Formation and Utility of Oxasilacyclopentenenes from Functionalized Alkynes

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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 were reported uncorrected. Analytical gas chromatography (GC) was performed on an Agilent 6850 series chromatograph, equipped with an Agilent 6850 auto sampler and a flame ionization detector (a fused silica capillary flash (30 m x 0.32 mm x 0.25 µm) wall-coated with HP-1 (J & W Scientific) was used with helium as the carrier gas) or on a gas chromatography-mass spectrometry (GC-MS) Thermo-Finnigan Trace Mass Spectrometer Plus quadrupole system with a fused silica capillary flash (30 m x 0.32 mm x 0.25 µm) wall-coated with DB-5 (J & W Scientific) using electron ionization (70 eV). 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, h = hexet, 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 silacyclopentenenes were stored and manipulated in an Innovative Technologies nitrogen atmosphere dry box. All reaction mixtures to form silacyclopentenenes and oxasilacyclopentenenes unless specified were prepared in the dry box. All other reactions unless specified were carried out 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. 4-triisopropylsilyloxy-2-butyne¹ (Table 1, entry 6) and cyclohexenesilacyclopropane^{2,3} (**1**) were constructed by known methods.

I. Ag_3PO_4 -catalyzed Construction of Silacycloprenes

5-(triisopropylsilyloxy)-3-penten-1-yne (**10**).

To a cooled (0 °C) solution of 3-penten-5-yn-1-ol (3.96 g, 46.3 mmol), imidazole (6.30 g, 92.6 mmol) and 12.0 mL of *N,N*-dimethylformamide was added triisopropylsilylchloride (10.4 mL, 48.6 mmol). The reaction mixture was allowed to warm to room temperature and stir for 21 h. The reaction mixture was diluted with 50 mL of water and extracted with Et_2O (3 x 40 mL). The organic extracts were rinsed with 1.0 N aqueous HCl (2 x 30 mL), saturated aqueous NaCl (30 mL), dried with MgSO_4 and concentrated *in vacuo* to give a yellow oil. Purification by column chromatography (hexanes to 3:97 CH_2Cl_2 :hexanes) afforded **10** as a colorless oil (6.80 g, 72%): ^1H NMR (CDCl_3 , 500 MHz) δ 6.31 (dt, J = 15.8, 3.9, 1H), 5.82 (dq, J = 15.8, 2.3, 1H), 4.33 (t, J = 3.0, 2H), 2.87 (d, J = 2.2, 1H), 1.07 (m, 21H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 144.6, 107.6, 82.4, 77.5, 63.1, 18.2, 12.2; IR (thin film) 3315, 2944, 2867, 1464, 882 cm^{-1} ; HRMS: (NH_3Cl) m/z calcd for $\text{C}_{14}\text{H}_{25}\text{OSi}$ ($\text{M}-\text{H}$) $^+$ 237.1675, found 237.1674. Anal. Calcd for $\text{C}_{14}\text{H}_{26}\text{OSi}$: C, 70.52; H, 10.99. Found: C, 70.25; H, 11.17.

Ag_3PO_4 -catalyzed silacycloprenation of alkynes typically utilized a 1:1 ratio of alkyne:cyclohexenesilacycloprenene **1**. In the following two examples, a small excess of **1** was used for increased yields. For substrate ratios, see experimental procedures for the *in situ* formation of oxasilacyclopentenenes from alkynes.

1,1-Di-*tert*-butyl-2-(3-(triisopropylsilyloxy)-1-propenyl)silacycloprenene (**2h**).

Representative Procedure for the silver-catalyzed silacycloprenation of synthesized alkynes:

To an NMR tube containing Ag_3PO_4 (0.005 g, 0.012 mmol) was added the alkyne (0.230 mL, 0.115 mmol, 0.500 M solution of alkyne and 0.133 M solution of PhSiMe_3 , the internal standard in C_6D_6), followed by **1** (0.270 mL, 0.135 mmol, 0.500 M solution of **1** and 0.133 M solution of PhSiMe_3 in C_6D_6). The reaction yield was determined to be 81% by ^1H NMR spectroscopy (compared to the PhSiMe_3 internal standard) using a single scan: ^1H NMR (C_6D_6 , 500 MHz) δ 7.91 (s, 1H), 6.81 (dt, J = 14.9, 1.7, 1H), 6.11 (dt, J = 14.8, 4.7, 1H), 4.29 (ddd, J = 4.7, 1.9, 0.5, 2H), 1.10 (s, 39H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 160.3, 144.7, 140.3, 125.1, 64.2, 30.5, 21.4, 18.6, 12.8; ^{29}Si NMR (C_6D_6 , 99.3 MHz) δ -67.5, 13.5.

1,1-Di-*tert*-butyl-2-(methoxymethyl)silacycloprenene (**2e**).

Representative Procedure for the silver-catalyzed silacycloprenation of commercially available alkynes:

To an NMR tube containing Ag_3PO_4 (0.006 g, 0.014 mmol) was added the alkyne (0.012 mL, 0.142 mmol), followed by **1** (0.600 mL, 0.150 mmol, 0.250 M solution of **1** and 0.133 M solution of PhSiMe_3 in C_6D_6). The reaction yield was determined to be 79% by ^1H NMR spectroscopy (compared to the PhSiMe_3 internal standard) using a single scan: ^1H NMR (C_6D_6 , 500 MHz) δ 8.05 (t, J = 1.9, 1H), 4.34 (d, J = 1.9, 1H), 3.26 (s, 3H), 1.05 (s, 18H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 162.9, 138.1, 73.7, 58.2, 30.3, 21.4; ^{29}Si NMR (C_6D_6 , 99.3 MHz) δ -66.6.

II. Characterization Data on Silacyclopropenes

Characterization Data for Silacyclopropenes by Thermal Silacyclopropenation

Isolation of silacyclopropenes generated by the silver-catalyzed silacyclopropenation was challenging, so, several of the reported silacyclopropenes were constructed by thermal silacyclopropenation and characterized. Thermal silacyclopropenation was found to provide increased yields with a sealed vessel under static vacuum (as described⁴). For internal alkynes, no solvent was utilized; terminal alkynes provided fewer by-products using toluene as solvent.

1,1-Di-tert-butyl-2-phenyl-3-methylsilacyclopropene (2a).

Representative Procedure for the thermal silacyclopropenation of alkynes:

A mixture of **1** (1.74 g, 7.75 mmol) and 1-phenyl-1-propyne (0.900 g, 7.75 mmol) was added to a vessel fitted with an air-free seal. The reaction mixture was degassed. The reaction mixture was heated to 90 °C for 72 h. After cooling to 22 °C, the reaction mixture was concentrated *in vacuo*. Purification by bulb-to-bulb distillation (90–100 °C/0.5 mm Hg) gave **2a** as a colorless liquid (1.57 g, 53%): ¹H NMR (C₆D₆, 500 MHz) δ 7.53 (dd, *J* = 8.0, 1.2, 2H), 7.25 (t, *J* = 7.7, 2H), 7.09 (m, 1H), 2.34 (s, 3H), 1.11 (s, 18H); ¹³C NMR (C₆D₆, 125 MHz) δ 152.6, 151.7, 137.9, 131.6, 130.5, 128.9, 32.0, 23.4, 17.5; ²⁹Si NMR (C₆D₆, 99.3 MHz) –68.4; IR (thin film) 3075, 2929, 2856, 1620, 1470, 822, 760 cm⁻¹; HRMS (EI/GCMS) *m/z* calcd for C₁₇H₂₆Si (M)⁺ 258.1804, found 258.1805. Anal. Calcd for C₁₇H₂₆Si: C, 79.00; H, 10.14. Found: C, 78.63; H, 9.99.

1,1-Di-tert-butyl-2,3-diethylsilacyclopropene (2b).⁵

The representative procedure for thermal silacyclopropenation of alkynes was followed using **1** (3.00 g, 13.4 mmol) and 3-hexyne (1.10 g, 13.4 mmol) at 90 °C for 48 h. Purification by bulb-to-bulb distillation (30–40 °C/0.5 mm Hg) gave **2b** as a colorless liquid (2.42 g, 81%) (spectral data matched that reported⁵): ¹H NMR (C₆D₆, 500 MHz) δ 2.45 (q, *J* = 8.5, 4H), 1.14 (t, *J* = 8.5, 6H), 1.11 (s, 18H); ¹³C NMR (C₆D₆, 125 MHz) δ 152.9, 30.6, 22.6, 21.3, 15.3; ²⁹Si NMR (C₆D₆, 99.3 MHz) –66.8; IR (thin film) 2942, 2961, 2855, 1470, 821 cm⁻¹; HRMS (EI/GCMS) *m/z* calcd for C₁₄H₂₈Si (M)⁺ 224.1960, found 224.1959. Anal. Calcd for C₁₄H₂₈Si: C, 74.91; H, 12.57. Found: C, 74.63; H, 12.53.

1,1-Di-tert-butyl-2-phenylsilacyclopropene (2c).

The representative procedure for thermal silacyclopropenation of alkynes was followed using **1** (3.30 g, 14.7 mmol), phenylacetylene (1.50 g, 14.7 mmol), and 15.0 mL of toluene at 90 °C for 72 h. Purification by bulb-to-bulb distillation (60–70 °C/0.5 mm Hg) gave **2c** as a colorless liquid (3.38 g, 94%): ¹H NMR (C₆D₆, 500 MHz) δ 8.31 (s, 1H), 7.57 (dd, *J* = 8.2, 1.3, 2H), 7.23 (t, *J* = 8.2, 2H), 7.11 (m, 1H), 1.10 (s, 18H); ¹³C NMR (C₆D₆,

125 MHz) δ 162.2, 139.2, 135.4, 129.6, 129.2, 128.9, 30.5, 21.5; ^{29}Si NMR (C_6D_6 , 99.3 MHz) δ -65.2; IR (thin film) 3021, 2929, 2856, 1470, 823, 744 cm^{-1} ; HRMS (EI/GCMS) m/z calcd for $\text{C}_{16}\text{H}_{24}\text{Si}$ (M) $^{+}$ 244.1647, found 244.1644. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{Si}$: C, 78.61; H, 9.90. Found: C, 78.57; H, 9.84.

1,1-Di-tert-butyl-2-butylsilacyclopropene (**2d**).

The representative procedure for thermal silacyclopropenation of alkynes was followed using **1** (2.19 g, 9.70 mmol), 1-hexyne (3.2 g, 39.0 mmol), and 5.0 mL of toluene at 90 °C for 48 h. Purification by bulb-to-bulb distillation (30–40 °C/0.5 mm Hg) gave **2d** as a colorless liquid (1.75 g, 80%) in a 96:4 mixture of **2d**:**1**: ^1H NMR (C_6D_6 , 500 MHz) δ 7.85 (t, J = 1.5, 1H), 2.51 (dt, J = 7.4, 1.5, 2H), 1.58 (m, 2H), 1.39 (h, J = 7.5, 2H), 1.09 (s, 18H), 0.92 (t, J = 7.3, 3H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 166.3, 137.8, 33.4, 31.8, 30.6, 23.3, 21.3, 14.6; ^{29}Si NMR (C_6D_6 , 99.3 MHz) δ -66.7; IR (thin film) 2959, 2856, 1559, 1470, 823 cm^{-1} ; HRMS (EI/GCMS) m/z calcd for $\text{C}_{14}\text{H}_{28}\text{Si}$ (M) $^{+}$ 224.1960, found 224.1960.

1,1-Di-tert-butyl-2-(triisopropylsilyloxymethyl)-3-methylsilacyclopropene (**2f**).

The representative procedure for thermal silacyclopropenation of alkynes was followed using **1** (0.660 g, 2.94 mmol) and triisopropylsilyloxy-2-butyne (0.665 g, 2.94 mmol) at 90 °C for 4 d. Purification by bulb-to-bulb distillation (140–150 °C/0.5 mm Hg) gave **2f** as a colorless liquid (0.525 g, 53%): ^1H NMR (C_6D_6 , 500 MHz) δ 4.81 (q, J = 1.5, 2H), 2.32 (t, J = 1.5, 3H), 1.12 (m, 21H), 1.08 (s, 18H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 151.2, 147.4, 64.4, 30.3, 21.7, 18.4, 15.8, 12.4; ^{29}Si NMR (C_6D_6 , 99.3 MHz) δ -65.4, 12.6; IR (thin film) 2942, 2866, 1646, 1470, 1085, 1052, 821 cm^{-1} ; HRMS (EI/GCMS) m/z calcd for $\text{C}_{18}\text{H}_{37}\text{OSi}_2$ [$\text{M}-\text{C}_3\text{H}_7$] $^{+}$ 325.2383, found 325.2372. Anal. Calcd for $\text{C}_{21}\text{H}_{44}\text{OSi}_2$: C, 68.40; H, 12.03. Found: C, 68.57; H, 12.04.

N-Benzyl-*N*-(1,1-Di-tert-butyl-2-silacyclopropenyl)-methylamine (**2g**).

The representative procedure for thermal silacyclopropenation of alkynes was followed using **1** (2.96 g, 13.2 mmol), *N*-methyl-*N*-propargylbenzylamine (2.03 mL, 12.0 mmol) and toluene (30.0 mL) at 90–100 °C for 7 d. Purification by bulb-to-bulb distillation (110–130 °C/0.5 mm Hg) gave **2g** as a pale yellow liquid (1.19 g, 34%): ^1H NMR (C_6D_6 , 500 MHz) δ 8.01 (t, J = 1.5, 1H), 7.45 (d, J = 7.7, 2H), 7.21 (t, J = 7.6, 2H), 7.11 (t, J = 7.4, 1H), 3.58 (s, 2H), 3.51 (s, 2H), 2.28 (s, 3H), 1.07 (s, 18H); ^{13}C NMR (C_6D_6 , 125 MHz) δ 163.5, 140.7, 139.1, 129.4, 128.9, 127.5, 62.4, 60.3, 43.0, 30.5, 21.5; ^{29}Si NMR (C_6D_6 , 99.3 MHz) δ -67.7; IR (thin film) 2933, 2856, 1646, 1471, 823 cm^{-1} ; HRMS (EI/GCMS) m/z calcd for $\text{C}_{19}\text{H}_{34}\text{NOSi}$ [$\text{M}+\text{H}_3\text{O}$] $^{+}$ 320.2410, found 320.2415.

III. Construction and Utility of Oxasilacyclopentenes

3a

2,2-Di-tert-butyl-4-phenyl-5-phenyloxasilacyclopentene (3a).

Representative procedure for the two-step, one-flask formation of oxasilacyclopentenes:

To a mixture of Ag_3PO_4 (0.042 g, 0.100 mmol) and toluene (4.0 mL) was added phenylacetylene (0.110 mL, 1.00 mmol), followed by **1** (0.225 g, 1.00 mmol). After 3 hours, the reaction mixture was cooled to -20°C . Benzaldehyde (0.305 mL, 3.00 mmol) was added, followed by CuBr_2 (0.033 g, 0.148 mmol). The reaction mixture was allowed to warm to 22°C over 1 hour. The reaction mixture was filtered through a short column of Davasil[®] with hexanes and concentrated *in vacuo* to give a colorless oil as a $\geq 99:1$ mixture of regioisomers (as determined by gas chromatography). Purification by column chromatography (12:88 to 18:82 CH_2Cl_2 :hexanes) gave **18** (0.276 g, 79%) as a colorless oil: GC t_R = 20.14 ($50\text{--}290^\circ\text{C}$, $10^\circ\text{C}/\text{min}$); ^1H NMR (CDCl_3 , 500 MHz) δ 7.29 (m, 4H), 7.19 (m, 6H), 6.57 (d, $J = 2.0$, 1H), 6.12 (d, $J = 2.0$, 1H), 1.07 (s, 9H), 1.05 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 162.2, 141.7, 137.4, 128.8, 128.5, 128.4, 128.0, 127.9, 126.8, 123.7, 86.3, 28.3, 27.7, 22.2, 20.6; IR (thin film) 2931, 2856, 1557, 1472, 1037, 823 cm^{-1} ; HRMS (NH_3Cl) m/z calcd for $\text{C}_{23}\text{H}_{30}\text{OSi}$ (M)⁺ 350.2066, found 350.2064. Anal. Calcd for $\text{C}_{23}\text{H}_{30}\text{OSi}$: C, 78.80; H, 8.63. Found: C, 78.52; H, 8.77.

3b

2,2-Di-tert-butyl-4-phenyl-5-propyloxasilacyclopentene (3b).

The representative procedure for the two-step, one flask formation of oxasilacyclopentenes was followed with phenylacetylene (0.147 mL, 1.34 mmol), **1** (0.300 g, 1.34 mmol) and Ag_3PO_4 (0.056 g, 0.134 mmol) for 3 hours and butyraldehyde (0.362 mL, 4.02 mmol) and CuBr_2 (0.045 g, 0.201 mmol) for 12 hours to provide a 99:1 unpurified mixture of regioisomers. Purification by column chromatography (12:88 CH_2Cl_2 :hexanes) gave **3b** (0.335 g, 79%) as a colorless oil: GC t_R = 16.55 ($50\text{--}290^\circ\text{C}$, $10^\circ\text{C}/\text{min}$); ^1H NMR (CDCl_3 , 500 MHz) δ 7.35 (m, 4H), 7.29 (m, 1H), 6.10 (d, $J = 1.8$, 1H), 5.13 (dt, $J = 9.9, 2.0$, 1H), 1.62 (m, 2H), 1.48 (m, 1H), 1.29 (q, $J = 9.9$, 1H), 1.07 (s, 9H), 1.01 (s, 9H), 0.89 (t, $J = 7.2$, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 165.4, 138.8, 128.6, 128.0, 126.6, 121.2, 83.7, 38.8, 28.2, 27.6, 21.7, 20.2, 19.8, 14.3; IR (thin film) 2931, 2857, 1556, 1472, 823, 754 cm^{-1} ; HRMS (NH_3Cl) m/z calcd for $\text{C}_{20}\text{H}_{32}\text{OSi}$ (M)⁺ 316.2222, found 316.2211. Anal. Calcd for $\text{C}_{20}\text{H}_{32}\text{OSi}$: C, 75.88; H, 10.19. Found: C, 75.72; H, 10.12.

3c

2,2-Di-tert-butyl-4-phenyl-5,5-diethyloxasilacyclopentene (3c).

The representative procedure for the two-step, one flask formation of oxasilacyclopentenes was followed with phenylacetylene (0.110 mL, 1.00 mmol), **1** (0.225 g, 1.00 mmol) and Ag_3PO_4 (0.042 g, 0.100 mmol) for 3 hours and 3-pentanone (0.318 mL, 3.00 mmol) and CuBr_2 (0.033 g, 0.148 mmol) for 1 hour to provide a $\geq 99:1$ unpurified mixture of regioisomers. Purification by column chromatography (hexanes to 1:99 CH_2Cl_2 :hexanes) gave **3c** (0.282 g, 85%) as a colorless oil: GC t_R = 10.46 ($100\text{--}250^\circ\text{C}$, $10^\circ\text{C}/\text{min}$); ^1H NMR (CDCl_3 , 500 MHz) δ 7.27 (m, 5H), 5.70 (s, 1H), 1.77 (m, 4H), 1.07 (s, 18H), 0.84 (t, $J = 7.5$, 6H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 171.7, 142.4, 128.0, 127.9, 127.2, 122.9, 90.3, 31.7, 28.6, 20.7, 9.4; IR (thin film) 2932, 2856, 1563, 1472, 977, 821 cm^{-1} ; HRMS (NH_3Cl) m/z calcd for $\text{C}_{21}\text{H}_{34}\text{OSi}$ (M)⁺ 330.2379, found 330.2381. Anal. Calcd for $\text{C}_{21}\text{H}_{34}\text{OSi}$: C, 76.30; H, 10.37. Found: C, 76.23; H, 10.49.

3d**2,2-Di-tert-butyl-4-phenyl-5-phenyl-5-methyloxasilacyclopentene (3d).**

The representative procedure for the two-step, one flask formation of oxasilacyclopentenes was followed with phenylacetylene (0.660 mL, 6.01 mmol), **1** (1.35 g, 6.01 mmol) and Ag_3PO_4 (0.251 g, 0.600 mmol) for 3 hours and acetophenone (2.10 mL, 18.0 mmol) and CuBr_2 (0.201 g, 0.900 mmol) for 2.5 hour to provide a >95:5 unpurified mixture of regioisomers (as determined by ^1H NMR spectroscopy). Purification by column chromatography (15:85 CH_2Cl_2 :hexanes) gave **3d** (1.83 g, 83%) as a white solid: mp = 78–79 °C; GC t_R = 20.56 (50–290 °C, 10 °C/min); ^1H NMR (CDCl_3 , 500 MHz) δ 7.44 (m, 2H), 7.30 (m, 2H), 7.23 (m, 6H), 6.44 (s, 1H), 1.88 (s, 3H), 1.10 (s, 9H), 0.91 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 166.7, 145.9, 138.6, 128.5, 128.1, 127.9, 127.8, 127.4, 127.2, 124.3, 88.9, 29.2, 28.6, 28.6, 21.0, 20.8; IR (thin film) 3058, 2931, 2857, 1543, 1473, 951, 823 cm^{-1} ; HRMS (NH_3Cl) m/z calcd for $\text{C}_{24}\text{H}_{32}\text{OSi}$ (M) $^+$ 364.2222, found 364.2227. Anal. Calcd for $\text{C}_{24}\text{H}_{32}\text{OSi}$: C, 79.06; H, 8.85. Found: C, 79.27; H, 8.93.

3e**2,2-Di-tert-butyl-4-phenyl-5-phenylethynyl-5-methyloxasilacyclopentene (3e).**

The representative procedure for the two-step, one flask formation of oxasilacyclopentenes was followed with phenylacetylene (0.110 mL, 1.00 mmol), **1** (0.225 g, 1.00 mmol) and Ag_3PO_4 (0.042 g, 0.100 mmol) for 3 hours and 4-phenyl-3-butyne-2-one (0.437 mL, 3.00 mmol) and CuBr_2 (0.033 g, 0.148 mmol) for 1 hour to provide a $\geq 99:1$ unpurified mixture of regioisomers. Purification by column chromatography (15:85 CH_2Cl_2 :hexanes) gave **3e** (0.311 g, 80%) as a pale yellow oil: GC t_R = 15.09 (100–250 °C, 10 °C/min); ^1H NMR (CDCl_3 , 500 MHz) δ 7.76 (m, 2H), 7.44 (m, 2H), 7.32 (m, 6H), 6.20 (s, 1H), 1.72 (s, 3H), 1.16 (s, 9H), 1.10 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 164.9, 138.3, 131.7, 128.5, 128.4, 128.3, 128.2, 128.0, 123.4, 122.7, 92.9, 85.2, 81.3, 30.0, 28.4, 28.2, 20.9, 20.5; IR (thin film) 2963, 2857, 1598, 1472, 1092, 957, 824 cm^{-1} ; HRMS (NH_3Cl) m/z calcd for $\text{C}_{26}\text{H}_{32}\text{OSi}$ (M) $^+$ 388.2222, found 388.2222. Anal. Calcd for $\text{C}_{26}\text{H}_{32}\text{OSi}$: C, 80.36; H, 8.30. Found: C, 80.46; H, 8.32.

3f**2,2-Di-tert-butyl-4-phenyl-5-ethoxyoxasilacyclopentene (3f).**

The representative procedure for the two-step, one flask formation of oxasilacyclopentenes was followed with phenylacetylene (0.110 mL, 1.00 mmol), **1** (0.225 g, 1.00 mmol) and Ag_3PO_4 (0.042 g, 0.100 mmol) for 3 hours and ethyl formate (0.242 mL, 3.00 mmol) and CuBr_2 (0.033 g, 0.148 mmol) for 1 hour to provide a $\geq 99:1$ unpurified mixture of regioisomers. Purification by column chromatography (10:90 CH_2Cl_2 :hexanes to 15:95 CH_2Cl_2 :hexanes) gave **3f** as a colorless oil (0.217 g, 68%): GC t_R = 16.43 (50–290 °C, 10 °C/min); ^1H NMR (CDCl_3 , 500 MHz) δ 7.59 (m, 2H), 7.35 (m, 2H), 7.29 (m, 1H), 6.54 (d, J = 0.8, 1H), 5.98 (d, J = 0.8, 1H), 3.97 (dq, J = 9.7, 7.1, 1H), 3.75 (dq, J = 9.6, 7.1, 1H), 1.26 (t, J = 7.1, 3H), 1.08 (s, 9H), 1.02 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 158.7, 135.7, 128.7, 128.5, 126.8, 123.0, 104.4, 63.6, 28.2, 27.7, 20.7, 20.2, 15.7; IR (thin film) 2961, 2930, 2857, 1472, 1030, 824 cm^{-1} ; HRMS (NH_3Cl) m/z calcd for $\text{C}_{19}\text{H}_{30}\text{O}_2\text{Si}$ (M) $^+$ 318.2015, found 318.2010. Anal. Calcd for $\text{C}_{19}\text{H}_{30}\text{O}_2\text{Si}$: C, 71.64; H, 9.49. Found: C, 71.41; H, 9.50.

4

2,2-Di-tert-butyl-4-trimethylsilyl-5-propyloxasilacyclopentene (4).

The representative procedure for the two-step, one flask formation of oxasilacyclopentenes was followed with trimethylsilylacetylene (0.141 mL, 1.00 mmol), **1** (0.225 g, 1.00 mmol) and Ag_3PO_4 (0.042 g, 0.100 mmol) for 3 hours and butyraldehyde (0.270 mL, 3.00 mmol) and CuI (0.029 g, 0.152 mmol) for 10 hours to provide a 96:4 unpurified mixture of regioisomers. Purification by column chromatography (7:93 CH_2Cl_2 :hexanes) gave **4** (0.243 g, 78%) as a colorless oil: GC t_R = 12.39 (50–290 °C, 10 °C/min); ^1H NMR (CDCl_3 , 500 MHz) δ 6.36 (d, J = 2.2, 1H), 4.73 (dt, J = 2.5, 10.0, 1H), 1.69 (m, 1H), 1.60 (m, 1H), 1.50 (m, 1H), 1.29 (m, 1H), 0.99 (s, 9H), 0.95–0.93 (t, J = 7.4, 3H; s, 9H), 0.13 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 172.1, 135.7, 87.7, 39.6, 28.3, 27.7, 21.4, 19.8, 19.8, 14.3, –0.5; IR (thin film) 2958, 2856, 1472, 1250, 1005, 823 cm^{-1} ; HRMS (NH_3Cl) m/z calcd for $\text{C}_{17}\text{H}_{35}\text{OSi}_2$ ($\text{M}-\text{H}$) $^+$ 311.2227, found 311.2235. Anal. Calcd for $\text{C}_{17}\text{H}_{36}\text{OSi}_2$: C, 65.31; H, 11.61. Found: C, 65.03; H, 11.64.

5

N-Benzyl-N-(2,2-Di-tert-butyl-5-phenyl-5-methyl-4-methyloxasilacyclopentenyl)methylamine (5).

To a vessel fitted with an air-free seal containing Ag_3PO_4 (0.042 g, 0.100 mmol) and C_7H_8 (4.0 mL) was added *N*-methyl-*N*-propargylbenzylamine (0.169 mL, 1.00 mmol) by syringe, followed by **1** (0.225 g, 1.00 mmol). The reaction mixture was heated to 80 °C for 40 h, then the reaction mixture was cooled to 22 °C. Acetophenone (0.350 mL, 3.00 mmol) was added, followed by CuI (0.058 g, 0.30 mmol). The reaction mixture was then heated to 110 °C for 3 hours. The reaction mixture was then cooled to 22 °C and filtered through a short column of Davasil[®] with hexanes and concentrated *in vacuo* to give a colorless oil as a 90:10 mixture of regioisomers. Purification by column chromatography (50:50 CHCl_3 :hexanes) gave **5** (0.305 g, 72%) as a yellow oil: GC t_R = 22.90 (50–290 °C, 10 °C/min); ^1H NMR (CDCl_3 , 500 MHz) δ 7.43 (m, 2H), 7.34 (m, 4H), 7.25 (m, 3H), 7.20 (m, 2H), 6.33 (t, J = 1.5, 1H), 3.52 (d, J = 3.1, 2H), 3.14 (dd, J = 4.8, 1.5, 1H), 2.25 (s, 3H), 1.77 (s, 3H), 1.06 (s, 9H), 0.89 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 165.8, 145.6, 139.6, 129.0, 128.5, 127.9, 127.2, 127.1, 126.8, 121.5, 88.2, 62.5, 59.8, 42.9, 28.9, 28.7, 28.6, 20.8, 20.7; IR (thin film) 2934, 2857, 1495, 822 cm^{-1} ; HRMS (ES) m/z calcd for $\text{C}_{27}\text{H}_{40}\text{NOSi}$ ($\text{M}+\text{H}$) $^+$ 422.2879, found 422.2882. Anal. Calcd for $\text{C}_{27}\text{H}_{39}\text{NOSi}$: C, 76.90; H, 9.32; N, 3.32. Found: C, 76.66; H, 9.49; N, 3.31.

6a

2,2-Di-tert-butyl-3-methyl-4-phenyl-5-phenyl-5-methyloxasilacyclopentene (6a).

The representative procedure for the two-step, one flask formation of oxasilacyclopentenes was followed with 1-phenyl-1-propyne (0.125 mL, 1.00 mmol), **1** (0.225 g, 1.00 mmol) and Ag_3PO_4 (0.042 g, 0.100 mmol) for 1.5 hours and acetophenone (0.350 mL, 3.00 mmol) and $\text{Cu}(\text{OTf})_2$ (0.054 g, 0.149 mmol) for 1 hour to provide a 97:3 unpurified mixture of regioisomers. Purification by column chromatography (12:88 CH_2Cl_2 :hexanes) gave **6a** (0.355 g, 94%) as a white solid. Crystallization by slow evaporation of CH_2Cl_2 and CH_3CN afforded crystals suitable for X-ray crystallographic analysis (crystallographic data is provided, *vide infra*): mp 103–104 °C; GC t_R = 13.51 (100–250 °C, 10 °C/min); ^1H NMR (CDCl_3 , 500 MHz) δ 7.32 (m, 3H), 7.17 (m, 5H), 6.91 (m, 2H), 1.78 (s, 3H), 1.62 (s, 3H), 1.22 (s, 9H), 1.13 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 161.0, 145.6, 139.0, 130.8, 130.0, 128.1, 127.2, 127.0, 126.7, 126.4, 89.2, 31.5, 29.0, 28.7, 21.3, 21.1, 16.1; IR (thin film)

2932, 2857, 1473, 938, 822 cm^{-1} ; HRMS (NH_3Cl) m/z calcd for $\text{C}_{25}\text{H}_{35}\text{OSi}$ ($\text{M} + \text{H}$)⁺ 379.2457, found 379.2464. Anal. Calcd for $\text{C}_{25}\text{H}_{34}\text{OSi}$: C, 79.31; H, 9.05. Found: C, 79.39; H, 9.17.

6b

2,2-Di-tert-butyl-3-methyl-4-phenyl-5-propyloxasilacyclopentene (**6b**).

The representative procedure for the two-step, one flask formation of oxasilacyclopentenes was followed with 1-phenyl-1-propyne (0.168 mL, 1.34 mmol), **1** (0.300 g, 1.34 mmol) and Ag_3PO_4 (0.056 g, 0.134 mmol) for 1.5 hours and butyraldehyde (0.362 mL, 4.02 mmol) and $\text{Cu}(\text{OTf})_2$ (0.073 g, 0.202 mmol) for 13 hours to provide a 95:5 unpurified mixture of regioisomers. Purification by column chromatography (5:95 CH_2Cl_2 :hexanes) gave **6b** (0.237 g, 54%) as a colorless oil: GC t_R = 16.57 (major), 16.82 (minor) (50–290 $^\circ\text{C}$, 10 $^\circ\text{C}/\text{min}$); ^1H NMR (CDCl_3 , 500 MHz) δ 7.34 (m, 2H), 7.26 (m, 1H), 7.07 (m, 2H), 4.82 (ddd, J = 9.3, 3.1, 1.9, 1H), 1.77 (s, 3H), 1.50 (m, 1H), 1.37 (m, 2H), 1.24 (m, 1H), 1.10 (s, 9H), 1.06 (s, 9H), 0.82 (t, J = 7.3, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 158.1, 138.5, 129.2, 128.4, 128.4, 127.0, 85.3, 38.7, 28.3, 27.9, 22.1, 20.5, 19.6, 15.6, 14.3; IR (thin film) 2931, 2856, 1591, 1474, 822 cm^{-1} ; HRMS (NH_3Cl) m/z calcd for $\text{C}_{21}\text{H}_{34}\text{OSi}$ (M)⁺ 330.2379, found 330.2376. Anal. Calcd for $\text{C}_{21}\text{H}_{34}\text{OSi}$: C, 76.30; H, 10.37. Found: C, 76.18; H, 10.27.

7

2,2-Di-tert-butyl-3-methyl-4-triisopropylsiloxy-5-methyl-5-phenyloxasilacyclopentene (**7**).

The representative procedure for the two-step, one flask formation of oxasilacyclopentenes was followed with alkyne 4-triisopropylsilyloxy-2-butyne (0.227 g, 1.00 mmol), **1** (0.225 g, 1.00 mmol) and Ag_3PO_4 (0.042 g, 0.100 mmol) for 3 hours and acetophenone (0.350 mL, 3.00 mmol) and $\text{Cu}(\text{OTf})_2$ (0.054 g, 0.149 mmol) for 13 hours to provide a 99:1 unpurified mixture of regioisomers. Purification by column chromatography (15:85 CH_2Cl_2 :hexanes) gave **7** (0.447 g, 91%) as a colorless oil: GC t_R = 23.17 (50–290 $^\circ\text{C}$, 10 $^\circ\text{C}/\text{min}$); ^1H NMR (CDCl_3 , 500 MHz) δ 7.43 (m, 2H), 7.25 (m, 2H), 7.19 (m, 1H), 4.57 (d, J = 11.5, 1H), 4.27 (d, J = 11.6, 1H), 2.03 (s, 3H), 1.78 (s, 3H), 1.15–1.04 (m, 30H), 0.81 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 157.2, 147.1, 133.9, 128.0, 127.2, 127.1, 89.1, 59.6, 29.5, 28.9, 28.8, 21.2, 21.1, 18.7, 18.6, 12.5; IR (thin film) 2942, 2865, 1602, 1463, 1099, 822 cm^{-1} ; HRMS (NH_3Cl) m/z calcd for $\text{C}_{29}\text{H}_{51}\text{O}_2\text{Si}_2$ ($\text{M} - \text{H}$)⁺ 487.3422, found 487.3418. Anal. Calcd for $\text{C}_{29}\text{H}_{52}\text{O}_2\text{Si}_2$: C, 71.24; H, 10.72. Found: C, 71.34; H, 10.87.

8

2,3-Diphenyl-3-penten-2-ol (**8**).

To a mixture of $\text{KO}t\text{-Bu}$ (0.133 g, 1.19 mmol), 1-methyl-2-pyrrolidinone (3.0 mL), THF (2.0 mL) and toluene (2.0 mL) was added **8** (0.150 g, 0.396 mmol), followed by 1.19 mL of a 1.0 M solution of TBAF in THF. After 13 hours, a second portion of TBAF (1.19 mL) was added. After 31 hours, the reaction mixture was diluted with H_2O (15 mL) and extracted with MTBE (3 $\times$ 15 mL). The organic extracts were rinsed with H_2O (3 $\times$ 10 mL), dried with Na_2SO_4 , and concentrated *in vacuo*. Purification by column chromatography (80:20 CH_2Cl_2 :hexanes) provided **8** (0.079 g, 84%) as a colorless oil: ^1H NMR (CDCl_3 , 500 MHz) δ 7.48 (m, 2H), 7.36 (m, 2H), 7.30 (m, 1H), 7.25 (m, 3H), 6.83 (m, 2H), 6.02 (q, J = 6.8, 1H), 1.99 (br s, 1H), 1.73 (s, 3H), 1.50 (d, J = 6.8, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 147.7, 147.0, 138.2, 130.2, 128.1, 128.1, 127.1, 126.9, 126.0, 122.2, 77.4, 29.6, 15.0; IR (thin film) 3459, 3055, 2979, 2859, 1600, 1492 cm^{-1} ; LRMS (EI/GCMS) m/z calcd for $\text{C}_{17}\text{H}_{16}$ ($\text{M} - \text{H}_2\text{O}$)⁺ 220, found 220. Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{O}$: C, 85.67; H, 7.61. Found: C, 85.41; H, 7.74.

Diol **9** was constructed in two-steps from oxasilacyclopentene **6b** (Scheme S-1). Hydrogenation of **6b** provided intermediate **A** in 99:1 diastereoselectivity. Oxidation of **A** provided the 1,3-diol **9**. Proof of stereochemistry was established by formation and analysis of acetal **B**. Experimental procedures for these transformations follow:

Scheme S-1

(3*R**, 4*R**, 5*R**)-2,2-Di-*tert*-butyl-3-methyl-4-phenyl-5-propyloxasilacyclopentane (**A**).

To an oven-dried 50 mL round-bottom flask equipped with a magnetic stir-bar was added **6b** (0.134 g, 0.405 mmol) and ethanol (20 mL). The reaction mixture was sparged for 5 minutes with H_2 gas, followed by addition of 20% $\text{Pd}(\text{OH})_2$ on carbon (0.057 g, 0.081 mmol). The reaction mixture was allowed to stir for 4 days under a balloon of hydrogen gas, upon which more $\text{Pd}(\text{OH})_2$ on carbon (0.014 g, 0.020 mmol) was added. The reaction mixture was allowed to stir for 1 more day under a balloon of hydrogen gas. The reaction mixture was passed over a short column of silica and concentrated *in vacuo* to provide the unpurified product as a 99:1 mixture of diastereomers (as determined by gas chromatography). Purification by column chromatography (5:95 CH_2Cl_2 :hexanes) provided **A** (0.113 g, 84%) as a clear oil: GC t_R = 17.48 (50–290 $^\circ\text{C}$, 10 $^\circ\text{C}/\text{min}$); ^1H NMR (CDCl_3 , 500 MHz) δ 7.28 (t, J = 7.5, 2H), 7.19 (t, J = 7.4, 1H), 7.06 (d, J = 7.0, 2H), 4.24 (ddd, J = 10.5, 7.7, 2.0, 1H), 3.08 (dd, J = 11.0, 8.3, 1H), 1.61 (p, J = 8.2, 1H), 1.51 (m, 2H), 1.41 (m, 1H), 1.30 (m, 1H), 1.14 (s, 9H), 1.08 (s, 9H), 0.85 (t, J = 7.1, 3H), 0.78 (d, J = 8.2, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 140.1, 129.4, 128.4, 126.1, 78.4, 54.7, 37.8, 28.9, 28.4, 22.5, 20.9, 19.1, 14.4, 13.2; IR (thin film) 2959, 2857, 1471, 822 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{21}\text{H}_{35}\text{OSi}$ ($\text{M}-\text{H}$) $^+$ 331.2457, found 317.2451. Anal. Calcd for $\text{C}_{21}\text{H}_{36}\text{OSi}$: C, 75.84; H, 10.91. Found: C, 76.08; H, 11.03.

(1*R**, 2*S**, 3*R**)-3-Phenyl-2,4-heptanediol (**9**).

To a cooled (0 $^\circ\text{C}$) slurry of KH (0.031 g, 1.60 mmol) in 0.8 mL of 1-methyl-2-pyrrolidinone (NMP) was added *tert*-butylhydroperoxide (0.107 mL, 0.8 mmol, 70% in H_2O) dropwise by syringe (no needle). A solution of **A** (0.086 g, 0.259) was then added in 1.0 mL of a 50:50 mixture of THF:toluene followed by 2.60 mL of a 1.0 M solution of TBAF in THF. The reaction was warmed (75 $^\circ\text{C}$) for 7 h, cooled, and diluted with 4 mL of a 1.3 M aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$. The resulting mixture was extracted with MTBE (3 x 15 mL). The organic extracts were washed with H_2O (3 x 10 mL), dried with Na_2SO_4 , and concentrated *in vacuo*. Purification by column chromatography (1:99 MeOH: CH_2Cl_2 to 2:98 MeOH: CH_2Cl_2) provided **9** (0.048 g, 89%) as a colorless solid: mp 68.5–69.5 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 500 MHz) δ 7.31 (m, 2H), 7.25 (m, 3H), 4.42 (dq, J = 6.5, 3.0, 1H), 4.17 (m, 1H), 2.70 (br s, 1H), 2.65–2.59 (br s, 1H; dd, J = 8.7, 3.1, 1H), 1.50 (m, 1H), 1.32 (m, 3H), 1.06 (d, J

= 6.5, 3H), 0.84 (t, J = 7.1, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 139.5, 129.8, 128.6, 127.0, 73.1, 68.3, 57.6, 38.1, 21.0, 19.0, 14.1; IR (thin film) 3382 (br), 2960, 1454, 1138 cm^{-1} ; HRMS: (EI/GCMS) m/z calcd for $\text{C}_{13}\text{H}_{18}\text{O}$ ($\text{M}-\text{H}_2\text{O}$) $^+$ 190.1358, found 190.1352. Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{O}_2$: C, 74.96; H, 9.68. Found: C, 74.52; H, 9.64.

(2*R, 4*R**, 5*S**, 6*R**)-4-Methyl-2-(nitrophenyl)-5-phenyl-6-propyl-1,3-dioxane (B).**

A flask fitted with a Dean-Stark trap and reflux condenser was charged with diol **9** (0.029 g, 0.139 mmol) and 4-nitrobenzaldehyde (0.021 g, 0.139 mmol) in 9 mL of benzene. CSA (<0.005 g) was added and the solution was heated to reflux for 22 h. The solution was cooled to 22 °C and 2–3 drops of Et_3N were added. The solution was concentrated *in vacuo* to afford a yellow oil as a 63:37 mixture of diastereomers. Purification by column chromatography (18:82 CH_2Cl_2 :hexanes to 20:80 CH_2Cl_2 :hexanes) gave **B** (0.046 g, 97%) as a colorless oil in three portions: the major isomer as a 99:1 mixture of diastereomers (0.0196 g); the minor isomer as a 94:6 mixture of diastereomers (0.0102 g); and a 55:45 mixture of diastereomers (0.016 g): **mixture**: IR (thin film) 2933, 2871, 1608, 1523, 1348, 1146 cm^{-1} ; HRMS (EI/GCMS) m/z calcd for $\text{C}_{20}\text{H}_{22}\text{NO}_4$ ($\text{M}-\text{H}$) $^+$ 340.1543, found 340.1546. Anal. Calcd for $\text{C}_{20}\text{H}_{23}\text{NO}_4$: C, 70.36; H, 6.79; N, 4.10. Found: C, 70.16; H, 6.95; N, 4.05. **major isomer**: GC t_R = 15.51 (100–250 °C, 10 °C/min); ^1H NMR (CDCl_3 , 500 MHz) δ 8.27 (dt, J = 8.9, 2.1, 2H), 7.77 (m, 2H), 7.50 (d, J = 7.0, 2H), 7.30 (m, 2H), 7.26 (m, 1H), 5.99 (s, 1H), 4.55 (dtd, J = 6.4, 6.4, 3.3, 1H), 4.25 (dd, J = 9.6, 5.7, 1H), 2.47 (d, J = 2.7, 1H), 2.26 (dtd, J = 14.8, 9.5, 5.2, 1H), 1.70 (m, 1H), 1.57 (m, 1H), 1.46 (m, 1H), 1.03 (d, J = 6.0, 3H), 0.99 (t, J = 7.4, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 148.3, 146.0, 141.2, 129.6, 128.4, 127.6, 127.0, 123.8, 93.9, 78.6, 71.5, 48.0, 33.4, 19.7, 19.5, 14.1. **minor isomer**: GC t_R = 15.87 (100–250 °C, 10 °C/min); ^1H NMR (CDCl_3 , 500 MHz) δ 8.24 (dt, J = 2.1, 8.9, 2H), 7.73 (m, 2H), 7.33 (t, J = 7.4, 2H), 7.26 (m, 1H), 7.13 (m, 2H), 6.02 (s, 1H), 4.46 (m, 2H), 3.28 (dd, J = 5.7, 10.9, 1H), 1.51 (m, 4H), 1.29 (d, J = 7.0, 3H), 0.88 (t, J = 7.1, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 148.3, 146.1, 138.8, 129.0, 128.9, 127.5, 127.2, 123.6, 92.6, 74.9, 73.8, 50.2, 35.7, 18.6, 14.2, 13.7.

2,2-Di-tert-butyl-4-(3-triisopropylsilyloxy-1-propenyl)-5,5-diethyloxasilacyclopentene (11).

The representative procedure for the two-step, one flask formation of oxasilacyclopentenenes was followed with alkyne **10** (0.483 g, 2.02 mmol), **1** (0.54 g, 2.43 mmol) and Ag_3PO_4 (0.085 g, 0.203 mmol) for 3 hours and 3-pentanone (0.642 mL, 6.06 mmol) and CuI (0.058 g, 0.305 mmol) for 12 hours to provide a 98:2 unpurified mixture of regioisomers. Purification by column chromatography (8:92 CH_2Cl_2 :hexanes to 10:90 CH_2Cl_2 :hexanes) gave **11** (0.513 g, 54%) as a colorless oil: GC t_R = 21.54 (minor), 21.71 (major), (50–290 °C, 10 °C/min); ^1H NMR (CDCl_3 , 500 MHz) δ 6.23 (d, J = 15.5, 1H), 6.11 (dt, J = 15.4, 4.3, 1H), 5.87 (s, 1H), 4.33 (dd, J = 4.3, 1.9, 2H), 1.76 (dq, J = 14.7, 7.4, 2H), 1.60 (dq, J = 15.3, 7.7, 2H), 1.10 (m, 21H), 1.01 (s, 18H), 0.97 (t, J = 7.5, 6H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 167.3, 131.9, 125.6, 116.7, 89.1, 63.9, 31.6, 28.7, 20.7,

18.2, 12.3, 9.3; IR (thin film) 2943, 2864, 1550, 1472, 822 cm^{-1} ; LRMS (EI/GCMS) m/z calcd for $\text{C}_{25}\text{H}_{49}\text{O}_2\text{Si}_2$ ($\text{M} - \text{C}_2\text{H}_5$)⁺ 437, found 437.

12

2,2-Di-tert-butyl-4-(3-triisopropylsiloxy-1-propenyl)-5-phenyl-5-methyloxasilacyclopentene (12).

The representative procedure for the two-step, one flask formation of oxasilacyclopentenenes was followed with alkyne **10** (0.449 g, 1.88 mmol), **1** (0.507 g, 2.26 mmol), and Ag_3PO_4 (0.079 g, 0.188 mmol) for 3 hours and acetophenone (0.658 mL, 5.64 mmol) and CuI (0.054 g, 0.282 mmol) for 2 hours to provide a 89:11 unpurified mixture of regioisomers. Purification by column chromatography (10:90 CH_2Cl_2 :hexanes to 13:87 CH_2Cl_2 :hexanes) gave **12** in two portions (0.468 g, 50%, 96:4 mixture of regioisomers, and 0.073 g, 8%, 23:77 mixture of regioisomers favoring the minor isomer) each as a colorless oil: GC t_R = 24.42 (major), 24.52 (minor) (50–290 $^\circ\text{C}$, 10 $^\circ\text{C}/\text{min}$). **major isomer:** ^1H NMR (CDCl_3 , 500 MHz) δ 7.47 (m, 2H), 7.24 (m, 2H), 7.18 (m, 1H), 6.39 (dt, J = 15.7, 2.0, 1H), 6.21 (s, 1H), 6.06 (dt, J = 15.7, 4.5, 1H), 4.34 (dd, J = 4.5, 1.9, 2H), 1.76 (s, 3H), 1.06 (m, 30H), 0.78 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 163.8, 146.2, 132.9, 127.8, 127.2, 127.0, 126.3, 121.2, 88.1, 63.9, 29.5, 28.5, 28.3, 20.70, 20.69, 18.2, 12.3; IR (thin film) 2932, 2859, 1694, 1470, 943, 822 cm^{-1} ; HRMS (NH_3Cl) m/z calcd for $\text{C}_{29}\text{H}_{49}\text{O}_2\text{Si}_2$ ($\text{M} - \text{CH}_3$)⁺ 485.3271, found 485.3269. Anal. Calcd for $\text{C}_{30}\text{H}_{52}\text{O}_2\text{Si}_2$: C, 71.93; H, 10.46. Found: C, 71.95; H, 10.63.

13

Oxasilacyclopentane 13.

To a vessel fitted with an air-free seal was added **11** (0.459 g, 0.983 mmol) in toluene (5.0 mL) followed by *N*-phenylmaleimide (0.221 g, 1.28 mmol). The vessel was sealed and heated to 130 $^\circ\text{C}$ for 6 days. The reaction mixture was concentrated *in vacuo* to give a yellow oil as a 99:1 mixture of diastereomers (as determined by gas chromatography). Purification by column chromatography (20:80 CHCl_3 :hexanes to 50:50 CHCl_3 :hexanes) gave **13** (0.475 g, 76%) as a pale yellow solid: mp 47–51 $^\circ\text{C}$; GC t_R = 36.69 (50–290 $^\circ\text{C}$, 10 $^\circ\text{C}/\text{min}$, 35 min at 290 $^\circ\text{C}$); ^1H NMR (CDCl_3 , 500 MHz) δ 7.46 (m, 2H), 7.37 (m, 1H), 7.31 (m, 2H), 5.54 (dd, J = 3.2, 2.3, 1H), 4.06 (dd, J = 9.6, 4.9, 1H), 4.01 (dd, J = 9.6, 3.7, 1H), 3.49 (dd, J = 8.6, 6.2, 1H), 3.10 (t, J = 8.7, 1H), 2.45 (dt, J = 6.4, 3.7, 1H), 2.37 (m, 1H), 1.90 (h, J = 7.2, 1H), 1.68 (dq, J = 14.7, 7.3, 1H), 1.52 (m, 1H), 1.38 (dq, J = 13.9, 7.5, 1H), 1.16 (s, 9H), 1.08 (m, 30H), 0.98 (t, J = 7.4, 3H), 0.74 (t, J = 7.5, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 179.5, 178.4, 146.5, 132.2, 129.4, 128.7, 126.6, 118.4, 84.9, 64.9, 40.5, 39.5, 38.2, 31.7, 29.3, 28.9, 28.6, 22.0, 21.4, 20.7, 18.3, 18.2, 12.2, 9.4, 8.2; IR (thin film) 2942, 2865, 1716, 1376 cm^{-1} ; HRMS (ES) m/z calcd for $\text{C}_{37}\text{H}_{62}\text{NO}_4\text{Si}_2$ ($\text{M} + \text{H}$)⁺ 640.4218, found 640.4225. Anal. Calcd for $\text{C}_{37}\text{H}_{61}\text{NO}_4\text{Si}_2$: C, 69.43; H, 9.61; N, 2.19. Found: C, 69.26; H, 9.58; N, 2.17.

14**Oxasilacyclopentane 14.**

To a vessel fitted with an air-free seal was added **12** (0.230 g, 0.459 mmol) in toluene (2.3 mL) followed by *N*-phenylmaleimide (0.103 g, 0.595 mmol). The vessel was sealed and heated to 130° C for 9 days. The reaction mixture was concentrated *in vacuo* to give a yellow oil as a 4:1 mixture of *exo:endo* diastereomers (as determined by ¹H NMR spectroscopy). Purification by column chromatography (20:80 CHCl₃:hexanes to CHCl₃) gave **14** in two portions (0.080 g, 26%, as a 1.1:1 major:minor mixture of diastereomers as a colorless oil, and 0.132 g, 43%, as a ≥97:3 mixture of diastereomers as a colorless solid). Crystallization by slow evaporation of CHCl₃ and CH₃CN afforded crystals suitable for X-ray crystallographic analysis (vide infra): **major isomer**: ¹H NMR (CDCl₃, 500 MHz) δ 7.59 (d, *J* = 7.2, 2H), 7.45 (m, 3H), 7.31 (m, 3H), 7.25 (m, 2H), 5.70 (t, *J* = 2.5, 1H), 4.07 (dd, *J* = 9.7, 4.5, 1H), 3.95 (dd, *J* = 9.6, 3.3, 1H), 3.52 (dd, *J* = 8.8, 7.0, 1H), 3.13 (t, *J* = 9.1, 1H), 2.57 (p, *J* = 3.4, 1H), 2.34 (m, 1H), 1.70 (s, 3H), 1.22 (s, 9H), 1.05 (s, 9H), 0.88 (m, 21H); ¹³C NMR (CDCl₃, 125 MHz) δ 179.1, 178.3, 146.8, 145.8, 132.1, 129.4, 128.7, 128.0, 126.9, 126.6, 126.3, 121.6, 84.4, 64.2, 40.6, 40.3, 39.1, 32.7, 28.8, 28.6, 28.3, 22.4, 20.9, 18.2, 18.1, 12.1; IR (thin film) 2940, 2863, 1716, 1376 cm⁻¹; HRMS (ES) *m/z* calcd for C₄₀H₅₉NO₄Si₂Na (M+Na)⁺ 696.3881, found 696.3884. Anal. Calcd for C₄₀H₅₉NO₄Si₂: C, 71.27; H, 8.82; N, 2.08. Found: C, 71.16; H, 8.93; N, 2.04.

IV. Regiochemistry Assignment of Oxasilacyclopentenes by NOE

The regiochemistry was assigned using DPFSG–NOE experiments, X-ray crystallography, and by analogy with ^1H NMR spectroscopy as compared to similar substrates determined by the previous methods. In several cases, the minor regioisomer could be isolated in sufficient quantity to provide NOE's of both isomers. A summary of the aforementioned data follows:

NOE Experiments:

2,2-Di-*tert*-butyl-4-phenyl-5,5-diethyloxasilacyclopentene (**3c**)

Major Isomer:

H_b : δ 5.70 ppm

H_a irradiated: No NOE observed to H_b

2,2-Di-*tert*-butyl-3-phenyl-5,5-diethyloxasilacyclopentene (**3c'**)

Minor Isomer:

H_d : δ 7.02 ppm

H_c irradiated: 1.8% NOE observed to H_d

2,2-Di-*tert*-butyl-4,5-diphenyl-5-methyloxasilacyclopentene (**3d**)

Major Isomer:

H_b : δ 6.44 ppm

H_a irradiated: No NOE observed to H_b

2,2-Di-*tert*-butyl-3,5-diphenyl-5-methyloxasilacyclopentene (**3d'**)

Minor Isomer:

H_d : δ 7.37 ppm

H_c irradiated: 6.8% NOE observed to H_d

2,2-Di-*tert*-butyl-4-trimethylsilyl-5-propyloxasilacyclopentene (**4**)

H_a irradiated: 4.2% NOE observed to **H_b**

N-Benzyl-*N*-(2,2-Di-*tert*-butyl-5-phenyl-5-methyl-4-methyloxasilacyclopentenyl)methylamine (**5**)

H_a irradiated: 9.6% NOE observed to **H_b**, 12.1% NOE observed to **H_c**

2,2-Di-*tert*-butyl-3-methyl-4-triisopropylsilyloxymethyl-5-methyl-5-phenyloxasilacyclopentene (**7**)

H_a irradiated: 3.0% NOE observed to **H_b**

Major Regioisomer Determined by Analogy: ^1H NMR spectroscopic analysis of substrates **3c** and **3d** display a large difference between the chemical shift of the vinyl hydrogens for each regioisomer. Several determinations of major regioisomers were carried out by analogy to this data.

Entry	Substrate	R ₁	R ₂	δ H _a ^a	δ H _b	Major Regioisomer
1	3c ^b	Et	Et	5.70	7.02	1,2-regioisomer
2	3d ^b	Ph	Me	6.44	7.37	1,2-regioisomer
3	3a	Ph	H	6.57	7.03	1,2-regioisomer
4	3b	Pr	H	6.10	6.96	1,2-regioisomer
5	3e	-CCPh	Me	6.20	6.82	1,2-regioisomer
6	3f	-OEt	H	6.31	6.71	1,2-regioisomer

^a In all cases, the major regioisomer is represented in H_a. ^b Major regioisomer determined by NOE data, discussed above.

The relative stereochemistry of diol **9** was established by NOE experiments and coupling constants of acetal **B**.

(2*R**, 4*R**, 5*S**, 6*R**)-4-Methyl-2-(nitrophenyl)-5-phenyl-6-propyl-1,3-dioxane (**B**)

B-Major:

H_a irradiated: 3.6% NOE observed to H_b, 14.0% NOE observed to H_c

H_d is a d, $J_{Hc\text{ to } Hd} = 3.1$ Hz, $J_{He\text{ to } Hd} = \text{ca. } 0$ Hz

B-Minor:

H_f irradiated: 2.9% NOE observed to H_g, NOE to H_h is present, however δ of H_h overlaps with H_i.

H_j is a dd, $J_{Hi\text{ to } Hj} = 5.8$ Hz, $J_{Hh\text{ to } Hj} = 10.9$ Hz

V. References

- (1) Trost, B. M.; Imi, K.; Indolese, A. F. *J. Am. Chem. Soc.* **1993**, *115*, 8831–8832.
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- (4) Tsai, D. J. S.; Midland, M. M. *J. Am. Chem. Soc.* **1985**, *107*, 3915–3918.
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VI. X-Ray Crystallography Data:

X-ray Data Collection, Structure Solution and Refinement for **6a**.

A colorless crystal of approximate dimensions 0.14 x 0.22 x 0.24 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 $P2_1/c$ 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 included using a riding model. There were two molecules of the formula unit present. The space group was monoclinic with beta approximately 90° (emulates orthorhombic crystal system). It was necessary to treat the structure as a twin and refine using the TWIN command. At convergence, $wR2 = 0.2072$ and $Goof = 1.029$ for 489 variables refined against 7669 data (Å). As a comparison for refinement on F, $R1 = 0.0713$ for those 4778 data with $I > 2.0\sigma(I)$.

6a

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.

Definitions:

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

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

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

The thermal ellipsoid plot is shown at the 40% probability level.

Table 1. Crystal data and structure refinement for **6a**.

Identification code	kaw42	
Empirical formula	C ₂₅ H ₃₄ O Si	
Formula weight	378.61	
Temperature	163(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ / <i>c</i>	
Unit cell dimensions	<i>a</i> = 14.6527(7) Å	$\alpha = 90^\circ$.
	<i>b</i> = 41.0065(19) Å	$\beta = 90.0080(10)^\circ$.
	<i>c</i> = 7.4830(3) Å	$\gamma = 90^\circ$.
Volume	4496.2(3) Å ³	
<i>Z</i>	8	

Density (calculated)	1.119 Mg/m ³
Absorption coefficient	0.116 mm ⁻¹
F(000)	1648
Crystal size	0.24 x 0.22 x 0.14 mm ³
Theta range for data collection	1.39 to 24.71°.
Index ranges	-17 ≤ <i>h</i> ≤ 17, -48 ≤ <i>k</i> ≤ 48, -8 ≤ <i>l</i> ≤ 8
Reflections collected	39061
Independent reflections	7669 [R(int) = 0.0998]
Completeness to theta = 24.71°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9840 and 0.9727
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7669 / 0 / 489
Goodness-of-fit on F ²	1.029
Final R indices [I>2sigma(I)]	R1 = 0.0713, wR2 = 0.1695
R indices (all data; 0.85Å)	R1 = 0.1304, wR2 = 0.2072
Extinction coefficient	0.0012(5)
Largest diff. peak and hole	0.775 and -0.612 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **6a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	9658(1)	859(1)	7317(2)	36(1)
O(1)	9643(3)	1147(1)	5761(5)	34(1)
C(1)	9524(3)	1476(1)	6409(7)	26(1)
C(2)	9404(4)	1446(1)	8461(7)	33(1)
C(3)	9471(4)	1148(1)	9169(8)	42(2)
C(4)	10362(3)	1678(1)	5859(7)	29(1)
C(5)	11008(4)	1553(1)	4690(7)	32(1)
C(6)	11737(4)	1737(1)	4120(8)	38(1)
C(7)	11838(4)	2057(1)	4686(8)	37(1)
C(8)	11195(4)	2189(1)	5821(8)	38(1)
C(9)	10454(4)	2001(1)	6412(7)	30(1)
C(10)	8672(4)	1617(1)	5497(7)	35(1)
C(11)	9179(4)	1742(1)	9557(7)	35(1)
C(12)	9842(5)	1880(2)	10674(8)	50(2)
C(13)	9608(7)	2140(2)	11797(8)	65(2)
C(14)	8719(7)	2258(2)	11818(10)	69(2)
C(15)	8073(5)	2122(2)	10722(10)	62(2)
C(16)	8299(5)	1859(1)	9604(8)	46(2)
C(17)	9364(6)	1074(2)	11135(9)	81(3)
C(18)	8671(4)	570(1)	6935(8)	40(2)
C(19)	8718(5)	400(2)	5130(10)	67(2)
C(20)	8584(5)	318(2)	8438(10)	70(2)
C(21)	7790(4)	777(2)	6935(8)	49(2)
C(22)	10820(5)	653(2)	7322(16)	92(3)
C(23)	10888(6)	363(2)	8430(20)	176(7)
C(24)	11048(6)	547(2)	5219(14)	104(4)
C(25)	11529(4)	917(2)	7855(13)	79(3)
Si(2)	4869(1)	865(1)	2304(2)	35(1)
O(2)	4877(2)	1153(1)	750(5)	32(1)
C(31)	4980(3)	1480(1)	1410(7)	29(1)

C(32)	5112(4)	1455(1)	3453(7)	31(1)
C(33)	5059(4)	1155(1)	4145(7)	39(2)
C(34)	4156(3)	1683(1)	856(7)	29(1)
C(35)	3505(4)	1553(1)	-331(7)	34(1)
C(36)	2773(4)	1743(1)	-909(8)	42(1)
C(37)	2669(4)	2057(1)	-323(7)	38(1)
C(38)	3300(4)	2192(1)	850(8)	37(1)
C(39)	4038(4)	2003(1)	1401(7)	34(1)
C(40)	5825(4)	1628(1)	509(7)	36(1)
C(41)	5333(4)	1746(1)	4555(7)	37(1)
C(42)	4684(5)	1887(1)	5676(8)	45(2)
C(43)	4909(6)	2144(2)	6798(8)	59(2)
C(44)	5779(7)	2262(2)	6823(10)	68(2)
C(45)	6452(5)	2128(2)	5753(10)	59(2)
C(46)	6222(4)	1868(1)	4638(9)	46(2)
C(47)	5186(6)	1080(2)	6122(8)	74(2)
C(48)	5871(4)	582(1)	1908(7)	37(1)
C(49)	5941(5)	307(2)	3266(10)	66(2)
C(50)	5814(5)	434(2)	11(8)	54(2)
C(51)	6737(4)	787(1)	1981(8)	47(2)
C(52)	3706(5)	659(2)	2375(14)	79(3)
C(53)	3453(6)	518(2)	550(20)	164(7)
C(54)	3680(6)	384(2)	3730(20)	193(8)
C(55)	3012(4)	921(2)	2873(12)	70(2)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **6a**.

Si(1)-O(1)	1.658(4)
Si(1)-C(3)	1.843(6)
Si(1)-C(18)	1.891(6)
Si(1)-C(22)	1.901(8)
O(1)-C(1)	1.447(6)
C(1)-C(10)	1.534(7)
C(1)-C(4)	1.537(7)
C(1)-C(2)	1.551(7)

C(2)-C(3)	1.338(8)
C(2)-C(11)	1.500(8)
C(3)-C(17)	1.510(9)
C(4)-C(5)	1.387(7)
C(4)-C(9)	1.393(7)
C(5)-C(6)	1.375(7)
C(6)-C(7)	1.386(7)
C(7)-C(8)	1.380(8)
C(8)-C(9)	1.403(7)
C(11)-C(16)	1.377(8)
C(11)-C(12)	1.402(8)
C(12)-C(13)	1.399(9)
C(13)-C(14)	1.390(10)
C(14)-C(15)	1.371(10)
C(15)-C(16)	1.402(8)
C(18)-C(19)	1.522(9)
C(18)-C(20)	1.534(8)
C(18)-C(21)	1.547(8)
C(22)-C(23)	1.453(12)
C(22)-C(25)	1.552(10)
C(22)-C(24)	1.667(14)
Si(2)-O(2)	1.658(4)
Si(2)-C(33)	1.841(6)
Si(2)-C(48)	1.893(6)
Si(2)-C(52)	1.902(7)
O(2)-C(31)	1.436(6)
C(31)-C(34)	1.523(7)
C(31)-C(40)	1.534(7)
C(31)-C(32)	1.544(7)
C(32)-C(33)	1.339(7)
C(32)-C(41)	1.486(8)
C(33)-C(47)	1.521(8)
C(34)-C(39)	1.386(7)
C(34)-C(35)	1.408(7)
C(35)-C(36)	1.392(7)

C(36)-C(37)	1.372(8)
C(37)-C(38)	1.389(8)
C(38)-C(39)	1.392(7)
C(41)-C(42)	1.393(8)
C(41)-C(46)	1.397(8)
C(42)-C(43)	1.387(9)
C(43)-C(44)	1.364(10)
C(44)-C(45)	1.384(11)
C(45)-C(46)	1.394(8)
C(48)-C(51)	1.523(8)
C(48)-C(49)	1.524(8)
C(48)-C(50)	1.546(8)
C(52)-C(54)	1.517(11)
C(52)-C(55)	1.526(9)
C(52)-C(53)	1.531(15)

O(1)-Si(1)-C(3)	94.0(2)
O(1)-Si(1)-C(18)	109.3(2)
C(3)-Si(1)-C(18)	113.7(3)
O(1)-Si(1)-C(22)	109.2(3)
C(3)-Si(1)-C(22)	114.7(4)
C(18)-Si(1)-C(22)	114.0(3)
C(1)-O(1)-Si(1)	115.6(3)
O(1)-C(1)-C(10)	107.4(4)
O(1)-C(1)-C(4)	108.4(4)
C(10)-C(1)-C(4)	109.3(4)
O(1)-C(1)-C(2)	105.7(4)
C(10)-C(1)-C(2)	112.2(4)
C(4)-C(1)-C(2)	113.5(4)
C(3)-C(2)-C(11)	122.6(5)
C(3)-C(2)-C(1)	117.2(5)
C(11)-C(2)-C(1)	120.1(5)
C(2)-C(3)-C(17)	124.1(6)
C(2)-C(3)-Si(1)	107.5(4)
C(17)-C(3)-Si(1)	128.3(5)

C(5)-C(4)-C(9)	118.2(5)
C(5)-C(4)-C(1)	121.0(5)
C(9)-C(4)-C(1)	120.6(5)
C(6)-C(5)-C(4)	121.5(5)
C(5)-C(6)-C(7)	120.5(5)
C(8)-C(7)-C(6)	119.1(5)
C(7)-C(8)-C(9)	120.5(5)
C(4)-C(9)-C(8)	120.2(5)
C(16)-C(11)-C(12)	119.5(6)
C(16)-C(11)-C(2)	120.2(5)
C(12)-C(11)-C(2)	120.0(6)
C(13)-C(12)-C(11)	119.7(7)
C(14)-C(13)-C(12)	120.1(7)
C(15)-C(14)-C(13)	119.9(7)
C(14)-C(15)-C(16)	120.4(7)
C(11)-C(16)-C(15)	120.3(6)
C(19)-C(18)-C(20)	110.2(5)
C(19)-C(18)-C(21)	106.9(5)
C(20)-C(18)-C(21)	107.5(5)
C(19)-C(18)-Si(1)	112.8(4)
C(20)-C(18)-Si(1)	112.0(4)
C(21)-C(18)-Si(1)	107.1(4)
C(23)-C(22)-C(25)	112.1(8)
C(23)-C(22)-C(24)	108.2(9)
C(25)-C(22)-C(24)	106.9(7)
C(23)-C(22)-Si(1)	115.2(6)
C(25)-C(22)-Si(1)	106.9(5)
C(24)-C(22)-Si(1)	107.1(6)
O(2)-Si(2)-C(33)	93.6(2)
O(2)-Si(2)-C(48)	108.7(2)
C(33)-Si(2)-C(48)	113.3(3)
O(2)-Si(2)-C(52)	110.1(3)
C(33)-Si(2)-C(52)	113.6(4)
C(48)-Si(2)-C(52)	115.3(3)
C(31)-O(2)-Si(2)	115.2(3)

O(2)-C(31)-C(34)	109.4(4)
O(2)-C(31)-C(40)	107.6(4)
C(34)-C(31)-C(40)	107.7(4)
O(2)-C(31)-C(32)	107.0(4)
C(34)-C(31)-C(32)	113.9(4)
C(40)-C(31)-C(32)	111.1(5)
C(33)-C(32)-C(41)	122.5(5)
C(33)-C(32)-C(31)	115.9(5)
C(41)-C(32)-C(31)	121.6(5)
C(32)-C(33)-C(47)	123.6(5)
C(32)-C(33)-Si(2)	108.3(4)
C(47)-C(33)-Si(2)	128.1(4)
C(39)-C(34)-C(35)	117.2(5)
C(39)-C(34)-C(31)	122.4(5)
C(35)-C(34)-C(31)	120.3(5)
C(36)-C(35)-C(34)	120.5(5)
C(37)-C(36)-C(35)	120.7(5)
C(36)-C(37)-C(38)	120.1(5)
C(37)-C(38)-C(39)	118.9(5)
C(34)-C(39)-C(38)	122.5(5)
C(42)-C(41)-C(46)	117.4(6)
C(42)-C(41)-C(32)	121.3(6)
C(46)-C(41)-C(32)	121.0(5)
C(43)-C(42)-C(41)	121.2(7)
C(44)-C(43)-C(42)	120.0(6)
C(43)-C(44)-C(45)	121.1(7)
C(44)-C(45)-C(46)	118.6(7)
C(45)-C(46)-C(41)	121.7(6)
C(51)-C(48)-C(49)	109.2(5)
C(51)-C(48)-C(50)	107.1(5)
C(49)-C(48)-C(50)	108.9(5)
C(51)-C(48)-Si(2)	107.7(4)
C(49)-C(48)-Si(2)	113.7(4)
C(50)-C(48)-Si(2)	110.0(4)
C(54)-C(52)-C(55)	110.1(8)

C(54)-C(52)-C(53)	108.1(9)
C(55)-C(52)-C(53)	108.8(7)
C(54)-C(52)-Si(2)	111.8(6)
C(55)-C(52)-Si(2)	107.0(5)
C(53)-C(52)-Si(2)	111.1(7)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **6a**. 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)	41(1)	26(1)	41(1)	6(1)	0(1)	-6(1)
O(1)	47(2)	28(2)	27(2)	-2(2)	9(2)	-4(2)
C(1)	33(3)	21(3)	24(3)	0(2)	-1(2)	-3(2)
C(2)	38(3)	38(3)	22(3)	-2(2)	-3(2)	-10(3)
C(3)	59(4)	35(3)	32(3)	5(3)	-13(3)	-14(3)
C(4)	38(3)	31(3)	17(3)	5(2)	0(2)	1(2)
C(5)	42(3)	24(3)	29(3)	1(2)	2(3)	-2(2)
C(6)	44(3)	33(3)	37(3)	3(3)	7(3)	3(3)
C(7)	38(3)	38(3)	36(3)	4(3)	3(3)	-8(3)
C(8)	51(4)	29(3)	34(3)	3(3)	0(3)	-3(3)
C(9)	42(3)	24(3)	24(3)	1(2)	4(2)	-4(2)
C(10)	38(3)	37(3)	29(3)	9(3)	-4(2)	-9(2)
C(11)	52(4)	39(3)	14(3)	2(3)	3(3)	-17(3)
C(12)	81(5)	41(4)	26(3)	4(3)	-1(3)	-19(3)
C(13)	130(8)	45(4)	21(4)	1(3)	5(4)	-39(4)
C(14)	134(8)	34(4)	40(4)	-12(3)	40(5)	-27(5)
C(15)	92(6)	36(4)	58(5)	-4(4)	35(4)	-9(3)
C(16)	66(4)	33(3)	38(4)	-6(3)	18(3)	-17(3)
C(17)	161(8)	54(5)	28(4)	16(3)	-16(4)	-32(5)
C(18)	51(4)	37(3)	34(3)	4(3)	0(3)	-15(3)
C(19)	79(5)	62(5)	61(5)	-23(4)	-8(4)	7(4)
C(20)	70(5)	61(4)	79(5)	36(4)	-20(4)	-39(4)
C(21)	46(4)	57(4)	44(4)	-5(3)	1(3)	-14(3)
C(22)	53(5)	48(4)	176(10)	49(6)	0(6)	-9(3)

C(23)	62(6)	86(7)	380(20)	108(10)	-40(9)	-2(5)
C(24)	93(7)	78(6)	142(9)	-19(6)	67(6)	-10(5)
C(25)	35(4)	70(5)	133(8)	47(5)	-18(4)	-4(3)
Si(2)	43(1)	26(1)	35(1)	5(1)	2(1)	3(1)
O(2)	44(2)	26(2)	25(2)	-3(2)	-4(2)	3(2)
C(31)	37(3)	23(3)	25(3)	1(2)	0(2)	0(2)
C(32)	43(3)	31(3)	18(3)	2(2)	4(2)	6(2)
C(33)	64(4)	32(3)	22(3)	4(3)	6(3)	14(3)
C(34)	34(3)	25(3)	28(3)	5(2)	2(2)	5(2)
C(35)	45(4)	24(3)	34(3)	2(2)	-1(3)	1(2)
C(36)	43(4)	43(4)	39(3)	5(3)	-11(3)	3(3)
C(37)	33(3)	39(3)	41(4)	3(3)	-4(3)	6(3)
C(38)	48(4)	25(3)	39(3)	0(3)	-1(3)	10(3)
C(39)	42(3)	35(3)	24(3)	3(3)	-2(2)	-3(3)
C(40)	41(3)	40(3)	27(3)	1(3)	4(3)	2(3)
C(41)	54(4)	34(3)	22(3)	1(3)	-6(3)	13(3)
C(42)	73(5)	39(3)	23(3)	-3(3)	1(3)	17(3)
C(43)	114(7)	38(4)	25(3)	1(3)	6(4)	32(4)
C(44)	132(8)	29(4)	44(5)	0(3)	-35(5)	20(4)
C(45)	82(5)	37(4)	57(5)	-8(4)	-34(4)	15(3)
C(46)	59(4)	37(3)	41(4)	-3(3)	-18(3)	11(3)
C(47)	148(8)	46(4)	27(4)	11(3)	19(4)	30(4)
C(48)	49(4)	29(3)	33(3)	0(2)	2(3)	6(3)
C(49)	71(5)	65(5)	64(5)	31(4)	19(4)	33(4)
C(50)	76(5)	48(4)	37(4)	-11(3)	11(3)	-12(3)
C(51)	49(4)	49(4)	41(4)	-2(3)	4(3)	11(3)
C(52)	52(4)	39(4)	147(8)	38(5)	-2(5)	8(3)
C(53)	66(6)	86(7)	340(20)	-119(10)	-70(9)	19(5)
C(54)	49(5)	121(8)	410(20)	195(12)	28(8)	4(5)
C(55)	47(4)	65(5)	98(6)	41(5)	18(4)	6(3)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **6a**.

	x	y	z	U(eq)
H(5A)	10946	1335	4274	38
H(6A)	12173	1644	3331	46
H(7A)	12344	2183	4298	45
H(8A)	11254	2409	6205	45
H(9A)	10014	2094	7192	36
H(10A)	8778	1632	4207	52
H(10B)	8543	1834	5980	52
H(10C)	8150	1473	5722	52
H(12A)	10448	1798	10669	60
H(13A)	10058	2236	12546	78
H(14A)	8559	2432	12591	83
H(15A)	7469	2206	10720	74
H(16A)	7843	1762	8875	55
H(17A)	9316	1279	11803	122
H(17B)	9896	951	11556	122
H(17C)	8811	944	11322	122
H(19A)	8188	256	4992	101
H(19B)	9279	270	5061	101
H(19C)	8717	563	4175	101
H(20A)	8061	175	8200	105
H(20B)	8494	430	9580	105
H(20C)	9143	186	8495	105
H(21A)	7261	635	6738	73
H(21B)	7822	940	5978	73
H(21C)	7727	888	8089	73
H(23A)	11502	270	8323	264
H(23B)	10436	202	8041	264
H(23C)	10773	422	9682	264
H(24A)	11641	437	5169	157

H(24B)	11064	742	4466	157
H(24C)	10571	399	4783	157
H(25A)	12142	821	7848	119
H(25B)	11390	998	9055	119
H(25C)	11504	1097	6998	119
H(35A)	3564	1335	-741	41
H(36A)	2341	1653	-1718	50
H(37A)	2164	2184	-720	45
H(38A)	3229	2409	1270	45
H(39A)	4477	2097	2180	40
H(40A)	5720	1644	-782	54
H(40B)	6356	1489	736	54
H(40C)	5938	1846	996	54
H(42A)	4077	1806	5671	54
H(43A)	4457	2238	7550	71
H(44A)	5926	2440	7587	82
H(45A)	7057	2211	5779	70
H(46A)	6682	1772	3915	55
H(47A)	5254	1285	6786	111
H(47B)	5734	946	6284	111
H(47C)	4652	962	6568	111
H(49A)	6467	169	2976	99
H(49B)	5382	175	3230	99
H(49C)	6018	398	4466	99
H(50A)	6333	288	-180	81
H(50B)	5830	610	-877	81
H(50C)	5244	311	-111	81
H(51A)	7268	647	1772	70
H(51B)	6790	889	3160	70
H(51C)	6712	956	1059	70
H(53A)	2857	411	624	247
H(53B)	3916	359	183	247
H(53C)	3426	694	-335	247
H(54A)	3074	283	3721	290
H(54B)	3807	471	4924	290

H(54C)	4141	220	3421	290
H(55A)	2401	824	2920	105
H(55B)	3022	1095	1974	105
H(55C)	3166	1012	4045	105

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

C(3)-Si(1)-O(1)-C(1)	1.3(4)
C(18)-Si(1)-O(1)-C(1)	118.1(4)
C(22)-Si(1)-O(1)-C(1)	-116.6(5)
Si(1)-O(1)-C(1)-C(10)	-122.3(4)
Si(1)-O(1)-C(1)-C(4)	119.7(4)
Si(1)-O(1)-C(1)-C(2)	-2.3(5)
O(1)-C(1)-C(2)-C(3)	2.7(7)
C(10)-C(1)-C(2)-C(3)	119.5(5)
C(4)-C(1)-C(2)-C(3)	-116.0(5)
O(1)-C(1)-C(2)-C(11)	-174.5(4)
C(10)-C(1)-C(2)-C(11)	-57.7(6)
C(4)-C(1)-C(2)-C(11)	66.8(6)
C(11)-C(2)-C(3)-C(17)	-2.3(10)
C(1)-C(2)-C(3)-C(17)	-179.4(6)
C(11)-C(2)-C(3)-Si(1)	175.3(4)
C(1)-C(2)-C(3)-Si(1)	-1.9(6)
O(1)-Si(1)-C(3)-C(2)	0.4(4)
C(18)-Si(1)-C(3)-C(2)	-112.7(4)
C(22)-Si(1)-C(3)-C(2)	113.6(5)
O(1)-Si(1)-C(3)-C(17)	177.8(6)
C(18)-Si(1)-C(3)-C(17)	64.7(7)
C(22)-Si(1)-C(3)-C(17)	-68.9(7)
O(1)-C(1)-C(4)-C(5)	9.3(6)
C(10)-C(1)-C(4)-C(5)	-107.5(5)
C(2)-C(1)-C(4)-C(5)	126.5(5)
O(1)-C(1)-C(4)-C(9)	-175.9(5)
C(10)-C(1)-C(4)-C(9)	67.3(6)
C(2)-C(1)-C(4)-C(9)	-58.7(7)
C(9)-C(4)-C(5)-C(6)	1.8(8)
C(1)-C(4)-C(5)-C(6)	176.7(5)
C(4)-C(5)-C(6)-C(7)	-0.9(9)
C(5)-C(6)-C(7)-C(8)	-0.4(9)
C(6)-C(7)-C(8)-C(9)	0.8(8)

C(5)-C(4)-C(9)-C(8)	-1.4(8)
C(1)-C(4)-C(9)-C(8)	-176.3(5)
C(7)-C(8)-C(9)-C(4)	0.1(8)
C(3)-C(2)-C(11)-C(16)	-98.5(7)
C(1)-C(2)-C(11)-C(16)	78.5(7)
C(3)-C(2)-C(11)-C(12)	75.1(7)
C(1)-C(2)-C(11)-C(12)	-107.8(6)
C(16)-C(11)-C(12)-C(13)	-1.3(8)
C(2)-C(11)-C(12)-C(13)	-175.0(5)
C(11)-C(12)-C(13)-C(14)	0.7(9)
C(12)-C(13)-C(14)-C(15)	-0.7(10)
C(13)-C(14)-C(15)-C(16)	1.3(10)
C(12)-C(11)-C(16)-C(15)	1.9(8)
C(2)-C(11)-C(16)-C(15)	175.6(5)
C(14)-C(15)-C(16)-C(11)	-1.9(9)
O(1)-Si(1)-C(18)-C(19)	60.9(5)
C(3)-Si(1)-C(18)-C(19)	164.4(4)
C(22)-Si(1)-C(18)-C(19)	-61.6(6)
O(1)-Si(1)-C(18)-C(20)	-174.1(4)
C(3)-Si(1)-C(18)-C(20)	-70.6(5)
C(22)-Si(1)-C(18)-C(20)	63.4(6)
O(1)-Si(1)-C(18)-C(21)	-56.4(4)
C(3)-Si(1)-C(18)-C(21)	47.1(5)
C(22)-Si(1)-C(18)-C(21)	-178.9(5)
O(1)-Si(1)-C(22)-C(23)	-171.1(9)
C(3)-Si(1)-C(22)-C(23)	85.0(9)
C(18)-Si(1)-C(22)-C(23)	-48.6(11)
O(1)-Si(1)-C(22)-C(25)	63.5(7)
C(3)-Si(1)-C(22)-C(25)	-40.4(7)
C(18)-Si(1)-C(22)-C(25)	-174.0(6)
O(1)-Si(1)-C(22)-C(24)	-50.8(5)
C(3)-Si(1)-C(22)-C(24)	-154.7(4)
C(18)-Si(1)-C(22)-C(24)	71.8(5)
C(33)-Si(2)-O(2)-C(31)	-2.3(4)
C(48)-Si(2)-O(2)-C(31)	-118.3(4)

C(52)-Si(2)-O(2)-C(31)	114.5(4)
Si(2)-O(2)-C(31)-C(34)	-120.5(4)
Si(2)-O(2)-C(31)-C(40)	122.8(4)
Si(2)-O(2)-C(31)-C(32)	3.3(5)
O(2)-C(31)-C(32)-C(33)	-3.2(7)
C(34)-C(31)-C(32)-C(33)	117.8(5)
C(40)-C(31)-C(32)-C(33)	-120.4(5)
O(2)-C(31)-C(32)-C(41)	173.8(4)
C(34)-C(31)-C(32)-C(41)	-65.2(7)
C(40)-C(31)-C(32)-C(41)	56.6(6)
C(41)-C(32)-C(33)-C(47)	2.0(9)
C(31)-C(32)-C(33)-C(47)	178.9(6)
C(41)-C(32)-C(33)-Si(2)	-175.3(4)
C(31)-C(32)-C(33)-Si(2)	1.7(6)
O(2)-Si(2)-C(33)-C(32)	0.3(4)
C(48)-Si(2)-C(33)-C(32)	112.5(4)
C(52)-Si(2)-C(33)-C(32)	-113.5(4)
O(2)-Si(2)-C(33)-C(47)	-176.8(6)
C(48)-Si(2)-C(33)-C(47)	-64.7(7)
C(52)-Si(2)-C(33)-C(47)	69.4(7)
O(2)-C(31)-C(34)-C(39)	175.8(5)
C(40)-C(31)-C(34)-C(39)	-67.6(6)
C(32)-C(31)-C(34)-C(39)	56.1(7)
O(2)-C(31)-C(34)-C(35)	-7.8(7)
C(40)-C(31)-C(34)-C(35)	108.8(5)
C(32)-C(31)-C(34)-C(35)	-127.5(5)
C(39)-C(34)-C(35)-C(36)	-0.4(8)
C(31)-C(34)-C(35)-C(36)	-177.0(5)
C(34)-C(35)-C(36)-C(37)	-0.6(9)
C(35)-C(36)-C(37)-C(38)	0.4(9)
C(36)-C(37)-C(38)-C(39)	0.6(8)
C(35)-C(34)-C(39)-C(38)	1.4(8)
C(31)-C(34)-C(39)-C(38)	178.0(5)
C(37)-C(38)-C(39)-C(34)	-1.6(8)
C(33)-C(32)-C(41)-C(42)	-76.4(7)

C(31)-C(32)-C(41)-C(42)	106.8(6)
C(33)-C(32)-C(41)-C(46)	97.3(7)
C(31)-C(32)-C(41)-C(46)	-79.5(7)
C(46)-C(41)-C(42)-C(43)	1.5(8)
C(32)-C(41)-C(42)-C(43)	175.3(5)
C(41)-C(42)-C(43)-C(44)	-0.2(9)
C(42)-C(43)-C(44)-C(45)	-0.6(10)
C(43)-C(44)-C(45)-C(46)	0.2(10)
C(44)-C(45)-C(46)-C(41)	1.1(9)
C(42)-C(41)-C(46)-C(45)	-1.9(8)
C(32)-C(41)-C(46)-C(45)	-175.8(5)
O(2)-Si(2)-C(48)-C(51)	58.5(4)
C(33)-Si(2)-C(48)-C(51)	-44.1(5)
C(52)-Si(2)-C(48)-C(51)	-177.4(5)
O(2)-Si(2)-C(48)-C(49)	179.6(4)
C(33)-Si(2)-C(48)-C(49)	77.0(5)
C(52)-Si(2)-C(48)-C(49)	-56.3(6)
O(2)-Si(2)-C(48)-C(50)	-57.9(4)
C(33)-Si(2)-C(48)-C(50)	-160.5(4)
C(52)-Si(2)-C(48)-C(50)	66.2(5)
O(2)-Si(2)-C(52)-C(54)	177.7(8)
C(33)-Si(2)-C(52)-C(54)	-78.8(8)
C(48)-Si(2)-C(52)-C(54)	54.3(9)
O(2)-Si(2)-C(52)-C(55)	-61.7(7)
C(33)-Si(2)-C(52)-C(55)	41.8(7)
C(48)-Si(2)-C(52)-C(55)	174.9(5)
O(2)-Si(2)-C(52)-C(53)	56.9(6)
C(33)-Si(2)-C(52)-C(53)	160.4(5)
C(48)-Si(2)-C(52)-C(53)	-66.5(6)

X-ray Data Collection, Structure Solution and Refinement for **14**.

A colorless crystal of approximate dimensions 0.15 x 0.21 x 0.30 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. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and 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 either located from a difference-Fourier map and refined (x,y,z and U_{iso}) or were included using a riding model. Carbon atoms C(17)-C(25) were disordered and included using multiple components with partial site-occupancy-factors. At convergence, $wR2 = 0.1324$ and $Goof = 1.039$ for 563 variables refined against 8952 data. As a comparison for refinement on F , $R1 = 0.0487$ for those 6432 data with $I > 2.0\sigma(I)$.

References.

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Definitions:

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

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

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

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

Table 1. Crystal data and structure refinement for **14**.

Identification code	kaw53 (Tim Clark)	
Empirical formula	C ₄₀ H ₅₉ N O ₄ Si ₂	
Formula weight	674.06	
Temperature	163(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P $\bar{1}$	
Unit cell dimensions	a = 9.034(2) Å	α = 73.068(4)°.
	b = 14.237(4) Å	β = 89.726(5)°.
	c = 16.346(4) Å	γ = 73.451(4)°.
Volume	1920.7(9) Å ³	
Z	2	
Density (calculated)	1.165 Mg/m ³	
Absorption coefficient	0.132 mm ⁻¹	
F(000)	732	
Crystal size	0.30 x 0.21 x 0.15 mm ³	
Theta range for data collection	1.31 to 28.31°.	
Index ranges	-11 ≤ h ≤ 11, -18 ≤ k ≤ 18, -20 ≤ l ≤ 21	
Reflections collected	20133	
Independent reflections	8952 [R(int) = 0.0332]	
Completeness to theta = 28.31°	93.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9805 and 0.9615	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8952 / 0 / 563	
Goodness-of-fit on F ²	1.039	
Final R indices [I > 2sigma(I)]	R1 = 0.0487, wR2 = 0.1175	
R indices (all data)	R1 = 0.0749, wR2 = 0.1324	
Largest diff. peak and hole	0.677 and -0.773 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **14**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	270(1)	1832(1)	3378(1)	16(1)
Si(2)	-3926(1)	8085(1)	1985(1)	30(1)
O(1)	-2413(2)	2862(1)	960(1)	27(1)
O(2)	-1372(2)	5940(1)	54(1)	23(1)
O(3)	-545(1)	2052(1)	4249(1)	18(1)
O(4)	-2865(2)	6876(1)	2340(1)	25(1)
N(1)	-2061(2)	4446(1)	315(1)	19(1)
C(1)	-1180(2)	2985(1)	2599(1)	16(1)
C(2)	-808(2)	3544(1)	1701(1)	17(1)
C(3)	-1861(2)	3535(2)	981(1)	20(1)
C(4)	-1418(2)	5128(2)	541(1)	19(1)
C(5)	-885(2)	4687(1)	1492(1)	17(1)
C(6)	-2062(2)	5291(1)	1982(1)	17(1)
C(7)	-2038(2)	4674(1)	2906(1)	18(1)
C(8)	-1713(2)	3662(1)	3173(1)	16(1)
C(9)	-1787(2)	3004(1)	4099(1)	17(1)
C(10)	-2696(2)	4614(2)	-537(1)	20(1)
C(11)	-2047(2)	3905(2)	-964(1)	25(1)
C(12)	-2619(3)	4076(2)	-1796(1)	29(1)
C(13)	-3826(3)	4940(2)	-2193(1)	33(1)
C(14)	-4463(3)	5641(2)	-1762(1)	35(1)
C(15)	-3906(2)	5488(2)	-926(1)	28(1)
C(16)	-1734(2)	6304(2)	1922(1)	21(1)
C(17)	-5087(6)	8260(4)	2903(3)	25(2)
C(18)	-5869(6)	7367(4)	3208(3)	34(1)
C(19)	-4226(5)	8311(3)	3661(3)	29(1)
C(20)	-5063(3)	8479(2)	932(2)	36(1)
C(21)	-5068(4)	7596(3)	579(2)	44(1)
C(22)	-6726(5)	9138(3)	916(3)	52(1)
C(23)	-2542(3)	8946(2)	1851(2)	29(1)

C(24)	-1307(3)	8734(2)	1241(2)	35(1)
C(25)	-3489(4)	10075(2)	1584(2)	33(1)
C(17B)	-5265(12)	8181(8)	2906(7)	12(3)
C(18B)	-6214(12)	7499(8)	3093(7)	28(3)
C(19B)	-4197(11)	8025(8)	3733(6)	28(2)
C(20B)	-5503(10)	7920(7)	1132(6)	14(2)
C(21B)	-4662(13)	7718(8)	301(7)	23(2)
C(22B)	-6957(11)	8791(8)	905(6)	17(2)
C(23B)	-3166(11)	8946(7)	1469(6)	18(2)
C(24B)	-1432(14)	8658(9)	1782(8)	35(3)
C(25B)	-4104(15)	10081(9)	1494(8)	29(2)
C(26)	-1583(2)	3519(1)	4775(1)	19(1)
C(27)	-2742(2)	4378(2)	4844(1)	22(1)
C(28)	-2542(3)	4874(2)	5433(1)	27(1)
C(29)	-1204(3)	4506(2)	5980(1)	29(1)
C(30)	-69(3)	3637(2)	5941(1)	29(1)
C(31)	-256(2)	3148(2)	5340(1)	23(1)
C(32)	-3320(2)	2735(2)	4177(1)	22(1)
C(33)	77(2)	590(2)	3249(1)	22(1)
C(34)	1227(3)	-368(2)	3864(2)	31(1)
C(35)	-1565(3)	520(2)	3422(2)	30(1)
C(36)	344(3)	582(2)	2317(1)	29(1)
C(37)	2327(2)	1913(2)	3452(1)	22(1)
C(38)	3299(3)	1628(2)	2740(2)	32(1)
C(39)	3177(3)	1207(2)	4326(2)	31(1)
C(40)	2219(2)	3024(2)	3406(2)	27(1)

Table 3. Bond lengths [Å] and angles [°] for **14**.

Si(1)-O(3)	1.6680(14)
Si(1)-C(33)	1.896(2)
Si(1)-C(1)	1.8994(19)
Si(1)-C(37)	1.901(2)
Si(2)-C(23B)	1.598(9)
Si(2)-O(4)	1.6438(15)
Si(2)-C(20)	1.860(3)
Si(2)-C(17)	1.862(5)
Si(2)-C(17B)	1.938(10)
Si(2)-C(23)	1.956(3)
Si(2)-C(20B)	2.105(8)
O(1)-C(3)	1.209(2)
O(2)-C(4)	1.210(2)
O(3)-C(9)	1.449(2)
O(4)-C(16)	1.420(2)
N(1)-C(3)	1.395(2)
N(1)-C(4)	1.396(2)
N(1)-C(10)	1.436(2)
C(1)-C(8)	1.517(2)
C(1)-C(2)	1.539(3)
C(2)-C(3)	1.521(3)
C(2)-C(5)	1.543(3)
C(4)-C(5)	1.519(3)
C(5)-C(6)	1.545(2)
C(6)-C(7)	1.506(3)
C(6)-C(16)	1.529(3)
C(7)-C(8)	1.321(3)
C(8)-C(9)	1.542(3)
C(9)-C(26)	1.530(3)
C(9)-C(32)	1.534(3)
C(10)-C(11)	1.384(3)
C(10)-C(15)	1.385(3)
C(11)-C(12)	1.386(3)

C(12)-C(13)	1.379(3)
C(13)-C(14)	1.379(4)
C(14)-C(15)	1.392(3)
C(17)-C(19)	1.498(7)
C(17)-C(18)	1.582(7)
C(20)-C(22)	1.523(5)
C(20)-C(21)	1.529(4)
C(23)-C(24)	1.518(4)
C(23)-C(25)	1.522(4)
C(17B)-C(18B)	1.439(15)
C(17B)-C(19B)	1.589(14)
C(20B)-C(22B)	1.487(12)
C(20B)-C(21B)	1.613(14)
C(23B)-C(24B)	1.550(15)
C(23B)-C(25B)	1.609(14)
C(26)-C(31)	1.391(3)
C(26)-C(27)	1.398(3)
C(27)-C(28)	1.389(3)
C(28)-C(29)	1.382(3)
C(29)-C(30)	1.382(3)
C(30)-C(31)	1.394(3)
C(33)-C(34)	1.534(3)
C(33)-C(35)	1.535(3)
C(33)-C(36)	1.545(3)
C(37)-C(38)	1.533(3)
C(37)-C(40)	1.536(3)
C(37)-C(39)	1.542(3)

O(3)-Si(1)-C(33)	110.82(8)
O(3)-Si(1)-C(1)	94.26(7)
C(33)-Si(1)-C(1)	110.64(9)
O(3)-Si(1)-C(37)	107.41(8)
C(33)-Si(1)-C(37)	115.75(9)
C(1)-Si(1)-C(37)	115.75(9)
C(23B)-Si(2)-O(4)	120.0(3)

C(23B)-Si(2)-C(20)	81.7(4)
O(4)-Si(2)-C(20)	116.10(11)
C(23B)-Si(2)-C(17)	120.6(4)
O(4)-Si(2)-C(17)	102.97(18)
C(20)-Si(2)-C(17)	115.37(19)
C(23B)-Si(2)-C(17B)	125.9(5)
O(4)-Si(2)-C(17B)	101.2(3)
C(20)-Si(2)-C(17B)	111.6(3)
C(17)-Si(2)-C(17B)	6.2(4)
C(23B)-Si(2)-C(23)	25.0(3)
O(4)-Si(2)-C(23)	108.07(10)
C(20)-Si(2)-C(23)	106.60(13)
C(17)-Si(2)-C(23)	107.30(18)
C(17B)-Si(2)-C(23)	113.5(3)
C(23B)-Si(2)-C(20B)	108.6(4)
O(4)-Si(2)-C(20B)	98.1(2)
C(20)-Si(2)-C(20B)	27.2(2)
C(17)-Si(2)-C(20B)	103.2(3)
C(17B)-Si(2)-C(20B)	97.6(4)
C(23)-Si(2)-C(20B)	133.5(3)
C(9)-O(3)-Si(1)	115.75(11)
C(16)-O(4)-Si(2)	128.92(13)
C(3)-N(1)-C(4)	112.51(15)
C(3)-N(1)-C(10)	123.59(16)
C(4)-N(1)-C(10)	123.53(16)
C(8)-C(1)-C(2)	114.82(15)
C(8)-C(1)-Si(1)	100.41(12)
C(2)-C(1)-Si(1)	123.33(13)
C(3)-C(2)-C(1)	113.06(15)
C(3)-C(2)-C(5)	103.49(15)
C(1)-C(2)-C(5)	118.64(15)
O(1)-C(3)-N(1)	124.55(17)
O(1)-C(3)-C(2)	127.59(18)
N(1)-C(3)-C(2)	107.84(15)
O(2)-C(4)-N(1)	124.34(17)

O(2)-C(4)-C(5)	127.73(17)
N(1)-C(4)-C(5)	107.86(15)
C(4)-C(5)-C(2)	103.65(14)
C(4)-C(5)-C(6)	108.33(15)
C(2)-C(5)-C(6)	114.42(15)
C(7)-C(6)-C(16)	110.67(15)
C(7)-C(6)-C(5)	111.92(15)
C(16)-C(6)-C(5)	109.68(15)
C(8)-C(7)-C(6)	123.76(17)
C(7)-C(8)-C(1)	123.70(17)
C(7)-C(8)-C(9)	125.68(16)
C(1)-C(8)-C(9)	110.62(15)
O(3)-C(9)-C(26)	109.23(14)
O(3)-C(9)-C(32)	107.53(15)
C(26)-C(9)-C(32)	110.06(15)
O(3)-C(9)-C(8)	106.57(14)
C(26)-C(9)-C(8)	113.28(15)
C(32)-C(9)-C(8)	109.96(15)
C(11)-C(10)-C(15)	121.28(19)
C(11)-C(10)-N(1)	118.77(18)
C(15)-C(10)-N(1)	119.92(18)
C(10)-C(11)-C(12)	119.3(2)
C(13)-C(12)-C(11)	120.3(2)
C(14)-C(13)-C(12)	119.9(2)
C(13)-C(14)-C(15)	120.9(2)
C(10)-C(15)-C(14)	118.4(2)
O(4)-C(16)-C(6)	109.34(15)
C(19)-C(17)-C(18)	109.0(4)
C(19)-C(17)-Si(2)	115.9(3)
C(18)-C(17)-Si(2)	109.4(3)
C(22)-C(20)-C(21)	109.2(3)
C(22)-C(20)-Si(2)	113.7(2)
C(21)-C(20)-Si(2)	114.9(2)
C(24)-C(23)-C(25)	111.5(2)
C(24)-C(23)-Si(2)	113.40(19)

C(25)-C(23)-Si(2)	109.8(2)
C(18B)-C(17B)-C(19B)	110.9(9)
C(18B)-C(17B)-Si(2)	116.6(7)
C(19B)-C(17B)-Si(2)	107.1(6)
C(22B)-C(20B)-C(21B)	112.7(8)
C(22B)-C(20B)-Si(2)	112.9(6)
C(21B)-C(20B)-Si(2)	110.0(6)
C(24B)-C(23B)-Si(2)	111.0(7)
C(24B)-C(23B)-C(25B)	111.5(9)
Si(2)-C(23B)-C(25B)	113.0(7)
C(31)-C(26)-C(27)	117.96(18)
C(31)-C(26)-C(9)	121.50(17)
C(27)-C(26)-C(9)	120.54(17)
C(28)-C(27)-C(26)	120.94(19)
C(29)-C(28)-C(27)	120.25(19)
C(28)-C(29)-C(30)	119.64(19)
C(29)-C(30)-C(31)	120.2(2)
C(26)-C(31)-C(30)	120.99(19)
C(34)-C(33)-C(35)	107.81(18)
C(34)-C(33)-C(36)	108.89(17)
C(35)-C(33)-C(36)	108.04(17)
C(34)-C(33)-Si(1)	112.80(15)
C(35)-C(33)-Si(1)	109.89(14)
C(36)-C(33)-Si(1)	109.28(14)
C(38)-C(37)-C(40)	108.87(18)
C(38)-C(37)-C(39)	108.44(18)
C(40)-C(37)-C(39)	107.63(17)
C(38)-C(37)-Si(1)	114.24(14)
C(40)-C(37)-Si(1)	107.51(13)
C(39)-C(37)-Si(1)	109.95(14)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **14**. 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)	17(1)	16(1)	15(1)	-6(1)	1(1)	-3(1)
Si(2)	36(1)	26(1)	19(1)	-5(1)	7(1)	4(1)
O(1)	36(1)	28(1)	19(1)	-6(1)	-1(1)	-15(1)
O(2)	29(1)	21(1)	18(1)	-4(1)	7(1)	-7(1)
O(3)	20(1)	16(1)	15(1)	-4(1)	1(1)	-1(1)
O(4)	34(1)	20(1)	20(1)	-9(1)	8(1)	-3(1)
N(1)	22(1)	22(1)	13(1)	-5(1)	3(1)	-7(1)
C(1)	16(1)	19(1)	13(1)	-5(1)	2(1)	-4(1)
C(2)	17(1)	19(1)	13(1)	-6(1)	3(1)	-3(1)
C(3)	20(1)	23(1)	16(1)	-7(1)	6(1)	-5(1)
C(4)	18(1)	23(1)	15(1)	-8(1)	6(1)	-4(1)
C(5)	17(1)	19(1)	16(1)	-6(1)	4(1)	-7(1)
C(6)	19(1)	18(1)	15(1)	-6(1)	3(1)	-4(1)
C(7)	18(1)	21(1)	15(1)	-7(1)	4(1)	-4(1)
C(8)	14(1)	20(1)	12(1)	-6(1)	1(1)	-4(1)
C(9)	17(1)	19(1)	13(1)	-4(1)	2(1)	-1(1)
C(10)	21(1)	30(1)	11(1)	-4(1)	4(1)	-12(1)
C(11)	25(1)	30(1)	20(1)	-7(1)	3(1)	-11(1)
C(12)	32(1)	43(1)	20(1)	-13(1)	6(1)	-19(1)
C(13)	33(1)	55(2)	15(1)	-6(1)	1(1)	-23(1)
C(14)	25(1)	47(1)	21(1)	3(1)	-3(1)	-6(1)
C(15)	24(1)	36(1)	21(1)	-6(1)	4(1)	-6(1)
C(16)	25(1)	20(1)	19(1)	-7(1)	6(1)	-5(1)
C(26)	21(1)	20(1)	15(1)	-5(1)	6(1)	-7(1)
C(27)	22(1)	25(1)	17(1)	-5(1)	5(1)	-4(1)
C(28)	32(1)	25(1)	23(1)	-10(1)	8(1)	-3(1)
C(29)	40(1)	31(1)	20(1)	-13(1)	5(1)	-11(1)
C(30)	30(1)	35(1)	21(1)	-12(1)	-3(1)	-5(1)
C(31)	23(1)	23(1)	19(1)	-7(1)	0(1)	-2(1)
C(32)	19(1)	28(1)	18(1)	-6(1)	4(1)	-8(1)

C(33)	28(1)	19(1)	21(1)	-8(1)	3(1)	-6(1)
C(34)	41(1)	20(1)	29(1)	-5(1)	0(1)	-4(1)
C(35)	36(1)	28(1)	34(1)	-13(1)	7(1)	-17(1)
C(36)	36(1)	31(1)	24(1)	-15(1)	4(1)	-10(1)
C(37)	19(1)	24(1)	22(1)	-8(1)	0(1)	-4(1)
C(38)	22(1)	43(1)	34(1)	-17(1)	8(1)	-7(1)
C(39)	23(1)	32(1)	33(1)	-10(1)	-5(1)	-2(1)
C(40)	19(1)	30(1)	34(1)	-11(1)	1(1)	-10(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **14**.

	x	y	z	U(eq)
H(6A)	-3123	5455	1699	21
H(17A)	-5939	8921	2687	30
H(18A)	-6489	7461	3687	51
H(18B)	-5062	6702	3394	51
H(18C)	-6539	7383	2731	51
H(19A)	-4936	8403	4106	44
H(19B)	-3796	8892	3485	44
H(19C)	-3381	7671	3890	44
H(20A)	-4547	8923	512	43
H(21A)	-5686	7872	24	66
H(21B)	-5517	7116	983	66
H(21C)	-4002	7235	503	66
H(22A)	-7257	9319	345	79
H(22B)	-6722	9768	1046	79
H(22C)	-7268	8753	1346	79
H(23A)	-1996	8787	2428	34
H(24A)	-649	9183	1205	53
H(24B)	-1804	8867	670	53
H(24C)	-671	8014	1454	53
H(25A)	-2791	10502	1521	50
H(25B)	-4195	10202	2024	50
H(25C)	-4091	10248	1036	50
H(17B)	-5978	8899	2743	15
H(18D)	-6828	7607	3572	42
H(18E)	-5550	6785	3251	42
H(18F)	-6910	7639	2586	42
H(19D)	-4834	8058	4217	43
H(19E)	-3690	8569	3618	43
H(19F)	-3408	7354	3875	43

H(20B)	-5798	7288	1435	17
H(21D)	-5404	7643	-93	34
H(21E)	-3787	7088	480	34
H(21F)	-4284	8300	10	34
H(22D)	-7645	8677	506	26
H(22E)	-6711	9433	632	26
H(22F)	-7475	8838	1426	26
H(23B)	-3208	8958	854	22
H(24D)	-901	7958	1774	53
H(24E)	-1345	8697	2368	53
H(24F)	-953	9139	1401	53
H(25D)	-3587	10575	1171	43
H(25E)	-4133	10091	2091	43
H(25F)	-5165	10268	1236	43
H(1)	-2040(20)	2701(16)	2511(13)	20(5)
H(2)	200(20)	3215(15)	1577(13)	17(5)
H(5)	110(20)	4773(16)	1580(13)	18(5)
H(7)	-2310(20)	5078(16)	3281(14)	23(6)
H(11)	-1190(30)	3319(19)	-676(15)	33(6)
H(12)	-2200(30)	3581(18)	-2091(15)	28(6)
H(13)	-4240(30)	5052(19)	-2772(17)	39(7)
H(14)	-5240(30)	6250(20)	-1995(17)	38(7)
H(15)	-4330(30)	5996(19)	-614(16)	38(7)
H(16A)	-1700(20)	6677(17)	1339(15)	22(5)
H(16B)	-700(30)	6125(17)	2204(15)	28(6)
H(27)	-3700(30)	4623(18)	4476(15)	31(6)
H(28)	-3370(30)	5463(17)	5470(14)	25(6)
H(29)	-1060(30)	4851(17)	6376(15)	27(6)
H(30)	880(30)	3377(19)	6329(17)	42(7)
H(31)	520(20)	2552(17)	5322(14)	21(5)
H(32A)	-3290(20)	2249(17)	4731(15)	21(5)
H(32B)	-4180(30)	3339(18)	4119(14)	26(6)
H(32C)	-3470(30)	2406(18)	3738(16)	32(6)
H(34B)	2360(30)	-404(17)	3760(15)	28(6)
H(34C)	1030(30)	-980(20)	3774(18)	49(8)

H(34A)	1120(30)	-380(20)	4463(18)	40(7)
H(35B)	-1630(30)	-130(20)	3350(16)	38(7)
H(35A)	-2350(30)	1090(20)	3007(17)	36(7)
H(35C)	-1790(30)	518(19)	4040(17)	40(7)
H(36A)	210(30)	-50(20)	2237(16)	36(7)
H(36B)	1380(30)	619(18)	2158(16)	35(6)
H(36C)	-420(30)	1140(20)	1918(17)	36(7)
H(38C)	3480(30)	900(20)	2777(16)	35(6)
H(38A)	4310(30)	1760(20)	2774(17)	46(7)
H(38B)	2800(30)	2080(20)	2136(18)	42(7)
H(39A)	3430(30)	460(20)	4374(16)	35(6)
H(39B)	2580(30)	1333(18)	4807(16)	32(6)
H(39C)	4180(30)	1331(19)	4405(16)	40(7)
H(40A)	3260(30)	3083(18)	3480(16)	35(6)
H(40C)	1580(30)	3271(18)	3843(15)	30(6)
H(40B)	1720(30)	3539(19)	2828(17)	36(7)

Table 6. Torsion angles [°] for **14**.

C(33)-Si(1)-O(3)-C(9)	-120.79(13)
C(1)-Si(1)-O(3)-C(9)	-6.81(13)
C(37)-Si(1)-O(3)-C(9)	111.88(13)
C(23B)-Si(2)-O(4)-C(16)	-41.9(4)
C(20)-Si(2)-O(4)-C(16)	53.7(2)
C(17)-Si(2)-O(4)-C(16)	-179.3(2)
C(17B)-Si(2)-O(4)-C(16)	174.6(3)
C(23)-Si(2)-O(4)-C(16)	-65.96(19)
C(20B)-Si(2)-O(4)-C(16)	75.1(3)
O(3)-Si(1)-C(1)-C(8)	24.43(12)
C(33)-Si(1)-C(1)-C(8)	138.57(11)
C(37)-Si(1)-C(1)-C(8)	-87.23(13)
O(3)-Si(1)-C(1)-C(2)	153.59(14)
C(33)-Si(1)-C(1)-C(2)	-92.27(16)
C(37)-Si(1)-C(1)-C(2)	41.93(17)
C(8)-C(1)-C(2)-C(3)	-116.98(17)
Si(1)-C(1)-C(2)-C(3)	120.18(16)
C(8)-C(1)-C(2)-C(5)	4.4(2)
Si(1)-C(1)-C(2)-C(5)	-118.40(16)
C(4)-N(1)-C(3)-O(1)	174.35(18)
C(10)-N(1)-C(3)-O(1)	-12.4(3)
C(4)-N(1)-C(3)-C(2)	-7.3(2)
C(10)-N(1)-C(3)-C(2)	165.96(16)
C(1)-C(2)-C(3)-O(1)	-34.1(3)
C(5)-C(2)-C(3)-O(1)	-163.74(19)
C(1)-C(2)-C(3)-N(1)	147.59(15)
C(5)-C(2)-C(3)-N(1)	17.96(18)
C(3)-N(1)-C(4)-O(2)	175.62(17)
C(10)-N(1)-C(4)-O(2)	2.4(3)
C(3)-N(1)-C(4)-C(5)	-7.0(2)
C(10)-N(1)-C(4)-C(5)	179.74(16)
O(2)-C(4)-C(5)-C(2)	-164.91(18)
N(1)-C(4)-C(5)-C(2)	17.84(18)

O(2)-C(4)-C(5)-C(6)	73.2(2)
N(1)-C(4)-C(5)-C(6)	-104.08(16)
C(3)-C(2)-C(5)-C(4)	-21.12(17)
C(1)-C(2)-C(5)-C(4)	-147.27(16)
C(3)-C(2)-C(5)-C(6)	96.64(17)
C(1)-C(2)-C(5)-C(6)	-29.5(2)
C(4)-C(5)-C(6)-C(7)	156.33(15)
C(2)-C(5)-C(6)-C(7)	41.3(2)
C(4)-C(5)-C(6)-C(16)	-80.43(18)
C(2)-C(5)-C(6)-C(16)	164.51(16)
C(16)-C(6)-C(7)-C(8)	-154.07(18)
C(5)-C(6)-C(7)-C(8)	-31.4(2)
C(6)-C(7)-C(8)-C(1)	5.9(3)
C(6)-C(7)-C(8)-C(9)	-175.37(16)
C(2)-C(1)-C(8)-C(7)	8.6(3)
Si(1)-C(1)-C(8)-C(7)	143.03(16)
C(2)-C(1)-C(8)-C(9)	-170.36(15)
Si(1)-C(1)-C(8)-C(9)	-35.90(16)
Si(1)-O(3)-C(9)-C(26)	-136.17(12)
Si(1)-O(3)-C(9)-C(32)	104.41(14)
Si(1)-O(3)-C(9)-C(8)	-13.45(17)
C(7)-C(8)-C(9)-O(3)	-145.22(18)
C(1)-C(8)-C(9)-O(3)	33.68(18)
C(7)-C(8)-C(9)-C(26)	-25.1(3)
C(1)-C(8)-C(9)-C(26)	153.82(15)
C(7)-C(8)-C(9)-C(32)	98.5(2)
C(1)-C(8)-C(9)-C(32)	-82.57(18)
C(3)-N(1)-C(10)-C(11)	-53.1(2)
C(4)-N(1)-C(10)-C(11)	119.4(2)
C(3)-N(1)-C(10)-C(15)	128.8(2)
C(4)-N(1)-C(10)-C(15)	-58.7(2)
C(15)-C(10)-C(11)-C(12)	0.0(3)
N(1)-C(10)-C(11)-C(12)	-178.06(17)
C(10)-C(11)-C(12)-C(13)	-0.2(3)
C(11)-C(12)-C(13)-C(14)	0.3(3)

C(12)-C(13)-C(14)-C(15)	-0.2(3)
C(11)-C(10)-C(15)-C(14)	0.1(3)
N(1)-C(10)-C(15)-C(14)	178.16(18)
C(13)-C(14)-C(15)-C(10)	0.0(3)
Si(2)-O(4)-C(16)-C(6)	-130.19(15)
C(7)-C(6)-C(16)-O(4)	-58.7(2)
C(5)-C(6)-C(16)-O(4)	177.31(15)
C(23B)-Si(2)-C(17)-C(19)	-63.7(6)
O(4)-Si(2)-C(17)-C(19)	73.4(4)
C(20)-Si(2)-C(17)-C(19)	-159.1(3)
C(17B)-Si(2)-C(17)-C(19)	147(4)
C(23)-Si(2)-C(17)-C(19)	-40.5(4)
C(20B)-Si(2)-C(17)-C(19)	175.0(4)
C(23B)-Si(2)-C(17)-C(18)	172.6(5)
O(4)-Si(2)-C(17)-C(18)	-50.3(4)
C(20)-Si(2)-C(17)-C(18)	77.2(4)
C(17B)-Si(2)-C(17)-C(18)	24(4)
C(23)-Si(2)-C(17)-C(18)	-164.1(3)
C(20B)-Si(2)-C(17)-C(18)	51.4(4)
C(23B)-Si(2)-C(20)-C(22)	-105.1(4)
O(4)-Si(2)-C(20)-C(22)	135.5(2)
C(17)-Si(2)-C(20)-C(22)	14.9(3)
C(17B)-Si(2)-C(20)-C(22)	20.3(4)
C(23)-Si(2)-C(20)-C(22)	-104.1(3)
C(20B)-Si(2)-C(20)-C(22)	83.1(6)
C(23B)-Si(2)-C(20)-C(21)	128.0(4)
O(4)-Si(2)-C(20)-C(21)	8.6(3)
C(17)-Si(2)-C(20)-C(21)	-112.0(3)
C(17B)-Si(2)-C(20)-C(21)	-106.6(4)
C(23)-Si(2)-C(20)-C(21)	129.0(2)
C(20B)-Si(2)-C(20)-C(21)	-43.7(5)
C(23B)-Si(2)-C(23)-C(24)	-64.5(8)
O(4)-Si(2)-C(23)-C(24)	58.5(2)
C(20)-Si(2)-C(23)-C(24)	-67.0(2)
C(17)-Si(2)-C(23)-C(24)	168.9(3)

C(17B)-Si(2)-C(23)-C(24)	169.9(4)
C(20B)-Si(2)-C(23)-C(24)	-62.4(4)
C(23B)-Si(2)-C(23)-C(25)	61.0(8)
O(4)-Si(2)-C(23)-C(25)	-175.99(18)
C(20)-Si(2)-C(23)-C(25)	58.6(2)
C(17)-Si(2)-C(23)-C(25)	-65.6(3)
C(17B)-Si(2)-C(23)-C(25)	-64.6(4)
C(20B)-Si(2)-C(23)-C(25)	63.1(4)
C(23B)-Si(2)-C(17B)-C(18B)	160.4(8)
O(4)-Si(2)-C(17B)-C(18B)	-59.0(8)
C(20)-Si(2)-C(17B)-C(18B)	65.1(8)
C(17)-Si(2)-C(17B)-C(18B)	-166(5)
C(23)-Si(2)-C(17B)-C(18B)	-174.5(7)
C(20B)-Si(2)-C(17B)-C(18B)	40.9(8)
C(23B)-Si(2)-C(17B)-C(19B)	-74.6(8)
O(4)-Si(2)-C(17B)-C(19B)	65.9(6)
C(20)-Si(2)-C(17B)-C(19B)	-170.0(5)
C(17)-Si(2)-C(17B)-C(19B)	-41(4)
C(23)-Si(2)-C(17B)-C(19B)	-49.6(7)
C(20B)-Si(2)-C(17B)-C(19B)	165.8(6)
C(23B)-Si(2)-C(20B)-C(22B)	-73.9(7)
O(4)-Si(2)-C(20B)-C(22B)	160.6(6)
C(20)-Si(2)-C(20B)-C(22B)	-65.3(7)
C(17)-Si(2)-C(20B)-C(22B)	55.2(7)
C(17B)-Si(2)-C(20B)-C(22B)	58.1(7)
C(23)-Si(2)-C(20B)-C(22B)	-74.8(7)
C(23B)-Si(2)-C(20B)-C(21B)	52.9(7)
O(4)-Si(2)-C(20B)-C(21B)	-72.5(6)
C(20)-Si(2)-C(20B)-C(21B)	61.5(6)
C(17)-Si(2)-C(20B)-C(21B)	-178.0(6)
C(17B)-Si(2)-C(20B)-C(21B)	-175.1(6)
C(23)-Si(2)-C(20B)-C(21B)	52.0(7)
O(4)-Si(2)-C(23B)-C(24B)	-31.3(9)
C(20)-Si(2)-C(23B)-C(24B)	-146.7(8)
C(17)-Si(2)-C(23B)-C(24B)	98.7(7)

C(17B)-Si(2)-C(23B)-C(24B)	102.7(8)
C(23)-Si(2)-C(23B)-C(24B)	35.6(7)
C(20B)-Si(2)-C(23B)-C(24B)	-142.7(7)
O(4)-Si(2)-C(23B)-C(25B)	-157.4(6)
C(20)-Si(2)-C(23B)-C(25B)	87.2(7)
C(17)-Si(2)-C(23B)-C(25B)	-27.4(9)
C(17B)-Si(2)-C(23B)-C(25B)	-23.4(10)
C(23)-Si(2)-C(23B)-C(25B)	-90.4(10)
C(20B)-Si(2)-C(23B)-C(25B)	91.2(8)
O(3)-C(9)-C(26)-C(31)	8.3(2)
C(32)-C(9)-C(26)-C(31)	126.15(19)
C(8)-C(9)-C(26)-C(31)	-110.3(2)
O(3)-C(9)-C(26)-C(27)	-171.35(16)
C(32)-C(9)-C(26)-C(27)	-53.5(2)
C(8)-C(9)-C(26)-C(27)	70.0(2)
C(31)-C(26)-C(27)-C(28)	2.8(3)
C(9)-C(26)-C(27)-C(28)	-177.49(18)
C(26)-C(27)-C(28)-C(29)	-1.8(3)
C(27)-C(28)-C(29)-C(30)	-0.5(3)
C(28)-C(29)-C(30)-C(31)	1.5(3)
C(27)-C(26)-C(31)-C(30)	-1.8(3)
C(9)-C(26)-C(31)-C(30)	178.58(19)
C(29)-C(30)-C(31)-C(26)	-0.4(3)
O(3)-Si(1)-C(33)-C(34)	-76.90(16)
C(1)-Si(1)-C(33)-C(34)	179.91(15)
C(37)-Si(1)-C(33)-C(34)	45.71(18)
O(3)-Si(1)-C(33)-C(35)	43.42(17)
C(1)-Si(1)-C(33)-C(35)	-59.77(17)
C(37)-Si(1)-C(33)-C(35)	166.03(14)
O(3)-Si(1)-C(33)-C(36)	161.82(14)
C(1)-Si(1)-C(33)-C(36)	58.63(16)
C(37)-Si(1)-C(33)-C(36)	-75.57(17)
O(3)-Si(1)-C(37)-C(38)	174.49(15)
C(33)-Si(1)-C(37)-C(38)	50.09(19)
C(1)-Si(1)-C(37)-C(38)	-81.76(17)

O(3)-Si(1)-C(37)-C(40)	-64.58(15)
C(33)-Si(1)-C(37)-C(40)	171.03(13)
C(1)-Si(1)-C(37)-C(40)	39.17(17)
O(3)-Si(1)-C(37)-C(39)	52.31(15)
C(33)-Si(1)-C(37)-C(39)	-72.08(16)
C(1)-Si(1)-C(37)-C(39)	156.07(13)

Chemical reaction scheme showing the synthesis of compound **2b** from compound **1**.

Compound **1** (a bicyclic silane) reacts with Ag_3PO_4 (10 mol%) in C_6D_6 at 22°C for 31 h to yield compound **2b** (a bicyclic silane with two ethyl groups).

¹H NMR spectrum of compound **2b** in CDCl_3 is shown. The spectrum displays peaks corresponding to the structure, with integration values provided for several signals.

¹³C NMR spectrum of compound **2b** in CDCl_3 is shown. The spectrum displays peaks corresponding to the structure, with integration values provided for several signals.

Current Data Parameters:

- USER: tclark
- EXPNO: TC-111-01-14
- PROCNO: 1

F2 - Acquisition Parameters:

- Date_: 20030730
- Time: 12.00
- INSTRUM: spect
- PROBHD: 5 mm broadband
- PULPROG: zg30
- TD: 65536
- SOLVENT: CDCl3
- RG: 32
- SWH: 8012.820 Hz
- FIDRES: 0.122266 Hz
- AQ: 4.084966 sec
- RG: 32
- DW: 62.400 usec
- DE: 4.00 usec
- TE: 300.2 K
- DELTA: 0.1000000 sec

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

- MVCL: 1H
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- PL2: 0.00 usec
- PL3: 0.00 usec
- PL4: 0.00 usec
- PL5: 0.00 usec
- PL6: 0.00 usec
- PL7: 0.00 usec
- PL8: 0.00 usec
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- PL199: 0.00 usec
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TC-III-63-2 (2.5 h at RT)
1H spectrum

TC-III-83-2 (1.25 h at RT)
1H spectrum

TC-III-114-2
1H spectrum

TC-III-131-2 (2.7 h at RT)
¹H spectrum

TC-III-130-Z (2.75 h at RT)
¹H spectrum

VIII. Selected Spectra

¹H spectrum

TC-IV-149-2
¹³C spectrum with ¹H decoupling

TC-IV-151-2
¹³C spectrum with ¹H decoupling

TTC-IV-80-3b (major diastereomer)
¹H spectrum

tc-IV-37c10210039_130615

10/21/2003 07:03:09 PM

tclark

RT: 19.64 - 21.27

RT: 20.07
AA: 3971930229NL:
2.18E9
TIC MS
ICIS
tc-IV-
37c1021003
9_130615 tc-IV-
37c10210039_130615#1353
RT: 19.93 AV: 1 NL: 6.76E6
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00] tc-IV-
37c10210039_130615#1364
RT: 20.07 AV: 1 NL: 1.80E8
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00] tc-IV-
37c10210039_130615#1428
RT: 20.90 AV: 1 NL: 1.97E6
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-16c09300079_111346

09/30/2003 05:29:58 PM

tr 3rk

RT: 15.75 - 17.52

NL: 1.44E9
TIC MS
ICIS
tc-IV-
16c0930007
9_111346

tc-IV-
16c09300079_111346#1088
RT: 16.52 AV: 1 NL: 1.94E8
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-
16c09300079_111346#1124
RT: 16.98 AV: 1 NL: 2.38E6
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-36c10210038_130615

10/21/2003 06:31:27 PM

tclark

RT: 17.28 - 17.78

NL:
3.51E9
TIC MS
ICIS
tc-IV-
36c1021003
8_130615

tc-IV-
36c10210038_130615#1167
RT: 17.53 AV: 1 NL: 2.22E8
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-
36c10210038_130615#1172
RT: 17.60 AV: 1 NL: 4.71E6
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-31-110160080_182822

10/16/2003 07:50:30 PM

tclark

RT: 21.80 - 22.68

RT: 22.24
MA: 6428998058NL:
2.76E9
TIC MS
tc-IV-31-
110160080-
182822tc-IV-31-
110160080_182822#1532
RT: 22.24 AV: 1 NL: 1.94E8
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00] tc-IV-31-
110160080_182822#1504
RT: 21.88 AV: 1 NL: 3.75E6
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-48c10310059_182234

11/03/2003 09:46:30 AM

tclark

RT: 16.17 - 16.72

NL:
2.70E9
TIC MS
ICIS
tc-IV-
48c1031005
9_182234

tc-IV-
48c10310059_182234#1097
RT: 16.63 AV: 1 NL: 7.60E5
T: (0,0) + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-
48c10310059_182234#1081
RT: 16.43 AV: 1 NL: 2.04E8
T: (0,0) + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-60c11120069_095433

11/12/2003 10:22:40 AM

tclark

RT: 10.55 - 13.99

RT: 12.35
AA: 6749585996NL:
3.53E9
TIC MS
ICIS
tc-IV-
60c1112006
9_095433

4

96:4

Relative Abundance

tc-IV-
60c11120069_095433#693
RT: 11.42 AV: 1 NL: 2.84E7
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00] tc-IV-
60c11120069_095433#765
RT: 12.35 AV: 1 NL: 2.48E8
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-77c12080124_175421

12/08/2003 07:13:00 PM

tclark

RT: 22.82 - 24.18

RT: 22.90

MA: 4438759270

NL:
2.28E9
TIC MS
tc-IV-
77c1208012
4_175421 tc-IV-
77c12080124_175421#1583
RT: 22.90 AV: 1 NL: 2.50E8
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00] tc-IV-
77c12080124_175421#1644
RT: 23.68 AV: 1 NL: 4.01E7
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-52c11040009_182533

11/04/2003 06:53:50 PM

TIC MS

RT: 19.47 - 22.13

RT: 20.56
AA: 2094717194NL:
1.17E9
TIC MS
ICIS
tc-IV-
52c1104000
9_182533

Relative Abundance

97:3

Relative Abundance

321.1

tc-IV-
52c11040009_182533#1402
RT: 20.56 AV: 1 NL: 1.98E8
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

137.0

279.0

243.1

145.1

323.2

363.1

364.2

425.9

551.2

623.1

tc-IV-
52c11040009_182533#1422
RT: 20.82 AV: 1 NL: 3.55E6
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

137.0

279.1

205.1

322.2

323.2

363.2

379.2

542.3

623.6

m/z

tc-IV-17c09300080_111346

09/30/2003 06:01:42 PM

tclark

RT: 14.36 - 21.83

NL: 1.93E9
TIC MS
ICIS
tc-IV-
17c09300080
0_111346

tc-IV-
17c09300080_111346#1092
RT: 16.57 AV: 1 NL: 2.03E8
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-
17c09300080_111346#1112
RT: 16.82 AV: 1 NL: 1.68E7
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-62c11210005_120957

11/21/2003 12:28:58 PM

tclark

RT: 22.53 - 23.79

NL:
1.58E8
TIC MS
ICIS
tc-IV-
62c1121000
5_120957

tc-IV-
62c11210005_120957#1532
RT: 22.74 AV: 1 NL: 2.84E5
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-
62c11210005_120957#1561
RT: 23.11 AV: 1 NL: 2.22E7
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-151c02200052_113918

02/20/2004 12:39:48 PM

tclark

RT: 20.76 - 22.60

NL:
1.62E9
TIC MS
ICIS
tc-IV-
151c022000
52_113918

tc-IV-
151c02200052_113918#1478
RT: 21.54 AV: 1 NL: 3.18E6
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-
151c02200052_113918#1491
RT: 21.71 AV: 1 NL: 1.05E8
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-49c10310060_182234

11/03/2003 10:18:10 AM

tclark

RT: 23.85 - 25.09

NL:
8.32E7
TIC MS
ICIS
tc-IV-
49c1031006
0_182234

tc-IV-
49c10310060_182234#1661
RT: 24.40 AV: 1 NL: 4.56E6
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-
49c10310060_182234#1669
RT: 24.51 AV: 1 NL: 6.20E5
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-152c02270058_190525

02/27/2004 07:18:35 PM

tclark

RT: 34.28 - 37.55

RT: 35.53
MA: 604416672NL:
8.56E7
TIC MS
tc-IV-
152c022700
58_190525 tc-IV-
152c02270058_190525#2552
RT: 35.91 AV: 1 NL: 8.52E5
T: (0,0) + c EI det=349.00
Full ms [50.00-750.00] tc-IV-
152c02270058_190525#2523
RT: 35.53 AV: 1 NL: 7.19E6
T: (0,0) + c EI det=349.00
Full ms [50.00-750.00]

tc-IV-34c10250007_172332

10/25/2003 05:23:46 PM

tclark

RT: 16.15 - 18.36

tc-IV-
34c10250007_172332#1091
RT: 16.55 AV: 1 NL: 6.59E5
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-
34c10250007_172332#1148
RT: 17.29 AV: 1 NL: 2.22E5
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]

tc-IV-
34c10250007_172332#1161
RT: 17.46 AV: 1 NL: 3.12E7
T: {0,0} + c EI det=349.00
Full ms [50.00-650.00]