date_: 2008324
 Time: 21.05
 INSTRUM: gpc500
 PULPROG: zgpg30
 FIDRES: 0.0956
 TOU: 65.56
 SOLVENT: CDCl3
 NS: 8
 DS: 2
 SWH: 8012.820 Hz
 FIDRES: 0.12286 Hz
 AQ: 4.0894686 sec
 RG: 390.0
 SF: 500.1354000 MHz
 DE: 6.00 mm
 TE: 300.0 K
 D1: 0.10000000 sec
 ===== CHANNEL f1 =====
 NUC1: ¹H
 P1: 12.00 dB
 PL1: 0.00 dB
 SFO1: 499.98498 MHz
 F2 - Processing parameters
 SI: 32768
 SF: 499.98498 MHz
 WDW: EM
 SSB: 0
 LB: 0.30 Hz
 GB: 0
 PC: 4.00
 F0: 0.00000000
 10 MHz plot parameters
 CX: 62.00 cm
 CY: 10.00 cm
 F1: 499.98498 MHz
 F2: -1.000 MHz
 FIDRES: 0.12286 Hz
 PPM0: 244.19432 Hz

Current Data Parameters

USER	SC131D
NAME	8C-11-01
EXPNO	5
PROCNO	1

F2 - Acquisition Parameters

Date_	20070414
Time	10:37
INSTRUM	gpr500
PROBHD	5 mm broadband
PULPROG	zgpg30
TD	65536
SF	500.135000 MHz
WDW	EM
SSB	0
LB	0.00 Hz
GB	0
PC	4.00

F2 - Processing parameters

SI	65536
WDW	EM
SSB	0
LB	0.00 Hz
GB	0
PC	4.00

ID parameters

CT	22.86 cm
PI	40.000 ppm
FI	500.135000 MHz
F2	-1.000 ppm
PRGM	0.45446 ppm/cm
QCX	241.30000 Hz/cm

===== CHANNEL f1 =====

NUC1	¹ H
PT	11.50 usec
PL1	-3.00 dB
PR1	500.135000 MHz

Current Data Parameters

USER	SCALD
NAME	SC-111-048
EXPNO	4
PROCNO	1

F2 - Acquisition Parameters

DATE_	02/08/2016
TIME	17:49
INSTRUM	DMG400
PROBHD	5 mm BBO-400
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	16015.820 Hz
FIDRES	0.09040 Hz
AQ	5.0958774 sec
RG	256
WM	62.500 Hz
DE	6.500 Hz
TE	300.2 K
D1	0.10000000 sec

===== CHANNEL f1 =====

NUCL1	¹ H
P1	13.00 Hz
PL1	-1.00 dB
NUC2	¹³ C
PC1	500.225015 MHz

F2 - Processing parameters

SI	5536
SD	500.225015 MHz
SR	0
SB	0
LB	0.30 Hz
GB	0
PC	4.00

1D FID parameters

EX	22.00 cm
NUC1	¹ H
PCP	13.00 Hz
PLP	-1.00 dB
PL2	-1.00 dB
PL3	-1.00 dB
PL4	-1.00 dB
PL5	-1.00 dB
PL6	-1.00 dB
PL7	-1.00 dB
PL8	-1.00 dB
PL9	-1.00 dB
PL10	-1.00 dB
PL11	-1.00 dB
PL12	-1.00 dB
PL13	-1.00 dB
PL14	-1.00 dB
PL15	-1.00 dB
PL16	-1.00 dB
PL17	-1.00 dB
PL18	-1.00 dB
PL19	-1.00 dB
PL20	-1.00 dB
PL21	-1.00 dB
PL22	-1.00 dB
PL23	-1.00 dB
PL24	-1.00 dB
PL25	-1.00 dB
PL26	-1.00 dB
PL27	-1.00 dB
PL28	-1.00 dB
PL29	-1.00 dB
PL30	-1.00 dB
PL31	-1.00 dB
PL32	-1.00 dB
PL33	-1.00 dB
PL34	-1.00 dB
PL35	-1.00 dB
PL36	-1.00 dB
PL37	-1.00 dB
PL38	-1.00 dB
PL39	-1.00 dB
PL40	-1.00 dB
PL41	-1.00 dB
PL42	-1.00 dB
PL43	-1.00 dB
PL44	-1.00 dB
PL45	-1.00 dB
PL46	-1.00 dB
PL47	-1.00 dB
PL48	-1.00 dB
PL49	-1.00 dB
PL50	-1.00 dB
PL51	-1.00 dB
PL52	-1.00 dB
PL53	-1.00 dB
PL54	-1.00 dB
PL55	-1.00 dB
PL56	-1.00 dB
PL57	-1.00 dB
PL58	-1.00 dB
PL59	-1.00 dB
PL60	-1.00 dB
PL61	-1.00 dB
PL62	-1.00 dB
PL63	-1.00 dB
PL64	-1.00 dB
PL65	-1.00 dB
PL66	-1.00 dB
PL67	-1.00 dB
PL68	-1.00 dB
PL69	-1.00 dB
PL70	-1.00 dB
PL71	-1.00 dB
PL72	-1.00 dB
PL73	-1.00 dB
PL74	-1.00 dB
PL75	-1.00 dB
PL76	-1.00 dB
PL77	-1.00 dB
PL78	-1.00 dB
PL79	-1.00 dB
PL80	-1.00 dB
PL81	-1.00 dB
PL82	-1.00 dB
PL83	-1.00 dB
PL84	-1.00 dB
PL85	-1.00 dB
PL86	-1.00 dB
PL87	-1.00 dB
PL88	-1.00 dB
PL89	-1.00 dB
PL90	-1.00 dB
PL91	-1.00 dB
PL92	-1.00 dB
PL93	-1.00 dB
PL94	-1.00 dB
PL95	-1.00 dB
PL96	-1.00 dB
PL97	-1.00 dB
PL98	-1.00 dB
PL99	-1.00 dB
PL100	-1.00 dB

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Current Data Parameters
 USER sc-111-075
 NAME 1
 EXPNO 1
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20041125
 Time_ 14.47
 INSTRUM spect
 PROBO 5 mm broadband
 PULPROG zgpg30
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 8042.833 Hz
 FIDRES 0.08063 Hz
 AQ 5.0980724 sec
 RG 181
 DM 62.400 sec
 DE 6.500 sec
 TE 300.0 K
 IE 0.10000000 sec
 ===== CHANNEL f1 =====
 NUC1 1H
 P1 11.50 usec
 PL1 -3.00 dB
 RF1 500.1555010 MHz
 SF01
 F2 - Processing parameters
 SI 500.1500298 MHz
 SF 500.1313130 MHz
 SCB 0
 LB 0.00 Hz
 GB 0
 PC 4.00
 =====
 1D NMR plot parameters
 CX 22.80 cm
 FIP 10.000 GHz
 SFO1 500.1313130 MHz
 FZ2 -11.000 MHz
 F2 -500.15 Hz
 PRNCH 0.4006 Ddr/Cs
 H2O 241.30000 Hz/Cs

Data File C:\HPCHEM\1\DATA\SAC\SCI002A.D

Sample Name: sc-I-002a

```

=====
Injection Date   : 6/5/2003 1:40:10 PM
Sample Name      : sc-I-002a                Location : Vial 12
Acq. Operator    : dms                      Inj       : 1
                                           Inj Volume: 1 µl
Acq. Method      : C:\HPCHEM\1\METHODS\STACIE.M
Last changed     : 3/28/2003 12:22:34 PM by jelena
Analysis Method  : C:\HPCHEM\1\METHODS\STACIE.M
Last changed     : 8/17/2004 9:11:11 AM by jelena
                  (modified after loading)
=====

```

```

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

```

```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Sample Amount  : 1.00000 [ng/ul] (not used in calc.)

```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	7.176	BP	0.0234	14.02498	7.72881	95.42600
2	7.380	MM	0.0213	6.72251e-1	5.25604e-1	4.57400

Totals : 14.69724 8.25441

Results obtained with enhanced integrator!

```

=====
*** End of Report ***
=====

```

Data File C:\HPCHEM\1\DATA\SAC\SC2206CR.D

Sample Name: sc-II-206cr

```

=====
Injection Date   : 6/2/2004 2:24:27 PM      Seq. Line :    2
Sample Name     : sc-II-206cr              Location  : Vial 2
Acq. Operator   : Jelena                   Inj       :    1
                                           Inj Volume: 1 µl

Acq. Method     : C:\HPCHEM\1\METHODS\STACIE.M
Last changed    : 5/24/2004 11:48:00 AM by Mike
Analysis Method : C:\HPCHEM\1\METHODS\STACIE.M
Last changed    : 11/23/2004 3:11:16 PM by jelena
                  (modified after loading)
=====

```

```

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

```

```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000

```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	12.842	BP	0.0258	227.61867	125.98470	97.04901
2	13.070	BP	0.0276	6.92124	3.58025	2.95099

Totals : 234.53991 129.56495

Results obtained with enhanced integrator!

```

=====
*** End of Report ***
=====

```

Data File C:\HPCHEM\1\DATA\SAC\010F0101.D

Sample Name: sc-III-046rxn

rxn start time 3:40

```

=====
Injection Date   : 9/19/2004 5:35:24 PM      Seq. Line :    1
Sample Name     : sc-III-046rxn             Location  : Vial 10
Acq. Operator   : Mike                      Inj       :    1
                                           Inj Volume: 1 µl

Acq. Method     : C:\HPCHEM\1\METHODS\STACIE1.M
Last changed    : 9/8/2004 2:58:58 PM by Mike
Analysis Method : C:\HPCHEM\1\METHODS\STACIE.M
Last changed    : 11/23/2004 3:12:55 PM by jelena
                  (modified after loading)
=====

```

```

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

```

```

Sorted By       : Signal
Multiplier      : 1.0000
Dilution        : 1.0000

```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	1.983	BV	0.0158	16.01445	15.86345	16.54448
2	2.197	BV	0.0182	12.88164	10.59907	13.30798
3	9.019	VV	0.0295	67.90025	35.19128	70.14754

```
Totals :                96.79634    61.65380
```

Results obtained with enhanced integrator!

```

=====
*** End of Report ***
=====

```

Data File C:\HPCHEM\1\DATA\SAC\2-56CR.D

Sample Name: sc-II-056crude

```

=====
Injection Date   : 8/13/2003 8:20:37 PM      Seq. Line :    1
Sample Name     : sc-II-056crude            Location  : Vial 12
Acq. Operator   : sbb                      Inj       :    1
                                           Inj Volume: 1 µl

Acq. Method     : C:\HPCHEM\1\METHODS\STACIE.M
Last changed    : 7/3/2003 5:53:32 PM by stevec
Analysis Method : C:\HPCHEM\1\METHODS\STACIE.M
Last changed    : 11/23/2004 3:17:01 PM by jelena
                  (modified after loading)
=====

```

```

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

```

```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution      : 1.0000

```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	15.273	MM	0.0435	11.89114	4.55235	10.25209
2	15.596	MM	0.0659	104.09628	26.31596	89.74791

Totals : 115.98741 30.86831

Results obtained with enhanced integrator!

```

=====
*** End of Report ***
=====

```

Data File C:\HPCHEM\1\DATA\SAC\SC2099CR.D

Sample Name: sc-II-099crude

```

=====
Injection Date   : 11/26/2003 9:38:42 AM      Seq. Line   :    1
Sample Name     : sc-II-099crude             Location    : Vial 3
Acq. Operator   : Glen                      Inj         :    1
                                           Inj Volume  : 1 µl

Acq. Method     : C:\HPCHEM\1\METHODS\STACIE.M
Last changed    : 9/17/2003 9:23:19 AM by scalad
Analysis Method : C:\HPCHEM\1\METHODS\STACIE.M
Last changed    : 11/23/2004 3:05:53 PM by jelena
                  (modified after loading)
=====

```

```

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

```

```

Sorted By      :      Signal
Multiplier     :      1.0000
Dilution       :      1.0000

```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	15.249	MM	0.0449	7.06826	2.62098	10.20037
2	15.573	BB	0.0404	62.22595	20.09649	89.79963

Totals : 69.29422 22.71746

Results obtained with enhanced integrator!

```

=====
*** End of Report ***
=====

```

Data File C:\HPCHEM\1\DATA\SAC\SC2109CR.D

Sample Name: sc-II-109

```

=====
Injection Date   : 1/7/2004 11:50:31 AM      Seq. Line :    1
Sample Name     : sc-II-109                 Location  : Vial 2
Acq. Operator   : STACIE                     Inj       :    1
                                           Inj Volume: 1 µl

Acq. Method     : C:\HPCHEM\1\METHODS\STACIE.M
Last changed    : 12/19/2003 1:43:34 PM by stevec
Analysis Method : C:\HPCHEM\1\METHODS\STACIE.M
Last changed    : 11/23/2004 3:07:50 PM by jelena
                  (modified after loading)
=====

```

```

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

```

```

Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000

```

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	15.246	BB	0.0320	13.80317	5.18770	11.00751
2	15.570	PB	0.0360	111.59454	37.18347	88.99249

Totals : 125.39771 42.37116

Results obtained with enhanced integrator!

```

=====
*** End of Report ***
=====

```