

# Synthesis of Bridgehead Allylsilanes and Stereoselective Reactions with Aldehydes

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## Experimental Section

**Instrumentation:** NMR measurements were conducted with Bruker instruments at 500 MHz for proton spectra and 125 MHz for carbon spectra. Chemical shifts are given in ppm values referenced to residual solvent peaks.<sup>1</sup> IR spectra were performed on a Perkin Elmer 1600 Series FTIR or MIDAC Prospect FT-IR spectrometer. High resolution mass spectral data were collected on a TOF instrument using electrospray ionization.

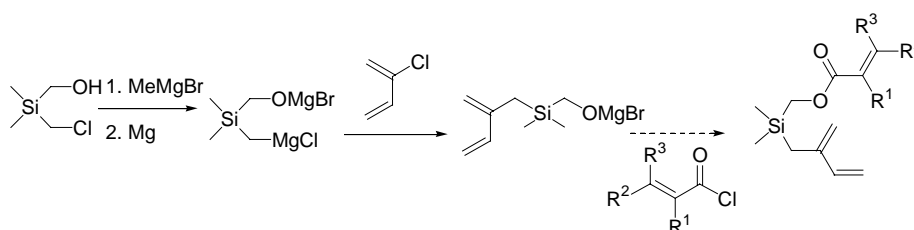
**General Procedures:** Toluene, THF, benzene, and CH<sub>2</sub>Cl<sub>2</sub> were purified by passage through alumina columns as described by Grubbs.<sup>2</sup> All reactions were performed under N<sub>2</sub> using oven or flame dried glassware and standard syringe and septa techniques. Removal of solvent *in vacuo* refers to use of a Büchi rotary evaporator. Reagents were purchased from VWR, Fisher, or Aldrich and generally used without purification. Benzaldehyde, butyraldehyde, and isobutyraldehyde were distilled at atmospheric pressure under N<sub>2</sub>. *m*-Nitrobenzaldehyde was recrystallized from hexanes and ether. TiCl<sub>4</sub> was stored under Ar in a glovebox. Trienes were stored at -20 °C as frozen solutions in benzene. The trienes were warmed to RT and concentrated *in vacuo* just

<sup>1</sup> Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, 62, 7512.

<sup>2</sup> Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F.J. *Organometallics* **1996**, 15, 1518.

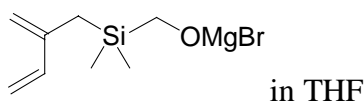
before use. TLC was performed with aluminum-backed silica gel 60 F<sub>254</sub> analytical plates from EMD. Visualization of compound spots was done with a short wave UV lamp followed by staining with either anisaldehyde or Seebach's stain (phosphomolybdic acid and Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>). Flash chromatography was performed on Geduran silica gel 60 (40-63 μm) from EMD.

### General Synthesis of Trienes



Hydroxymethyl(2-methylene-3-butenyl)dimethylsilane magnesium bromide salt solution was prepared in bulk and reacted with the appropriate acid chlorides.

### Hydroxymethyl(2-methylene-3-butenyl)dimethylsilane magnesium bromide salt solution

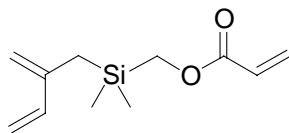


Chloromethyldimethylhydroxymethylsilane<sup>3</sup> (43.13 g, 311 mmol) and a few crystals of 1,10-phenanthroline were dissolved in THF (300 mL) and the solution was cooled to -30 °C. To this solution was added CH<sub>3</sub>MgBr (3.0 M, 104 mL, 311 mmol) dropwise, keeping

<sup>3</sup> Prepared according to Whitney, J. M.; Parnes, J. S.; Shea, K. J. *J. Org. Chem.* **1997**, 62, 8962, with the following modification in the conversion of bis(hydroxymethyl)dimethylsilane to chloromethyldimethylhydroxymethylsilane: 1) The chloroform used in this reaction was found to work best after extended storage over 4 Å molecular sieves in the presence of ambient lighting. Presumably, HCl is developed over time and catalyzes the reaction. 2) The solvent used to triturate triphenylphosphine oxide must be ether, as hexanes do not adequately solvate the product.

the solution  $< -30\text{ }^{\circ}\text{C}$ . Upon completion of addition, the solution became heterogeneous. The mixture was allowed to warm to  $0\text{ }^{\circ}\text{C}$  and solids dissolved. Magnesium turnings (7.56 g, 311 mmol) were added in one portion and the reaction was refluxed for 12 h. The reaction was cooled to  $0\text{ }^{\circ}\text{C}$  and  $\text{NiCl}_2\text{dppp}$  catalyst (3.37 g, 62.2 mmol) was added followed by freshly distilled chloroprene (43.31 mL, 466.6 mmol) in a dropwise manner. An exotherm was observed after some of the chloroprene was added. The reaction was heated to a mild reflux for 3 h to complete the coupling. The reaction mixture was then used directly for dienophile coupling after determining the concentration of an aliquot via titration with 5 M HCl and phenolphthalein as an indicator.

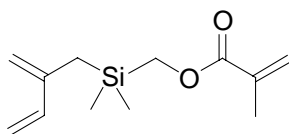
### Dimethyl(2-methylene-3-butenyl)silylmethyl acrylate [5a]



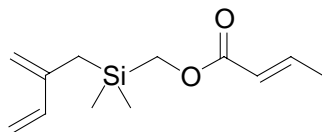
Hydroxymethyl(2-methylene-3-butenyl)dimethylsilane magnesium bromide salt solution (0.80 M, 20 mL, 16 mmol) was cooled to  $-30\text{ }^{\circ}\text{C}$  under  $\text{N}_2$ . Acryloylchloride (1.43 mL, 17.6 mmol) was injected quickly and the reaction was warmed to RT over 30 min. Water was added to quench the reaction and the organics were extracted with hexanes. The combined hexane extracts were dried over  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo*. The residue was purified by  $\text{SiO}_2$  flash chromatography (95:5 hexanes:EtOAc) to give the product as a colorless oil. Yield: 3.10 g, 92%. Rf 0.45 (90:10 hexane:EtOAc).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) 6.39 (dd,  $J = 17.8, 10.6\text{ Hz}$ , 1 H), 6.38 (dd,  $J = 17.5, 1.70\text{ Hz}$ , 1 H), 6.13 (dd,  $J = 17.5, 10.6\text{ Hz}$ , 1 H), 5.79 (dd,  $J = 10.1, 1.67\text{ Hz}$ , 1 H), 5.13 (d,  $J = 17.9\text{ Hz}$ , 1 H), 5.06 (d,  $J = 12.6\text{ Hz}$ , 1 H), 4.94 (d,  $J = 1.48\text{ Hz}$ , 1 H), 4.84 (s, 1 H), 3.87 (s, 2 H),

1.81 (d,  $J = 0.84$  Hz, 2 H), 0.085 (s, 6 H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ) 166.80, 142.84, 139.46, 130.00, 128.29, 114.82, 113.61, 56.34, 17.96, -4.53. IR 2928, 1727, 1403. HRMS EI  $[\text{M}-\text{C}_5\text{H}_7]$  found 143.0550, calculated for  $\text{C}_6\text{H}_{11}\text{O}_2\text{Si}$  143.0528.

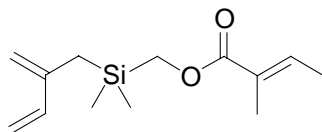
### Dimethyl(2-methylene-3-butenyl)silylmethyl methacrylate [5b]



Hydroxymethyl(2-methylene-3-butenyl)dimethylsilane magnesium bromide salt solution (0.80 M, 20 mL, 16 mmol) was cooled to  $-30\text{ }^{\circ}\text{C}$  under  $\text{N}_2$ . Methacryloyl chloride (1.72 mL, 17.6 mmol) was injected quickly and the reaction warmed to RT over 30 min. Water was added to quench the reaction and the organics were extracted with hexanes. The combined hexanes extracts were dried over  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo*. The yellow oil residue was purified by  $\text{SiO}_2$  flash chromatography (95:5 hexanes:EtOAc) to give the desired triene as a colorless oil. Yield 2.93 g, 82%. Rf 0.55 (90:10 hexanes:EtOAc).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) 6.37 (dd,  $J = 17.2, 10.8$  Hz, 1 H), 6.06 (d,  $J = 0.69$  Hz, 1 H), 5.51 (m, 1 H), 5.11 (d,  $J = 17.3$  Hz, 1 H), 5.05 (d,  $J = 10.3$  Hz, 1 H), 4.93 (d,  $J = 1.15$  Hz, 1 H), 4.83 (s, 1 H), 3.83 (s, 2 H), 1.93 (m, 3 H), 1.80 (d,  $J = 0.97$  Hz, 2 H), 0.079 (s, 6 H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ) 169.14, 142.89, 139.64, 136.48, 124.89, 114.92, 113.69, 56.54, 18.41, 18.24, -4.33. IR 1720, 1335, 1161, 845. HRMS CI  $[\text{M}-\text{C}_4\text{H}_5\text{O}]$  found 155.0966, calculated for  $\text{C}_8\text{H}_{15}\text{OSi}$  155.0892.

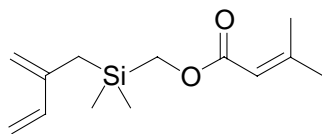
**Dimethyl(2-methylene-3-butenyl)silylmethyl crotonate [5c]**

Hydroxymethyl(2-methylene-3-butenyl)dimethylsilane magnesium bromide salt solution (0.80 M, 20 mL, 16 mmol) was cooled to -30 °C under N<sub>2</sub>. Crotonoyl chloride (1.98 mL, 17.6 mmol) was injected quickly and the reaction was warmed to RT over 30 min. Water was added to quench the reaction and the organics were extracted with hexane. The combined organics were dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by SiO<sub>2</sub> flash chromatography (95:5 hexanes:EtOAc) to give the product as a colorless oil. Yield: 3.41 g, 95%. R<sub>f</sub> 0.57 (90:10 hexane:EtOAc). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 6.94 (dq, *J* = 7.02, 6.95 Hz, 1 H), 6.36 (dd, *J* = 17.4, 10.8 Hz, 1 H), 5.84 (dd, *J* = 15.5, 1.72 Hz, 1 H), 5.11 (d, *J* = 17.8 Hz, 1 H), 5.04 (d, *J* = 11.0 Hz, 1 H), 4.92 (d, *J* = 0.93 Hz, 1 H), 4.83 (s, 1 H), 3.81 (d, *J* = 3.46 Hz, 2 H), 1.86 (dd, *J* = 6.95, 1.57 Hz, 3 H), 1.8 (s, 2 H), 0.064 (s, 6 H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) 167.29, 144.06, 142.94, 139.67, 122.66, 114.91, 113.71, 56.07, 18.15, 17.89, -4.39. IR 1724, 841. HRMS CI [M-CH<sub>3</sub>] found 209.0997, calculated for C<sub>11</sub>H<sub>17</sub>O<sub>2</sub>Si 209.0998.

**Dimethyl(2-methylene-3-butenyl)silylmethyl tiglate [5d]**

Hydroxymethyl(2-methylene-3-butenyl)dimethylsilane magnesium bromide salt solution (0.80 M, 20 mL, 16 mmol) was cooled to -30 °C under N<sub>2</sub>. Tiglyl chloride (2.09 g, 17.6 mmol) was injected quickly and the reaction was warmed to RT over 30 min. Water was added to quench the reaction and the organics were extracted with hexanes. The combined organics were dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by SiO<sub>2</sub> flash chromatography (95:5 hexanes:EtOAc) to give the product as a colorless oil. Yield: 3.46 g, 95%. R<sub>f</sub> 0.25 (95:5 hexane:EtOAc). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 6.80 (dd, *J* = 5.59, 1.40 Hz, 1 H), 6.36 (dd, *J* = 17.4, 10.2 Hz, 1 H), 5.10 (d, *J* = 17.3 Hz, 1 H), 5.03 (d, *J* = 11.3 Hz, 1 H), 4.90 (t, *J* = 1.00 Hz, 1 H), 4.82 (s, 1 H), 3.80 (s, 3 H), 1.75-1.82 (m, 8 H), 0.064 (s, 6 H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) 168.81, 142.84, 139.54, 128.70, 114.88, 113.70, 56.17, 18.21, 14.22, 12.08, -4.35. IR 1712, 737. HRMS CI [M+H] found 239.1470, calculated for C<sub>13</sub>H<sub>23</sub>O<sub>2</sub>Si 239.1467.

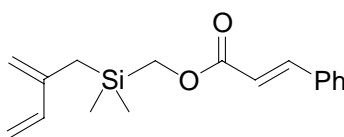
### Dimethyl(2-methylene-3-butenyl)silylmethyl 2,2-dimethylacrylate [5e]



Hydroxymethyl(2-methylene-3-butenyl)dimethylsilane magnesium bromide salt solution (0.80 M, 20 mL, 16 mmol) was cooled to -30 °C under N<sub>2</sub>. 2,2-Dimethylacroyl chloride (1.78 mL, 17.6 mmol) was injected quickly and the reaction was warmed to RT over 30 min. Water was added to quench the reaction and the organics were extracted with hexanes. The combined organics were dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by SiO<sub>2</sub> flash chromatography (95:5 hexanes:EtOAc) to give the product as a colorless oil. Yield: 2.7 g, 71%. R<sub>f</sub> 0.59 (90:10 hexane:EtOAc).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) 6.36 (dd,  $J = 17.2, 10.9$  Hz, 1 H), 5.67 (t,  $J = 1.26$  Hz, 1 H), 5.11 (d,  $J = 17.8$  Hz, 1 H), 5.04 (d,  $J = 10.7$  Hz, 1 H), 4.92 (d,  $J = 1.52$  Hz, 1 H), 4.83 (s, 1 H), 3.76 (d,  $J = 3.56$  Hz, 2 H), 2.14 (d,  $J = 1.37$  Hz, 3 H), 1.88 (d,  $J = 1.21$  Hz, 3 H), 1.79 (d,  $J = 0.77$  Hz, 2 H), 0.062 (s, 6 H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ) 167.51, 155.86, 143.00, 139.68, 116.04, 114.90, 113.75, 55.29, 27.28, 20.13, 18.15, -4.34. IR 1716, 1142. HRMS CI  $[\text{M}-\text{CH}_3]$  found 223.1151, calculated for  $\text{C}_{12}\text{H}_{19}\text{O}_2\text{Si}$  223.1155.

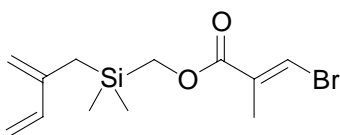
### Dimethyl(2-methylene-3-butenyl)silylmethyl cinnamate [5f]



Chloromethyldimethylhydroxysilane (3.33 g, 24 mmol) was dissolved in THF (25 mL) and cooled to  $-35\text{ }^{\circ}\text{C}$ . Methylmagnesium bromide (2.76 M, 9.56 mL, 26.4 mmol) was added dropwise keeping the temp below  $-20\text{ }^{\circ}\text{C}$ . The heterogeneous reaction was then warmed to RT and stirred for 20 min. Magnesium turnings (0.64 g, 26.4 mmol) were added in one portion and then external heating was applied to bring the solution to reflux for 12 h. The magnesium had been mostly consumed at this point. The reaction was cooled to  $0\text{ }^{\circ}\text{C}$  and the  $\text{NiCl}_2\text{dppp}$  catalyst (0.39 g, 0.72 mmol) was added. Freshly distilled chloroprene (3.36 mL, 36 mmol) was then added dropwise. The solution exothermed and became heterogeneous. It was then poured into saturated aqueous  $\text{NH}_4\text{Cl}$  and extracted with  $\text{Et}_2\text{O}$ . The combined ether abstracts were dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated *in vacuo*. The resulting oily orange residue was purified by  $\text{SiO}_2$  flash chromatography (95:5 hexanes:EtOAc) to give the desired triene as a colorless

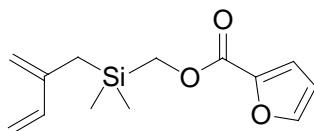
oil. Yield 5.87 g, 85%. Rf 0.44 (90:10 hexanes:EtOAc).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) 7.66 (d,  $J = 16.0$  Hz, 1 H), 7.53 (m, 2 H), 7.39 (m, 3 H), 6.45 (d,  $J = 16.1$  Hz, 1 H), 6.40 (dd,  $J = 17.4, 10.7$  Hz, 1 H), 5.15 (d,  $J = 17.5$  Hz, 1 H), 5.08 (d,  $J = 10.7$  Hz, 1 H), 4.94 (d,  $J = 0.68$  Hz, 1 H), 4.87 (s, 1 H), 3.92 (s, 2 H), 1.83 (s, 2 H), 0.12 (s, 6 H).  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ) 167.61, 144.22, 142.73, 139.49, 134.26, 130.00, 128.66, 127.85, 117.93, 114.89, 113.67, 56.41, 18.01, -4.44. IR 1712, 1639, 1587, 1331, 1162, 845. HRMS CI  $[\text{M}-\text{C}_5\text{H}_7]$  found 219.0860, calculated for  $\text{C}_{12}\text{H}_{15}\text{O}_2\text{Si}$  219.0843.

**Dimethyl(2-methylene-3-butenyl)silylmethyl *E*-2-bromomethacrylate [5g]**



Prepared as described by Whitney, et. al.<sup>3</sup>

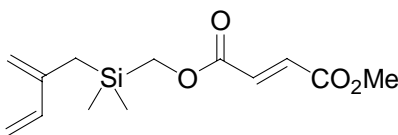
**Dimethyl(2-methylene-3-butenyl)silylmethyl furylate [5h]**



Hydroxymethyl(2-methylene-3-butenyl)dimethylsilane magnesium bromide salt solution (0.80 M, 20 mL, 16 mmol) was cooled to  $-30^\circ\text{C}$  under  $\text{N}_2$ . Furoyl chloride (1.74 mL, 17.6 mmol) was injected quickly and the reaction was warmed to RT over 30 min. Water was added to quench the reaction and the organics were extracted with hexanes. The

combined organics were dried over  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo*. The residue was purified by  $\text{SiO}_2$  flash chromatography (95:5 hexanes:EtOAc) to give the product as a colorless oil. Yield: 3.85 g, 96%.  $R_f$  0.42 (95:5 hexanes:EtOAc).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) 7.56 (t,  $J = 0.84$  Hz, 1 H), 7.12 (d,  $J = 3.12$  Hz, 1 H), 6.49 (dd,  $J = 3.43, 1.69$  Hz, 1 H), 6.37 (dd,  $J = 17.7, 10.7$  Hz, 1 H), 5.13 (d,  $J = 17.4$  Hz, 1 H), 5.05 (d,  $J = 11.4$  Hz, 1 H), 4.94 (s, 1 H), 4.86 (s, 1 H), 3.99 (s, 2 H), 1.84 (d,  $J = 0.56$  Hz, 2 H), 0.12 (s, 6 H).  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ ) 159.55, 146.12, 144.87, 142.82, 139.65, 117.34, 115.08, 113.83, 111.67, 56.94, 18.15, -4.31. IR 1722, 1315, 1119, 841, 764. HRMS CI  $[\text{M}-\text{CH}_3]$  found 235.0799, calculated for  $\text{C}_{12}\text{H}_{15}\text{O}_3\text{Si}$  235.0791.

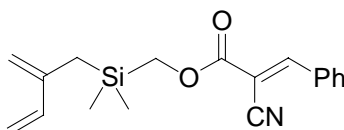
### Dimethyl(2-methylene-3-butenyl)silylmethyl methyl fumarate [5i]



Hydroxymethyl(2-methylene-3-butenyl)dimethylsilane magnesium bromide salt solution (0.80 M, 20 mL, 16 mmol) was cooled to  $-30$  °C under  $\text{N}_2$ . Methyl fumaroyl chloride (2.60 g, 17.6 mmol) was added quickly and the reaction was warmed to RT over 30 min. Water was added to quench the reaction and the organics were extracted with hexanes. The combined organics were dried over  $\text{MgSO}_4$ , filtered, and concentrated *in vacuo*. The residue was purified by  $\text{SiO}_2$  flash chromatography (95:5 hexanes:EtOAc) to give the product as a colorless oil. Yield: 3.03 g, 71%.  $R_f$  0.63 (90:10 hexane:EtOAc).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) 6.85 (d,  $J = 15.8$  Hz, 1 H), 6.78 (d,  $J = 15.8$  Hz, 1 H), 6.34 (dd,  $J = 17.5, 10.7$  Hz, 1 H), 5.07 (d,  $J = 17.3$  Hz, 1 H), 5.02 (d,  $J = 10.3$  Hz, 1 H), 4.91 (s, 1 H), 4.80 (s, 1 H), 3.88 (s, 2 H), 3.77 (s, 3 H), 1.78 (s, 2 H), 0.06 (s, 6 H).  $^{13}\text{C}$  NMR (75.4

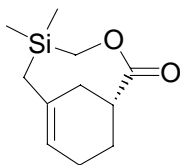
MHz, CDCl<sub>3</sub>) 165.63, 165.43, 142.66, 139.59, 133.78, 132.87, 115.12, 113.80, 57.53, 52.24, 18.09, -4.37. IR 2360, 1727, 1588, 1307, 1154, 849. HRMS CI [M+1] found 269.1205, calculated for C<sub>13</sub>H<sub>21</sub>O<sub>4</sub>Si 269.1209.

### Dimethyl(2-methylene-3-butenyl)silylmethyl *E*-2-cyanocinnamate [5j]



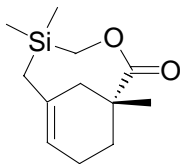
Hydroxymethyl(2-methylene-3-butenyl)dimethylsilane magnesium bromide salt solution (0.80 M, 20 mL, 16 mmol) was cooled to -30 °C under N<sub>2</sub>. *E*-2-Cyanocinnamoyl chloride (3.37 g, 17.6 mmol) was added quickly and the reaction was warmed to RT over 30 min. Water was added to quench the reaction and the organics were extracted with hexanes. The combined organics were dried over MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by SiO<sub>2</sub> flash chromatography (95:5 hexanes:EtOAc) to give the product as a white powder. Yield: 3.58 g, 72%. R<sub>f</sub> 0.34 (90:10 hexane:EtOAc). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 8.21 (s, 1 H), 7.96 (m, 2 H), 7.52 (m, 3 H), 6.38 (dd, *J* = 17.5, 10.7 Hz, 1 H), 5.15 (d, *J* = 17.5 Hz, 1 H), 5.07 (d, *J* = 10.7 Hz, 1 H), 4.95 (d, *J* = 1.1 Hz, 1 H), 4.87 (s, 1 H), 4.01 (s, 2 H), 1.86 (d, *J* = 0.08 Hz, 2 H), 0.14 (s, 6 H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) 165.41, 154.83, 142.67, 139.59, 133.26, 131.48, 131.06, 129.26, 115.25, 113.96, 102.91, 58.93, 18.08, -4.37. IR 2922, 2359, 1731, 1613, 1463. HRMS CI [M-C<sub>5</sub>H<sub>7</sub>] found 244.0793, calculated for C<sub>13</sub>H<sub>13</sub>NO<sub>2</sub>Si 244.0795.

### 5,5-Dimethyl-3-oxa-5-sila-bicyclo[5.3.1]unde-7-en-2-one [4a]



In a dry re-sealable glass tube, dimethyl(2-methylene-3-butenyl)silylmethyl acrylate (210 mg, 0.998 mmol) was dissolved in toluene (100 mL, 0.01 M) and the solution was sparged with N<sub>2</sub> gas for 10 min. The solution was then heated at 200 °C for a total of 6.75 h, and then allowed to cool to RT. The toluene was removed under reduced pressure to yield a colorless oil. The oil was purified by flash chromatography on SiO<sub>2</sub> (95:5 hexanes:EtOAc) to give the product as a colorless oil. Yield: 168 mg, 80%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 5.29 (d, *J* = 3.95 Hz, 1 H), 4.39 (d, *J* = 14.0 Hz, 1 H), 3.56 (d, *J* = 14.0 Hz, 1 H), 2.89 (m, 1 H), 2.41 (dt, *J* = 13.4, 1.75 Hz, 1 H), 2.11 (m, 2 H), 1.94 (s, 1 H), 1.90 (s, 1 H), 1.66 (d, *J* = 13.5 Hz, 1 H), 1.63 (m, 1 H), 1.45 (d, *J* = 13.5 Hz, 1 H), 0.13 (s, 3 H), 0.06 (s, 3 H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) 177.91, 136.55, 121.51, 60.14, 41.75, 35.90, 25.51, 22.75, 21.44, -1.26, -1.78. IR 2929, 1727, 1254, 839. HRMS CI [M+H] found 211.1148, calculated for C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>Si.

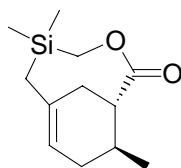
### 1,5,5-Trimethyl-3-oxa-5-sila-bicyclo[5.3.1]undec-7-en-2-one [4b]



In a dry, re-sealable glass tube, dimethyl(2-methylene-3-butenyl)silylmethyl methacrylate (224 mg, 0.999 mmol) was dissolved in toluene (100 mL, 0.01 M) and the N<sub>2</sub> was bubbled through the solution for 10 min. The solution was then heated at 200 °C for a total of 8.75 h, and then allowed to cool to RT. The toluene was removed *in vacuo* to

yield a colorless oil. The oil was purified by flash chromatography on SiO<sub>2</sub> (95:5 hexanes:EtOAc) to give the product as a colorless oil. Yield: 201 mg, 90%. R<sub>f</sub> 0.52 (10:90 hexanes:EtOAc). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 5.28 (m, 1 H), 4.37 (d, *J* = 14.0 Hz, 1 H), 3.60 (d, *J* = 14.0 Hz, 1 H), 2.10-2.28 (m, 4 H), 1.70-1.93 (m, 2 H), 1.46 (dd, *J* = 13.5, 1.46 Hz, 1 H), 1.36 (m, 1 H), 1.22 (s, 3 H), 0.20 (s, 3 H), 0.08 (s, 3 H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) 179.59, 136.38, 121.30, 60.11, 47.52, 43.63, 31.81, 25.65, 23.04, 22.79, -0.94, -1.82. IR 1731, 802. HRMS CI [M+1] found 225.1317, calculated for C<sub>12</sub>H<sub>21</sub>O<sub>2</sub>Si 225.1311.

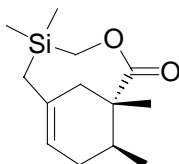
### 5,4,10-Trimethyl-3-oxa-5-sila-bicyclo[5.3.1]undec-7-en-2-one [4c]



In a dry, re-sealable glass tube, dimethyl(2-methylene-3-butenyl)silylmethyl crotonate (224 mg, 0.999 mmol) was dissolved in toluene (100 mL, 0.01 M) and the N<sub>2</sub> was bubbled through the solution for 10 min. The solution was then heated at 200 °C for a total of 66 h, and then allowed to cool to RT. The toluene was removed *in vacuo* to yield a colorless oil. The oil was purified by flash chromatography on SiO<sub>2</sub> (95:5 hexanes:EtOAc) to give the product as a wax. Yield: 210 mg, 94%. R<sub>f</sub> 0.50 (10:90 EtOAc:hexanes). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 5.41 (d, *J* = 1.02 Hz, 1 H), 4.48 (d, *J* = 13.5 Hz, 1 H), 3.57 (d, *J* = 14.0 Hz, 1 H), 2.28-2.55 (m, 4 H), 1.97 (dd, *J* = 12.5, 1.76 Hz, 1 H), 1.73 (m, 1 H), 1.51 (d, *J* = 13.9 Hz, 1 H), 1.36 (m, 1 H), 1.00 (d, *J* = 7.24 Hz, 3 H), 0.12 (s, 6 H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) 177.65, 137.49, 122.59, 59.62, 49.60, 32.80,

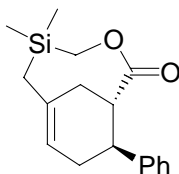
31.25, 27.86, 25.00, 21.20, -1.58. IR 1736, 1157. HRMS CI [M+1] found 225.1306, calculated for C<sub>12</sub>H<sub>21</sub>O<sub>2</sub>Si 225.1311.

**1,5,5,10-Tetramethyl-3-oxa-5-sila-bicyclo[5.3.1]undec-7-en-2-one [4d]**



In a dry re-sealable glass tube, dimethyl(2-methylene-3-butenyl)silylmethyl tiglate (120 mg, 0.503 mmol) was dissolved in toluene (50 mL, 0.01 M) and N<sub>2</sub> was bubbled through the solution for 10 min. The solution was then heated at 200 °C for a total of 100 h, and then allowed to cool to RT. The toluene was removed under reduced pressure to yield a yellow oil. The oil was purified by flash chromatography on SiO<sub>2</sub> (95:5 hexanes:EtOAc) to give the product as a colorless oil. Yield: 93 mg, 77%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 5.24 (d, *J* = 0.26 Hz, 1 H), 4.38 (d, *J* = 14.1 Hz, 1 H), 3.59 (d, *J* = 14.1 Hz, 1 H), 2.45 (m, 2 H), 2.06 (d, *J* = 13.2 Hz, 1 H), 1.91 (d, *J* = 13.2 Hz, 1 H), 1.71 (d, *J* = 13.5 Hz, 1 H), 1.45 (d, *J* = 13.4 Hz, 1 H), 1.13 (s, 3 H), 0.88 (d, *J* = 6.74 Hz, 3 H), 0.18 (s, 3 H), 0.07 (s, 3 H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) 180.24, 137.16, 121.27, 59.89, 51.07, 38.74, 32.78, 31.18, 25.30, 19.74, 17.50, -1.01, -1.79. IR 2960, 1736, 1454, 1142, 846. HRMS CI [M+1] found 239.1472, calculated for C<sub>13</sub>H<sub>23</sub>O<sub>2</sub>Si 239.1476.

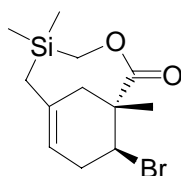
**5,5-Dimethyl-10-phenyl-3-oxa-5-sila-bicyclo[5.3.1]undec-7-en-2-one [4f]**



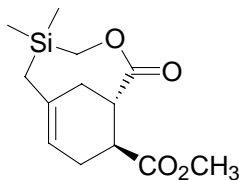
In a dry re-sealable glass tube, dimethyl(2-methylene-3-butenyl)silylmethyl cinnamate (430 mg, 1.5 mmol) was dissolved in toluene (115 mL, 0.013 M) and N<sub>2</sub> was bubbled through the solution for 10 min. The solution was then heated at 200 °C for a total of 40 h, and then allowed to cool to RT. The toluene was removed under reduced pressure to yield a yellow oil. The oil was purified by flash chromatography on SiO<sub>2</sub> (95:5 hexanes:EtOAc) to give the product as a colorless solid. Yield: 413 mg, 96%. Mp: 72.8-74.5 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 7.25 (m, 5 H), 5.49 (s, 1 H), 4.49 (d, *J* = 14.0 Hz, 1 H), 3.70 (m, 1 H), 3.67 (d, *J* = 14 Hz, 1 H), 2.98 (m, 1 H), 2.66 (m, 2 H), 2.24 (d, *J* = 13.3 Hz, 1 H), 2.07 (d, *J* = 16.6 Hz, 1 H), 1.79 (d, *J* = 13.5 Hz, 1 H), 1.58 (d, *J* = 13.0 Hz, 1 H), 0.16 (s, 3 H), 0.15 (s, 3 H). <sup>13</sup>C NMR (75.4 Hz, CDCl<sub>3</sub>) 177.59, 146.65, 137.44, 128.48, 127.55, 126.09, 121.49, 60.58, 49.56, 39.49, 33.14, 30.53, 25.52, -1.45, -1.69. IR (KBr pellet, cm<sup>-1</sup>): 3053, 3025, 2995, 2952, 2926, 2912, 2880, 2844, 1726, 1416, 1306, 1281, 1255, 1245, 1158, 1148, 839, 802, 749, 709. HRMS EI [M<sup>+</sup>] found 286.1384, calculated for C<sub>17</sub>H<sub>22</sub>O<sub>2</sub>Si C<sub>17</sub>H<sub>22</sub>O<sub>2</sub>Si 286.1389.

### 10-Bromo-1,5,5-trimethyl-3-oxa-5-sila-bicyclo[5.3.1]undec-7-en-2-one

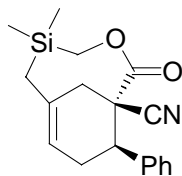
[4g]



Prepared as described by Whitney, et. al.<sup>3</sup>

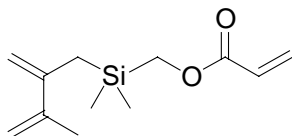
**5,5-Dimethyl-2-oxo-3-oxa-5-sila-bicyclo[5.3.1]undec-7-ene-10-carboxylic acid methyl ester [4i]**

1-[Dimethyl(2-methylene-3-butenyl)]silylmethyl methyl fumarate (160 mg, 0.596 mmol) was dissolved in N<sub>2</sub> purged benzene (60 mL) and heated to reflux. After 2.8 d, the benzene was removed *in vacuo* to yield a yellow oily solid. The solid was dissolved in hexane and passed through a plug of SiO<sub>2</sub>, and then concentrated *in vacuo* to give the product as a white wax. Yield: 130 mg, 81%. R<sub>f</sub> 0.28 (10:90 EtOAc:hexanes). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 5.35 (d, *J* = 6.1 Hz, 1 H), 4.48 (d, *J* = 13.9 Hz, 1 H), 3.68 (s, 3 H), 3.59 (d, *J* = 13.9 Hz, 1 H), 3.34 (m, 2 H), 2.51 (m, 1 H), 2.42 (dd, *J* = 8.7, 7.2 Hz, 1 H), 2.10 (m, 1 H), 2.01 (dd, *J* = 13.1, 1.7 Hz, 1 H), 1.72 (d, *J* = 13.6 Hz, 1 H), 1.51 (d, *J* = 13.6 Hz, 1 H), 0.11 (s, 3 H), 0.10 (s, 3 H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) 176.73, 175.82, 137.97, 120.18, 60.19, 51.94, 44.96, 39.78, 34.10, 25.08, 24.99, -1.58. IR 2919, 1737, 1455, 838. HRMS CI [M+1] found 269.1205, calculated for C<sub>13</sub>H<sub>21</sub>O<sub>4</sub>Si 269.1209.

**5,5-Dimethyl-2-oxo-10-phenyl-3-oxa-5-sila-bicyclo[5.3.1]undec-7-ene-1-carbonitrile [4j]**

In a dry re-sealable glass tube, dimethyl(2-methylene-3-butenyl)silylmethyl *E*-2-cyanocinnamate (100 mg, 0.321 mmol) was dissolved in toluene (32 mL, 0.01 M) and N<sub>2</sub> was bubbled through the solution for 10 min. The solution was then heated at 200 °C for a total of 45 h, and then allowed to cool to RT. The toluene was removed *in vacuo* and the residue was purified by flash chromatography on SiO<sub>2</sub> (95:5 hexanes:EtOAc) to give a mixture of regioisomers as a wax. The minor isomer is present as 5% of the product. R<sub>f</sub> 0.26 (90:10 hexanes:EtOAc). Yield: 89 mg, 89%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 7.27-7.40 (m, 5 H), 5.33 (m, 1 H), 4.51 (d, *J* = 14.2 Hz, 1 H), 3.87 (d, *J* = 13.6 Hz, 1 H), 3.84 (m, 1 H), 2.63-2.77 (m, 3 H), 2.40 (d, *J* = 18 Hz, 1 H), 1.88 (d, *J* = 13.6 Hz, 1 H), 1.59 (d, *J* = 13.4 Hz, 1 H), 0.27 (s, 3 H), 0.18 (s, 3 H). <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) 169.48, 140.93, 134.30, 129.73, 129.15, 128.45, 127.61, 121.94, 117.28, 62.88, 49.81, 42.03, 36.38, 30.18, 25.58, -1.16, -1.88. IR 2256, 1743, 1253, 837. HRMS CI [M+1] found 312.1386, calculated for C<sub>18</sub>H<sub>22</sub>NO<sub>2</sub>Si 312.1419.

**[Dimethyl-(3-methyl-2-methylene-but-3-enyl)-silanyl]-methyl acrylate**  
**[12]**

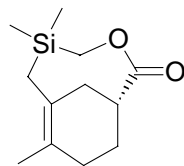


Chloromethylhydroxymethyldimethylsilane (4.9 g, 35 mmol) was dissolved in dry THF (90 ml) under N<sub>2</sub> and a few crystals of 1,10-phenanthroline monohydrate were added as an internal indicator. The solution was cooled below -30 °C and magnetically stirred as MeMgBr (3.0 M in ether) was added dropwise until the mix became cloudy and acquired a slight pink tint (about 11 mL). The mixture was allowed to warm to rt and all solids dissolved. The pink solution was transferred via cannula to a flask with excess Mg

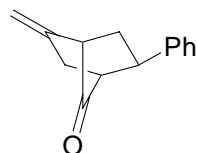
turnings (4.8 g) that had been activated by stirring overnight under N<sub>2</sub>. Initiation of the Grignard reaction was immediate. A condenser and magnetic stirring were used as the mixture exothermed. Heating was applied to maintain reflux for 1 h. After cooling and standing at RT for 24 h, the Grignard solution was transferred to another flask containing NidpppCl<sub>2</sub> (0.67 g, 1.0 mmol) in order to separate the solution from the remaining solid Mg. Freshly prepared 2-chloro-3-methyl-buta-1,3-diene<sup>4</sup> (5 mL, 51 mmol) was added dropwise as the mixture was magnetically stirred. The mixture was left to stir at RT for 3 h, and then transferred via cannula to an ice-cooled flask containing acryloyl chloride (4.0 g, 44 mmol) in 50 mL of THF. This mixture was stirred for 1 h at RT. The mixture was partitioned between Et<sub>2</sub>O (500 mL) and saturated aqueous NH<sub>4</sub>Cl. The organic layer was washed twice with saturated aqueous NaCl, dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvents were removed *in vacuo*. The residue was purified by silica gel flash chromatography using EtOAc:hexanes (5:95) to give the product as a colorless liquid. Yield: 1.54 g (19%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.27 (dd, *J* = 17.4, 1.7 Hz, 1 H), 6.05 (dd, *J* = 17.4, 10.5 Hz, 1 H), 5.70 (dd, *J* = 10.5, 1.5 Hz, 1 H), 4.88-4.94 (m, 3 H), 4.72 (s, 1 H), 3.76 (s, 2 H), 1.81-1.83 (m, 3 H), 1.78-1.80 (m, 2 H), -0.03 (s, 6 H). <sup>13</sup>C NMR (125 MHz, DCCl<sub>3</sub>) δ 167.1, 144.4, 143.4, 130.2, 113.7, 111.3, 56.8, 21.1, 20.9, -4.2. IR (NaCl film): 3084, 2956, 2903, 1723, 1632, 1590, 1404, 1303, 1249, 1180, 1053, 984, 888, 845, 813 cm<sup>-1</sup>.

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<sup>4</sup> Carothers, W. H.; Coffman, D. D. *J. Am. Chem. Soc.* **1932**, *54*, 4071.

**5,5,8-trimethyl-3-oxa-5-sila-bicyclo[5.3.1]undec-7-en-2-one [13]**

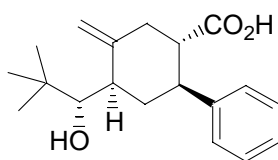
The triene (170 mg, 0.75 mmol) was dissolved in 50 mL of dry toluene to give a 0.015 M solution. The solution was transferred to a heavy-walled re-sealable glass tube and was heated in an oil bath at 200 °C for 48 h. The toluene was removed *in vacuo* and the residue was purified by silica gel flash chromatography using EtOAc:hexanes (5:95) to give the product as a colorless liquid (104 mg, 61 %).  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  4.49 (d,  $J = 13.9$  Hz, 1 H), 3.42 (d,  $J = 14.2$  Hz, 1 H), 2.65 (m, 1 H), 2.30-2.37 (m, 2 H), 2.04 (ddd,  $J = 16.0, 9.3, 3.9$  Hz, 1 H), 1.74-1.90 (m, 4 H), 1.52 (s, 3 H), 1.37-1.45 (m, 1 H), 1.17 (d,  $J = 13.4$  Hz, 1 H), 0.02 (s, 3 H), -0.08 (s, 3 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  177.5, 59.7, 41.8, 37.4, 28.2, 23.7, 22.7, 19.9, -0.2, -0.9. EIMS  $m/z$  (%) = 224 (64), 143 (69), 91 (100). IR (NaCl film): 2903, 1734, 1446, 1404, 1340, 1297, 1249, 1159, 1138, 1053, 989, 957, 840  $\text{cm}^{-1}$ . TOF ES-HRMS  $m/z$ : (M-H) found 223.1156, calc for  $\text{C}_{12}\text{H}_{19}\text{O}_2\text{Si}$  223.1154.

**2-Methylene-5-phenyl-bicyclo[2.2.1]heptan-7-one [14]**

In a glovebox, the phenyl-substituted bridgehead allylsilane (50 mg, 0.174 mmol) was dissolved in THF (10 mL) and TASf (53 mg, 0.191 mmol) was added in one portion. The reaction instantly became yellow and was filtered through a plug of  $\text{SiO}_2$ . The filtrate was concentrated to a yellow oil and characterized crude. Rf 0.57 (90:10

hexanes:EtOAc).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ) 7.29 (m, 5 H), 5.08 (s, 1 H), 4.83 (s, 1 H), 3.62 (dd,  $J = 4.82$  Hz, 1 H), 2.75 (d,  $J = 4.53$  Hz, 1 H), 2.36-2.52 (m, 4 H), 2.39 (dd,  $J = 12.6, 5.9$  Hz, 1 H). IR 1728. HRMS EI  $[\text{M}^+]$  found 198.1039, calculated for  $\text{C}_{14}\text{H}_{14}\text{O}$  198.1045.

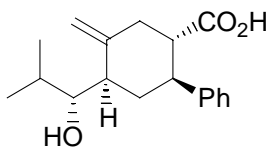
**4-(1-Hydroxy-2,2-dimethyl-propyl)-5-methylene-2-phenyl-cyclohexane carboxylic acid [16a]**



In a 2-neck schlenck flask was combined 325 mg (1.65 mmol) of 2,6-di-*tert*-butyl-4-methylpyridine and 315 mg (1.65 mmol) of  $\text{TiCl}_4$  using glovebox techniques. Dichloromethane (10 mL) was added, and the solution was stirred magnetically and cooled in a dry ice-acetone bath. Pivaldehyde (0.180 mL, 1.65 mmol) was added neat and the reaction mixture became green and cloudy. After stirring for 5 min with dry ice-acetone cooling, 4 mL of a solution of the allylsilane (444 mg, 1.55 mmol) in dichloromethane was added and the reaction mixture immediately became clear and deep red. The reaction mixture warmed to RT overnight, and was then quenched by pouring the reaction mixture into a separatory funnel containing saturated aqueous  $\text{NaHCO}_3$ . The aqueous layer was then made acidic with 2 N HCl, and the product was extracted 3 times with  $\text{CHCl}_3$  and once with EtOAc. The combined organic layer was dried over sodium sulfate, and the solvents were removed *in vacuo*. The residue was purified by flash chromatography on silica gel using a gradient of EtOAc in hexanes (20:80 – 50:50) to

give the product as 234 mg of a slightly yellow oil that crystallized upon standing. Yield: 0.234 g (50%). Mp: 128.8-133.3 °C. <sup>1</sup>H NMR (500 MHz, DCCl<sub>3</sub>): δ 7.21-7.26 (m, 2H), 7.14-7.19 (m, 3H), 4.93 (d, *J* = 5.9 Hz, 2H), 3.75 (s, 1H), 3.03 (app td, *J* = 12.5, 3.5 Hz, 1H), 2.64-2.72 (m, 2H), 2.45 (app d, *J* = 11.9 Hz, 1H), 2.38 (t, *J* = 13.3 Hz, 1H), 2.01-2.08 (m, 1H), 1.60 (qtr, *J* = 12.8 Hz, 1H), 0.93 (s, 9H). <sup>13</sup>C NMR (125 MHz, DCCl<sub>3</sub>): δ 179.6, 148.8, 143.8, 128.9, 127.8, 127.1, 108.1, 78.0, 51.7, 46.6, 43.7, 40.7, 36.20, 36.16, 27.2. IR (KBr cm<sup>-1</sup>): 3431, 3031, 2952, 2891, 2639, 1709, 1654, 1458, 1363, 1309, 1282, 1253, 1234, 1152, 1082, 980, 905, 769, 698. TOF ES-HRMS *m/z*: (M+Na) found 325.1784, calc for C<sub>19</sub>H<sub>26</sub>O<sub>3</sub>Na 325.1780.

**4-(1-Hydroxy-2-methyl-propyl)-5-methylene-2-phenyl-cyclohexanecarboxylic acid [16b]**



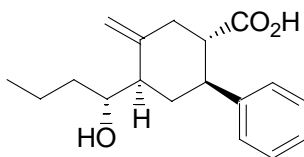
In a 25 mL Schlenck flask was combined TiCl<sub>4</sub> (168 mg, 0.88 mmol) and 4-methyl-2,6-di-*tert*-butylpyridine (166 mg, 81 mmol) in 5 mL of dry CH<sub>2</sub>Cl<sub>2</sub>. This mixture was magnetically stirred under N<sub>2</sub> and cooled in a dry ice-acetone bath. Freshly distilled isobutyraldehyde (80 μL, 63 mg, 0.87 mmol) was added. Stirring was continued and the reaction mixture turned grey-green and cloudy. After 5 min, a solution of the allylsilane

(200 mg, 0.7 mmol) in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> was added in a steady stream and the reaction was allowed to warm to rt. After stirring for 2 d, the reaction mixture was quenched with water and poured into a separatory funnel. The aqueous layer was made acidic with 2 N HCl. The organic layer was then separated, and the aqueous layer was extracted 3 times with EtOAc (3 x 15 mL). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was triturated with hexanes and filtered. The solids were washed with hexanes, and then were dissolved in EtOAc. The solvents were removed *in vacuo* to give the product as a white powder.

Yield: 0.149 g (74%). Mp: 182.8-185.0 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 11.8-12.2 (s.br., 1 H), 7.14-7.29 (m, 5 H), 4.91 (s, 1 H), 4.79 (s, 1 H), 4.27 (d, *J* = 5.9 Hz, 1 H), 2.95 (app. td, *J* = 12, 3.4 Hz, 1 H), 2.52-2.59 (m, 2 H), 2.20-2.30 (m, 2 H), 1.91 (dt, *J* = 13.2, 3.4 Hz, 1 H), 1.71 (sext., *J* = 6.6 Hz, 1 H), 1.39 (qtr., *J* = 12.5 Hz, 1 H), 0.86 (app. d, *J* = 6.6 Hz, 6 H). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ 175.2, 147.8, 144.4, 128.3, 127.3, 126.3, 107.9, 74.3, 50.7, 45.8, 44.1, 40.2, 35.6, 30.5, 20.0, 18.3. IR (KBr pellet, cm<sup>-1</sup>): 3275, 3076, 3030, 2963, 2934, 2907, 2877, 2630, 2534, 1676, 1646, 1292, 1261, 993, 977, 901, 702. ESI-HRMS *m/z* [M+Na] found 311.1628, calculated for C<sub>18</sub>H<sub>24</sub>O<sub>3</sub>Na 311.1623.

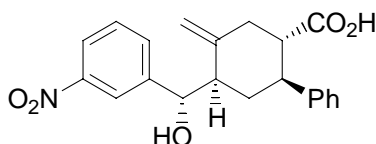
#### 4-(1-Hydroxy-butyl)-5-methylene-2-phenyl-cylcohexanecarboxylic acid

[16c]



In a 25 mL Schlenck flask was combined  $\text{TiCl}_4$  (168 mg, 0.88 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (166 mg, 81 mmol) in 5 mL of dry  $\text{CH}_2\text{Cl}_2$ . This mixture was magnetically stirred under  $\text{N}_2$  and cooled in a dry ice-acetone bath. Freshly distilled butyraldehyde (78  $\mu\text{L}$ , 63 mg, 0.87 mmol) was added. Stirring was continued and the reaction mixture turned reddish brown and cloudy. After 5 min, a solution of the allylsilane (200 mg, 0.7 mmol) in 2 mL of  $\text{CH}_2\text{Cl}_2$  was added in a rapid stream. The reaction mixture was allowed to warm to RT and was stirred for 2 d. The reaction mixture was then quenched with water and poured into a separatory funnel. The aqueous layer was made acidic with 2 N HCl. The organic layer was then separated, and the aqueous layer was extracted with EtOAc (3 x 15 mL). The combined organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered, and the solvents removed *in vacuo*. The residue was purified by silica gel flash chromatography (hexanes: EtOAc, 2:1, Rf 0.1) to give the product as an off-white solid. Yield: 0.160 g (79%). Mp: 150.0-152.8 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{DCCl}_3$ ):  $\delta$  7.22-7.34 (m, 5H), 5.04 (s, 1H), 4.94 (s, 1H), 4.09-4.13 (m, 1H), 3.03 (td,  $J$  = 12.0, 3.3 Hz, 1H), 2.69-2.78 (m, 2H), 2.44 (t,  $J$  = 12.8 Hz, 1H), 2.23 (app. d,  $J$  = 12.0 Hz, 1H), 2.09 (app. dt,  $J$  = 13.0, 3.9 Hz, 1H), 1.49-1.66 (m, 4H), 1.37-1.46 (m, 1H), 0.99 (t,  $J$  = 6.8 Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DCCl}_3$ ):  $\delta$  179.5, 146.8, 143.3, 128.6, 127.4, 126.9, 108.5, 70.9, 50.8, 46.8, 46.1, 40.1, 37.4, 34.0, 19.6, 14.2. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3265, 3078, 3065, 3029, 2957, 2934, 2907, 2873, 2862, 2546, 1674, 1648, 1297, 700. ESI-HRMS  $m/z$   $[\text{M}+\text{Na}]^+$  found 311.1625, calculated for  $\text{C}_{18}\text{H}_{24}\text{O}_3\text{Na}$  311.1623.

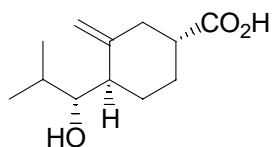
**4-[Hydroxy-(3-nitro-phenyl)-methyl]-5-methylene-2-phenyl-cyclohexanecarboxylic acid [16d]**



In a 25 mL schlenk flask was combined  $\text{TiCl}_4$  (168 mg, 0.89 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (161 mg, 0.78 mmol) under  $\text{N}_2$ . The solids were dissolved in 5 mL of  $\text{CH}_2\text{Cl}_2$  and the magnetically stirred solution was cooled with a dry ice-acetone bath. *m*-Nitrobenzaldehyde (132 mg, 0.87 mmol) was added in one portion, and the solution was allowed to warm to RT to dissolve the aldehyde. The solution was re-cooled in the dry ice-acetone bath and after 5 min, the allylsilane (200 mg, 0.70 mmol) was added as a solution in 2 mL of  $\text{CH}_2\text{Cl}_2$ . The mixture was allowed to slowly warm to RT and was stirred for 48 h. The reaction mixture was then quenched with water and poured into a separatory funnel. The organic layer was then separated, and the aqueous layer was extracted with EtOAc (3 x 15 mL). The combined organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered, and the solvents removed *in vacuo*. The residue was purified by  $\text{SiO}_2$  flash chromatography (hexanes: EtOAc, 5:1 to 0:1) to give the product as an off-white solid. Yield: 0.172 g (67%). Mp: 187.8-189.1 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  11.96 (s.br., 1H), 8.19 (s.br., 1H), 8.07 (dd,  $J$  = 8.1, 1.9 Hz, 1H), 7.82 (d,  $J$  = 7.8 Hz, 1H), 7.60

(t,  $J=8.0$  Hz, 1H), 7.11-7.24 (m, 5H), 5.51 (d.br.,  $J=5.1$  Hz, 1H), 5.14 (s, 1H), 4.99 (d,  $J=6.8$  Hz, 2H), 2.82 (td,  $J=11.6, 4.2$  Hz, 1H), 2.51-2.60 (m, 3H), 2.32 (t,  $J=12.4$  Hz, 1H), 1.49-1.62 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DCCl}_3$ ):  $\delta$  174.9, 147.9, 147.7, 146.5, 144.0, 133.0, 129.4, 128.2, 127.3, 126.3, 121.6, 120.8, 108.9, 70.5, 50.6, 48.0, 45.6, 39.6, 33.4. IR (KBr pellet,  $\text{cm}^{-1}$ ): 3442, 3087, 3030, 2931, 2868, 1707, 1648, 1529, 1350, 1285, 1179, 1095, 904, 700. ESI-HRMS  $m/z$   $[\text{M}+\text{Na}]^+$  found 390.1319, calculated for  $\text{C}_{21}\text{H}_{21}\text{NO}_5\text{Na}$  390.1317.

#### 4-(1-Hydroxy-2-methyl-propyl)-3-methylene-cyclohexanecarboxylic acid [17]

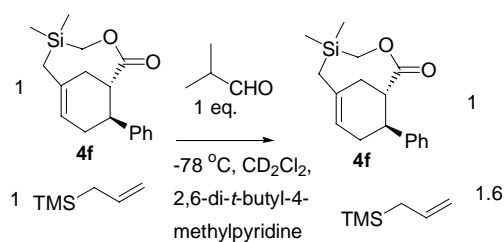


In a 25 mL schlenk flask was combined  $\text{TiCl}_4$  (209 mg, 1.1 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (205 mg, 1.0 mmol) under  $\text{N}_2$ . The solids were dissolved in 2.5 mL  $\text{CH}_2\text{Cl}_2$  and the magnetically stirred solution was cooled with a dry ice-acetone bath. Isobutyraldehyde (101  $\mu\text{L}$ , 1.1 mmol) was added in one portion and the mixture became heterogeneous and orange. After 5 min, a solution of the allylsilane (200 mg, 0.95 mmol) in 1 mL  $\text{CH}_2\text{Cl}_2$  was added. The flask that contained this solution was washed with 1 mL  $\text{CH}_2\text{Cl}_2$  and this wash was added to the reaction flask. The reaction was slowly allowed

to warm to RT and stirred for 48 h. The reaction was quenched with 15 mL water and the layers were separated. The aqueous layer was extracted with three 15 mL portions of EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvents were removed *in vacuo*. The viscous liquid residue was purified via SiO<sub>2</sub> flash chromatography using a gradient from 2:1 to 1:1 hexanes:EtOAc to give the product as a yellow oil.

Yield: 0.156 g (77%). <sup>1</sup>H NMR (500 MHz, DCCl<sub>3</sub>): δ 4.92 (s, 1 H), 4.81 (s, 1 H), 3.62-3.65 (m, 1 H), 2.52-2.60 (m, 1 H), 2.45-2.53 (m, 1 H), 2.29 (t, *J* = 11.5 Hz, 1 H), 2.17-2.24 (m, 1 H), 2.07-2.15 (m, 1 H), 1.87-1.94 (m, 1 H), 1.77-1.86 (m, 1 H), 1.62-1.73 (m, 1 H), 1.42-1.54 (m, 1 H), 0.98 (d, *J* = 6.6 Hz, 3 H), 0.90 (d, *J* = 6.6 Hz, 1 H). <sup>13</sup>C NMR (125 MHz, DCCl<sub>3</sub>): δ 180.8, 147.5, 108.9, 76.0, 44.4, 43.9, 38.1, 30.4, 27.4, 25.1, 19.7, 18.1. IR (NaCl thin film, cm<sup>-1</sup>): 3423, 3084, 2962, 2875, 1706, 1646, 1449, 1282, 1227, 1182, 1074, 974, 909, 734. TOF ES-HRMS *m/z*: (M+Na) found 235.1308, calc for C<sub>12</sub>H<sub>20</sub>O<sub>3</sub>Na 235.1310.

## Competition study



TiCl<sub>4</sub> (42 mg, 0.22 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (41 mg, 0.20 mmol) were combined in a 25 mL schlenk flask and dissolved in 0.75 mL CD<sub>2</sub>Cl<sub>2</sub>. The mixture was cooled in a dry ice-acetone bath and isobutyraldehyde (19 μL, 0.21 mmol) was

added via syringe. After 5 min, a solution of **4f** (60 mg, 0.21 mmol) and trimethylallylsilane (33  $\mu$ L, 0.21 mmol) in 0.75 mL of CD<sub>2</sub>Cl<sub>2</sub> was added rapidly. The mixture was stirred with dry ice-acetone bath cooling for 1.5 h, and then allowed to warm to RT. The mixture was transferred to an NMR tube and analysis was performed immediately. The <sup>1</sup>H resonances of the remaining allylsilanes were quantified by integration of the alkene proton of the bridgehead allylsilane (a broad singlet at 5.50 ppm) and one of the alkene protons of trimethylallylsilane (multiplet at 5.81 ppm).

#### X-ray Data Collection, Structure Solution and Refinement for **16c**.

A colorless crystal of approximate dimensions 0.10 x 0.28 x 0.30 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART<sup>1</sup> 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 SAINT<sup>2</sup> and SADABS<sup>3</sup> to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL<sup>4</sup> program. The diffraction symmetry was *2/m* and the systematic absences were consistent with the centrosymmetric monoclinic space group *P2<sub>1</sub>/c* which was later determined to be correct.

The structure was solved by direct methods and refined on F<sup>2</sup> by full-matrix least-squares techniques. The analytical scattering factors<sup>5</sup> 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<sub>iso</sub>) or were included using a riding model. There was one-half molecule of hexane solvent present per formula unit. The solvent was located about an inversion center. It was necessary to constrain the thermal parameters and the carbon-carbon distances associated with the solvent molecule. Least-squares analysis yielded wR2 = 0.2243 and Goof = 1.037 for 216 variables refined against 3935 data. As a comparison for refinement on F, R1 = 0.0689 for those 2793 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 2.10, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 2002.
  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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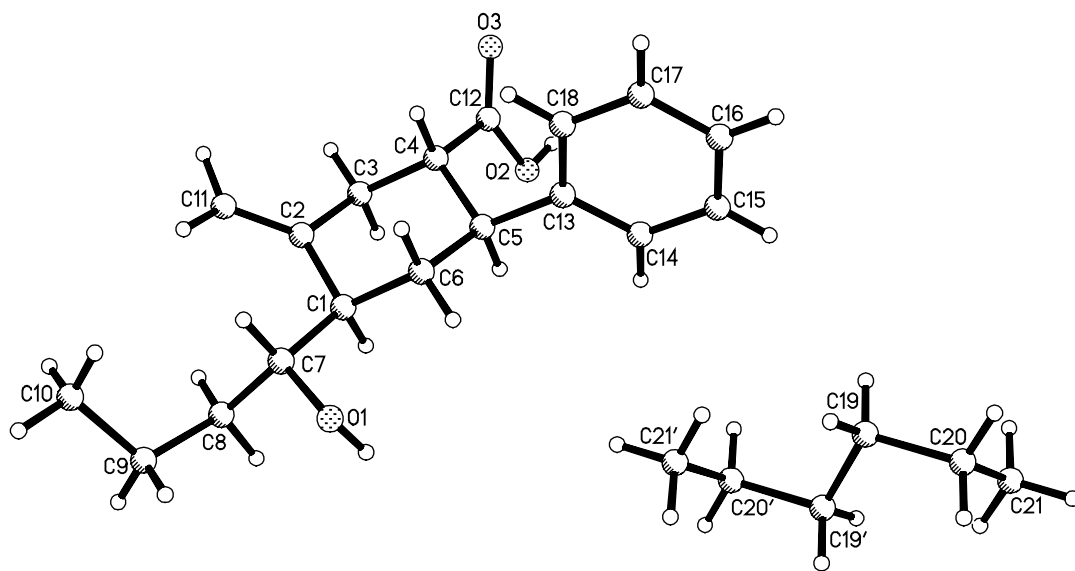
## Definitions:

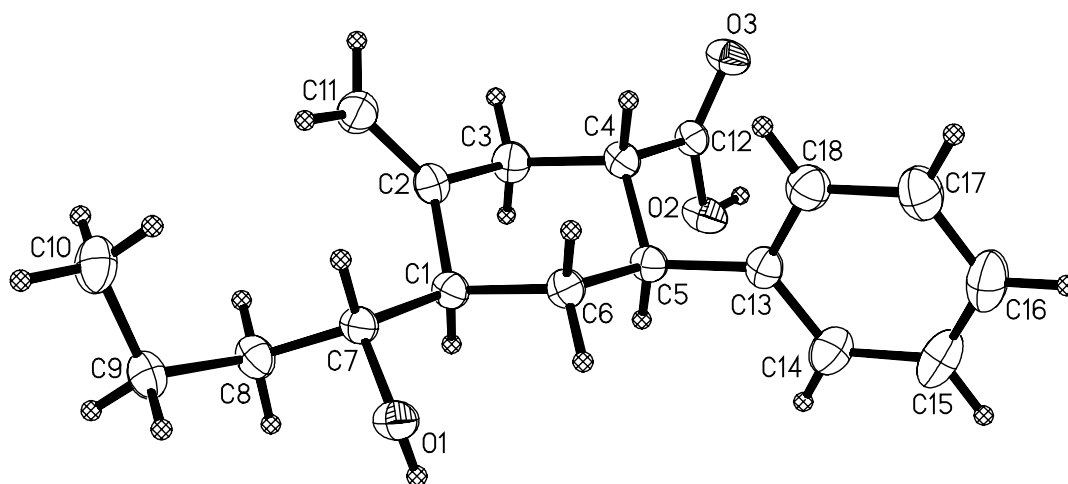
$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$$

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

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.



Table 1. Crystal data and structure refinement for **16c**.

Identification code	kjs50 (Ryan Lauchli)	
Empirical formula	$\text{C}_{18} \text{H}_{24} \text{O}_3 \cdot \frac{1}{2}(\text{C}_6\text{H}_{14})$	
Formula weight	331.46	
Temperature	158(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 6.0054(5)$ Å	$\alpha = 90^\circ$ .
	$b = 20.4908(18)$ Å	$\beta = 96.822(2)^\circ$ .
	$c = 15.7065(14)$ Å	$\gamma = 90^\circ$ .
Volume	$1919.1(3)$ Å <sup>3</sup>	
Z	4	
Density (calculated)	1.147 Mg/m <sup>3</sup>	
Absorption coefficient	0.075 mm <sup>-1</sup>	
F(000)	724	
Crystal color	colorless	
Crystal size	0.30 x 0.28 x 0.10 mm <sup>3</sup>	
Theta range for data collection	1.64 to 26.37°.	
Index ranges	$-7 \leq h \leq 7, -25 \leq k \leq 25, -19 \leq l \leq 18$	
Reflections collected	18745	

Independent reflections	3935 [R(int) = 0.0430]
Completeness to theta = 26.37°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9926 and 0.9779
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3935 / 3 / 216
Goodness-of-fit on F <sup>2</sup>	1.037
Final R indices [I>2sigma(I) = 2793 data]	R1 = 0.0689, wR2 = 0.1967
R indices (all data; 0.80)	R1 = 0.0980, wR2 = 0.2243
Largest diff. peak and hole	0.894 and -0.635 e.Å <sup>-3</sup>

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ )for **16c**. U(eq) is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
O(1)	4205(3)	2759(1)	5107(1)	26(1)
O(2)	-2644(3)	2446(1)	1353(1)	30(1)
O(3)	-156(3)	2288(1)	429(1)	29(1)
C(1)	2708(4)	3050(1)	3641(2)	22(1)
C(2)	3149(4)	3395(1)	2821(2)	24(1)
C(3)	1366(5)	3260(1)	2081(2)	27(1)
C(4)	1198(4)	2519(1)	1902(2)	22(1)
C(5)	757(4)	2147(1)	2715(2)	22(1)
C(6)	2583(4)	2313(1)	3458(2)	23(1)
C(7)	4380(4)	3220(1)	4425(2)	22(1)
C(8)	4021(4)	3910(1)	4751(2)	27(1)
C(9)	5875(5)	4156(1)	5424(2)	28(1)
C(10)	8053(5)	4299(2)	5064(2)	35(1)
C(11)	4961(5)	3737(2)	2711(2)	31(1)
C(12)	-580(4)	2399(1)	1153(2)	21(1)
C(13)	599(4)	1414(1)	2578(2)	24(1)
C(14)	-1244(5)	1069(2)	2798(2)	35(1)
C(15)	-1384(6)	396(2)	2698(2)	45(1)
C(16)	319(6)	58(2)	2385(2)	42(1)
C(17)	2163(6)	390(2)	2169(2)	37(1)
C(18)	2301(5)	1062(1)	2262(2)	31(1)
C(19)	-4472(18)	-277(3)	4761(7)	195(3)
C(20)	-5286(15)	-935(5)	5085(8)	195(3)
C(21)	-7861(15)	-963(6)	4919(8)	195(3)

Table 3. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **16c**.

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O(1)-C(7)	1.442(3)
O(2)-C(12)	1.318(3)
O(3)-C(12)	1.215(3)
C(1)-C(2)	1.520(4)
C(1)-C(7)	1.533(3)
C(1)-C(6)	1.538(4)
C(2)-C(11)	1.323(4)
C(2)-C(3)	1.509(4)
C(3)-C(4)	1.544(4)
C(4)-C(12)	1.513(3)
C(4)-C(5)	1.537(4)
C(5)-C(13)	1.518(4)
C(5)-C(6)	1.542(3)
C(7)-C(8)	1.528(4)
C(8)-C(9)	1.528(4)
C(9)-C(10)	1.514(4)
C(13)-C(18)	1.390(4)
C(13)-C(14)	1.391(4)
C(14)-C(15)	1.390(5)
C(15)-C(16)	1.374(5)
C(16)-C(17)	1.376(5)
C(17)-C(18)	1.386(4)
C(19)-C(19)#1	1.5395(10)
C(19)-C(20)	1.5399(10)
C(20)-C(21)	1.5388(10)
C(2)-C(1)-C(7)	114.3(2)
C(2)-C(1)-C(6)	107.9(2)
C(7)-C(1)-C(6)	112.6(2)
C(11)-C(2)-C(3)	121.1(3)
C(11)-C(2)-C(1)	125.8(2)
C(3)-C(2)-C(1)	112.8(2)
C(2)-C(3)-C(4)	110.2(2)
C(12)-C(4)-C(5)	113.0(2)

C(12)-C(4)-C(3)	109.1(2)
C(5)-C(4)-C(3)	110.5(2)
C(13)-C(5)-C(4)	112.8(2)
C(13)-C(5)-C(6)	110.6(2)
C(4)-C(5)-C(6)	110.0(2)
C(1)-C(6)-C(5)	111.9(2)
O(1)-C(7)-C(8)	109.4(2)
O(1)-C(7)-C(1)	110.5(2)
C(8)-C(7)-C(1)	111.9(2)
C(9)-C(8)-C(7)	114.7(2)
C(10)-C(9)-C(8)	113.3(2)
O(3)-C(12)-O(2)	123.0(2)
O(3)-C(12)-C(4)	123.4(2)
O(2)-C(12)-C(4)	113.6(2)
C(18)-C(13)-C(14)	117.7(3)
C(18)-C(13)-C(5)	121.9(2)
C(14)-C(13)-C(5)	120.4(3)
C(15)-C(14)-C(13)	121.1(3)
C(16)-C(15)-C(14)	120.2(3)
C(15)-C(16)-C(17)	119.6(3)
C(16)-C(17)-C(18)	120.3(3)
C(17)-C(18)-C(13)	121.1(3)
C(19)#1-C(19)-C(20)	108.6(10)
C(21)-C(20)-C(19)	109.2(9)

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Symmetry transformations used to generate equivalent atoms:

#1 -x-1,-y,-z+1

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **16c**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
O(1)	19(1)	37(1)	19(1)	1(1)	-1(1)	-2(1)
O(2)	18(1)	49(1)	22(1)	-5(1)	-2(1)	3(1)
O(3)	21(1)	45(1)	21(1)	-6(1)	0(1)	0(1)
C(1)	18(1)	26(1)	21(1)	-2(1)	0(1)	0(1)
C(2)	26(1)	23(1)	23(1)	-2(1)	0(1)	1(1)
C(3)	30(1)	26(1)	22(1)	3(1)	-3(1)	0(1)
C(4)	17(1)	26(1)	21(1)	-3(1)	-1(1)	1(1)
C(5)	19(1)	26(1)	19(1)	-1(1)	-1(1)	0(1)
C(6)	21(1)	26(1)	20(1)	0(1)	-2(1)	-1(1)
C(7)	18(1)	27(1)	19(1)	-1(1)	1(1)	-1(1)
C(8)	20(1)	32(2)	27(1)	-6(1)	-1(1)	1(1)
C(9)	28(1)	29(1)	27(1)	-6(1)	-2(1)	0(1)
C(10)	26(2)	35(2)	42(2)	-6(1)	-5(1)	-3(1)
C(11)	34(2)	32(2)	26(2)	1(1)	2(1)	-6(1)
C(12)	20(1)	23(1)	20(1)	-1(1)	0(1)	1(1)
C(13)	24(1)	25(1)	20(1)	1(1)	-5(1)	-2(1)
C(14)	30(2)	32(2)	43(2)	2(1)	5(1)	-4(1)
C(15)	42(2)	33(2)	57(2)	8(2)	1(2)	-13(1)
C(16)	53(2)	24(2)	46(2)	3(1)	-5(2)	-4(1)
C(17)	43(2)	28(2)	38(2)	-2(1)	2(1)	4(1)
C(18)	30(2)	31(2)	31(2)	0(1)	3(1)	-1(1)

Table 5. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **16c**.

	x	y	z	U(eq)
H(1B)	1190	3191	3772	26
H(3A)	1739	3490	1563	32
H(3B)	-98	3425	2220	32
H(4A)	2670	2369	1735	26
H(5A)	-714	2300	2880	26
H(6A)	2259	2080	3981	27
H(6B)	4055	2160	3312	27
H(7A)	5930	3192	4254	26
H(8A)	3891	4213	4256	32
H(8B)	2580	3921	4998	32
H(9A)	5354	4559	5687	34
H(9B)	6156	3824	5882	34
H(10A)	9175	4451	5525	52
H(10B)	7801	4637	4622	52
H(10C)	8594	3900	4810	52
H(14A)	-2427	1298	3019	42
H(15A)	-2661	169	2848	53
H(16A)	224	-403	2318	50
H(17A)	3348	157	1956	44
H(18A)	3579	1285	2107	37
H(1)	2770(70)	2760(17)	5240(20)	41(9)
H(2)	-3570(60)	2390(17)	890(20)	41(9)
H(11A)	5310(60)	3888(17)	2140(20)	41(9)
H(11B)	6170(50)	3798(16)	3160(20)	31(8)
H(19A)	-2817	-252	4868	234
H(19B)	-4923	-236	4136	234
H(20A)	-4630	-1298	4783	234

H(20B)	-4794	-980	5707	234
H(21A)	-8386	-1380	5129	293
H(21B)	-8337	-925	4303	293
H(21C)	-8501	-603	5221	293

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Table 6. Torsion angles [°] for **16c**.

C(7)-C(1)-C(2)-C(11)	10.0(4)
C(6)-C(1)-C(2)-C(11)	-116.1(3)
C(7)-C(1)-C(2)-C(3)	-175.3(2)
C(6)-C(1)-C(2)-C(3)	58.6(3)
C(11)-C(2)-C(3)-C(4)	116.3(3)
C(1)-C(2)-C(3)-C(4)	-58.7(3)
C(2)-C(3)-C(4)-C(12)	-179.4(2)
C(2)-C(3)-C(4)-C(5)	55.9(3)
C(12)-C(4)-C(5)-C(13)	58.1(3)
C(3)-C(4)-C(5)-C(13)	-179.4(2)
C(12)-C(4)-C(5)-C(6)	-177.9(2)
C(3)-C(4)-C(5)-C(6)	-55.4(3)
C(2)-C(1)-C(6)-C(5)	-57.6(3)
C(7)-C(1)-C(6)-C(5)	175.3(2)
C(13)-C(5)-C(6)-C(1)	-177.3(2)
C(4)-C(5)-C(6)-C(1)	57.5(3)
C(2)-C(1)-C(7)-O(1)	-165.3(2)
C(6)-C(1)-C(7)-O(1)	-41.7(3)
C(2)-C(1)-C(7)-C(8)	72.6(3)
C(6)-C(1)-C(7)-C(8)	-163.8(2)
O(1)-C(7)-C(8)-C(9)	67.7(3)
C(1)-C(7)-C(8)-C(9)	-169.5(2)
C(7)-C(8)-C(9)-C(10)	70.8(3)
C(5)-C(4)-C(12)-O(3)	-135.2(3)
C(3)-C(4)-C(12)-O(3)	101.6(3)
C(5)-C(4)-C(12)-O(2)	46.8(3)
C(3)-C(4)-C(12)-O(2)	-76.4(3)
C(4)-C(5)-C(13)-C(18)	54.9(3)
C(6)-C(5)-C(13)-C(18)	-68.8(3)
C(4)-C(5)-C(13)-C(14)	-127.4(3)
C(6)-C(5)-C(13)-C(14)	109.0(3)
C(18)-C(13)-C(14)-C(15)	-0.4(4)
C(5)-C(13)-C(14)-C(15)	-178.2(3)
C(13)-C(14)-C(15)-C(16)	0.5(5)

C(14)-C(15)-C(16)-C(17)	-0.1(5)
C(15)-C(16)-C(17)-C(18)	-0.4(5)
C(16)-C(17)-C(18)-C(13)	0.4(5)
C(14)-C(13)-C(18)-C(17)	0.0(4)
C(5)-C(13)-C(18)-C(17)	177.8(3)
C(19)#1-C(19)-C(20)-C(21)	59.2(15)

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Symmetry transformations used to generate equivalent atoms:

#1 -x-1,-y,-z+1

#### X-ray Data Collection, Structure Solution and Refinement for **4f**.

A colorless crystal of approximate dimensions 0.23 x 0.50 x 0.50 mm was mounted on a glass fiber and transferred to a Siemens P4 diffractometer. The XSCANS<sup>1</sup> program package was used to determine the Laue symmetry, crystal class, unit-cell parameters and for data collection. Intensity data were collected at 296 K using a 2 $\theta$ / $\omega$  scan technique with MoK $\alpha$  radiation. The raw data were processed with a local version of CARESS<sup>2</sup> which employs a modified version of the Lehman-Larsen algorithm to obtain intensities and standard deviations from the measured 96-step profiles. Subsequent calculations were carried out using the SHELXTL<sup>3</sup> program. All data were corrected for Lorentz and polarization effects and placed on an approximately absolute scale. The diffraction symmetry was *mmm* and the systematic absences were consistent with space group *Pca*2<sub>1</sub> which was later determined to be correct.

The structure was solved by direct methods and refined on F<sup>2</sup> by full-matrix least-squares techniques. The analytical scattering factors<sup>4</sup> for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0873 and GOF = 1.074 for 182 variables refined against 1272 data (0.93Å). As a comparison for refinement on F, R1 = 0.0356 for those 1101 data with I > 2.0 $\sigma$ (I). The absolute structure was assigned by refinement of the Flack<sup>5</sup> parameter.

## References.

6. XSCANS Software Users Guide, Version 2.1, Siemens Analytical X-Ray Systems, Inc.; Madison, WI 1994.
7. Broach, R. W. CARESS, Argonne National Laboratory, Illinois, 1978.
8. Sheldrick, G. M. SHELXTL Version 6.12, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 2001
9. International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer Academic Publishers.
10. Flack, H. D. Acta. Cryst., A39, 876-881, 1983.

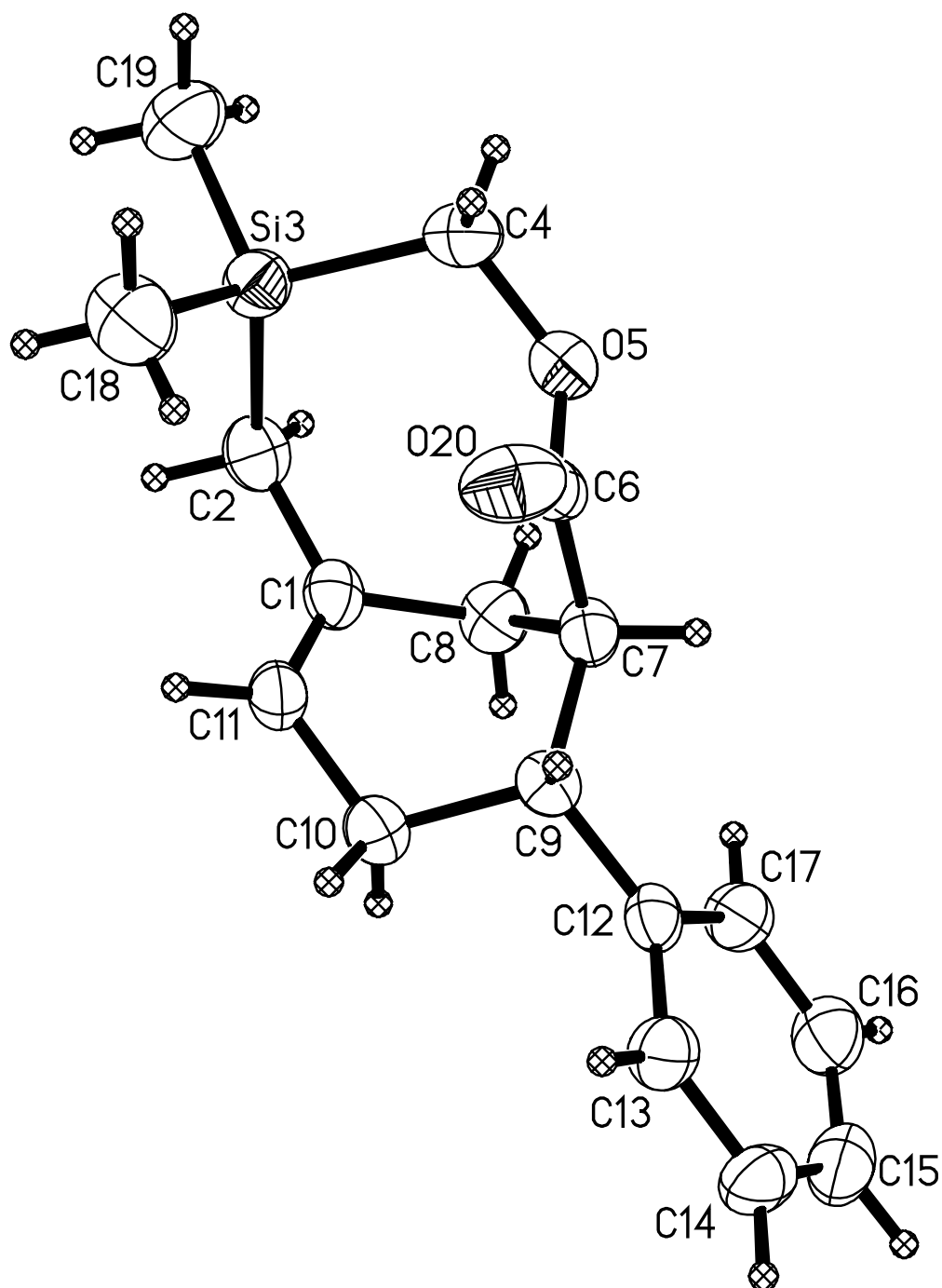
## Definitions:

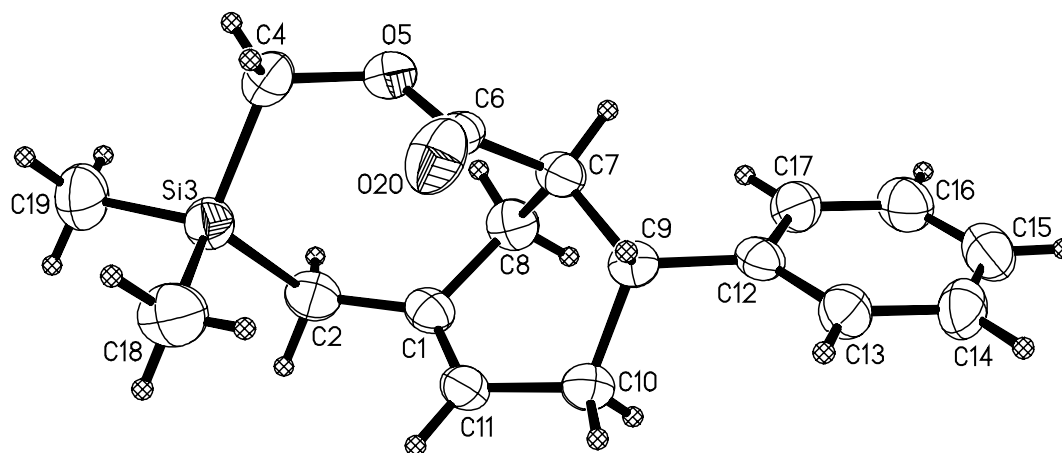
$$wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2] ]^{1/2}$$

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

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 30% probability level.



Table 1. Crystal data and structure refinement for **4f**.

Identification code	jmw2_05 (John Whitney)	
Empirical formula	C <sub>17</sub> H <sub>22</sub> O <sub>2</sub> Si	
Formula weight	286.44	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	<i>Pca</i> 2 <sub>1</sub>	
Unit cell dimensions	<i>a</i> = 10.0069(13) Å	$\alpha = 90^\circ$ .
	<i>b</i> = 17.429(3) Å	$\beta = 90^\circ$ .
	<i>c</i> = 9.1617(15) Å	$\gamma = 90^\circ$ .
Volume	1597.9(4) Å <sup>3</sup>	
<i>Z</i>	4	
Density (calculated)	1.191 Mg/m <sup>3</sup>	
Absorption coefficient	0.146 mm <sup>-1</sup>	
<i>F</i> (000)	616	
Crystal color	colorless	
Crystal size	0.50 x 0.50 x 0.23 mm <sup>3</sup>	
Theta range for data collection	2.34 to 22.50°.	
Index ranges	$-1 \leq h \leq 10$ , $-1 \leq k \leq 18$ , $-1 \leq l \leq 9$	

Reflections collected	1539
Independent reflections	1272 [R(int) = 0.0116]
Completeness to theta = 22.50°	99.4 %
Absorption correction	None
Max. and min. transmission	0.9671 and 0.9305
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	1272 / 1 / 182
Goodness-of-fit on F <sup>2</sup>	1.074
Final R indices [I>2sigma(I) = 1101 data]	R1 = 0.0356, wR2 = 0.0823
R indices (all data)	R1 = 0.0446, wR2 = 0.0873
Absolute structure parameter	-0.1(2)
Extinction coefficient	0.0016(8)
Largest diff. peak and hole	0.178 and -0.140 e.Å <sup>-3</sup>

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

	x	y	z	U(eq)
C(1)	-1044(4)	6837(2)	1660(5)	58(1)
C(2)	-1183(4)	6312(2)	2968(5)	70(1)
Si(3)	199(1)	6318(1)	4361(2)	65(1)
C(4)	521(5)	7336(3)	5006(6)	82(1)
O(5)	-43(3)	7893(2)	4006(3)	79(1)
C(6)	563(5)	7966(2)	2717(5)	62(1)
C(7)	-434(4)	8194(2)	1558(5)	58(1)
C(8)	-1607(4)	7644(2)	1718(6)	67(1)
C(9)	155(4)	8129(2)	22(5)	54(1)
C(10)	-59(4)	7307(2)	-624(7)	68(1)
C(11)	-281(4)	6696(2)	531(5)	65(1)
C(12)	-340(4)	8720(2)	-1056(4)	54(1)
C(13)	390(4)	8877(2)	-2301(6)	67(1)
C(14)	-30(5)	9409(3)	-3319(6)	80(1)
C(15)	-1199(6)	9803(2)	-3088(7)	84(2)
C(16)	-1933(5)	9652(2)	-1883(7)	82(1)
C(17)	-1522(4)	9119(2)	-873(6)	70(1)
C(18)	1743(4)	5900(3)	3556(7)	98(2)
C(19)	-335(6)	5755(3)	5992(7)	102(2)
O(20)	1718(3)	7829(2)	2524(4)	91(1)

Table 3. Bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **4f**.

C(1)-C(11)	1.309(6)
C(1)-C(2)	1.514(6)
C(1)-C(8)	1.516(5)
C(2)-Si(3)	1.882(5)
Si(3)-C(18)	1.861(5)
Si(3)-C(19)	1.866(6)
Si(3)-C(4)	1.897(5)
C(4)-O(5)	1.449(5)
O(5)-C(6)	1.334(5)
C(6)-O(20)	1.193(5)
C(6)-C(7)	1.510(6)
C(7)-C(8)	1.523(5)
C(7)-C(9)	1.531(6)
C(9)-C(12)	1.511(6)
C(9)-C(10)	1.564(5)
C(10)-C(11)	1.518(6)
C(12)-C(13)	1.382(6)
C(12)-C(17)	1.382(5)
C(13)-C(14)	1.381(7)
C(14)-C(15)	1.374(6)
C(15)-C(16)	1.352(7)
C(16)-C(17)	1.374(6)
C(11)-C(1)-C(2)	124.5(4)
C(11)-C(1)-C(8)	114.7(4)
C(2)-C(1)-C(8)	119.9(4)
C(1)-C(2)-Si(3)	117.8(3)
C(18)-Si(3)-C(19)	110.4(3)
C(18)-Si(3)-C(2)	109.8(2)
C(19)-Si(3)-C(2)	109.2(2)
C(18)-Si(3)-C(4)	110.4(2)
C(19)-Si(3)-C(4)	106.9(2)
C(2)-Si(3)-C(4)	110.0(2)
O(5)-C(4)-Si(3)	111.3(3)

C(6)-O(5)-C(4)	116.5(4)
O(20)-C(6)-O(5)	123.5(5)
O(20)-C(6)-C(7)	126.0(5)
O(5)-C(6)-C(7)	110.3(4)
C(6)-C(7)-C(8)	106.0(4)
C(6)-C(7)-C(9)	111.8(3)
C(8)-C(7)-C(9)	109.8(4)
C(1)-C(8)-C(7)	107.2(3)
C(12)-C(9)-C(7)	115.1(3)
C(12)-C(9)-C(10)	109.4(4)
C(7)-C(9)-C(10)	111.3(4)
C(11)-C(10)-C(9)	113.5(4)
C(1)-C(11)-C(10)	120.3(4)
C(13)-C(12)-C(17)	117.0(4)
C(13)-C(12)-C(9)	120.1(4)
C(17)-C(12)-C(9)	123.0(4)
C(14)-C(13)-C(12)	122.0(4)
C(15)-C(14)-C(13)	119.4(5)
C(16)-C(15)-C(14)	119.4(5)
C(15)-C(16)-C(17)	121.3(5)
C(16)-C(17)-C(12)	121.0(5)

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
C(1)	53(2)	51(2)	70(3)	-6(2)	-9(3)	-6(2)
C(2)	62(2)	66(2)	81(4)	-7(3)	2(3)	-8(2)
Si(3)	67(1)	62(1)	65(1)	3(1)	-1(1)	0(1)
C(4)	107(4)	81(3)	56(3)	5(3)	-9(3)	-6(3)
O(5)	114(2)	65(2)	58(3)	-8(2)	-2(2)	0(2)
C(6)	78(3)	57(2)	51(3)	-6(2)	-2(3)	-18(2)
C(7)	60(2)	49(2)	64(3)	-5(2)	-3(3)	1(2)
C(8)	53(2)	73(3)	75(3)	-3(3)	1(2)	10(2)
C(9)	51(2)	56(2)	54(2)	-5(2)	0(2)	0(2)
C(10)	80(3)	62(2)	61(3)	-8(3)	1(3)	12(2)
C(11)	79(3)	50(2)	66(3)	-8(2)	-14(3)	11(2)
C(12)	57(2)	45(2)	61(4)	-8(2)	-8(2)	-3(2)
C(13)	69(3)	63(3)	69(3)	2(3)	0(3)	-9(2)
C(14)	99(4)	74(3)	65(3)	14(3)	-12(3)	-30(3)
C(15)	100(4)	60(3)	93(4)	7(3)	-36(4)	-7(3)
C(16)	85(3)	72(3)	89(4)	-2(3)	-18(4)	16(3)
C(17)	74(3)	69(2)	67(3)	-1(3)	-7(3)	15(2)
C(18)	77(3)	113(4)	104(4)	-18(3)	-8(3)	17(3)
C(19)	124(4)	92(3)	91(4)	24(3)	-2(4)	-5(3)
O(20)	66(2)	128(3)	80(2)	20(2)	-14(2)	-20(2)

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

	x	y	z	U(eq)
H(2A)	-1278	5791	2610	84
H(2B)	-2009	6443	3463	84
H(4A)	131	7406	5966	98
H(4B)	1477	7419	5086	98
H(7A)	-737	8722	1731	69
H(8A)	-2060	7729	2639	80
H(8B)	-2242	7721	932	80
H(9A)	1122	8204	115	65
H(10A)	-826	7317	-1272	82
H(10B)	717	7169	-1202	82
H(11A)	128	6220	436	78
H(13A)	1188	8616	-2458	80
H(14A)	475	9499	-4154	95
H(15A)	-1484	10171	-3755	101
H(16A)	-2732	9913	-1735	99
H(17A)	-2046	9026	-54	84
H(18A)	1566	5385	3237	147
H(18C)	2439	5895	4277	147
H(18D)	2020	6205	2737	147
H(19C)	-509	5234	5709	153
H(19D)	-1133	5976	6393	153
H(19A)	361	5765	6712	153

Table 6. Torsion angles [°] for **4f**.

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C(11)-C(1)-C(2)-Si(3)	77.7(5)
C(8)-C(1)-C(2)-Si(3)	-90.8(4)
C(1)-C(2)-Si(3)-C(18)	-68.0(4)
C(1)-C(2)-Si(3)-C(19)	170.7(3)
C(1)-C(2)-Si(3)-C(4)	53.6(4)
C(18)-Si(3)-C(4)-O(5)	103.8(4)
C(19)-Si(3)-C(4)-O(5)	-136.0(4)
C(2)-Si(3)-C(4)-O(5)	-17.5(4)
Si(3)-C(4)-O(5)-C(6)	-71.0(5)
C(4)-O(5)-C(6)-O(20)	-27.0(6)
C(4)-O(5)-C(6)-C(7)	149.5(4)
O(20)-C(6)-C(7)-C(8)	127.4(5)
O(5)-C(6)-C(7)-C(8)	-49.0(5)
O(20)-C(6)-C(7)-C(9)	7.8(6)
O(5)-C(6)-C(7)-C(9)	-168.6(4)
C(11)-C(1)-C(8)-C(7)	-52.3(5)
C(2)-C(1)-C(8)-C(7)	117.3(4)
C(6)-C(7)-C(8)-C(1)	-53.5(5)
C(9)-C(7)-C(8)-C(1)	67.5(5)
C(6)-C(7)-C(9)-C(12)	-146.1(3)
C(8)-C(7)-C(9)-C(12)	96.5(4)
C(6)-C(7)-C(9)-C(10)	88.7(4)
C(8)-C(7)-C(9)-C(10)	-28.7(5)
C(12)-C(9)-C(10)-C(11)	-150.7(4)
C(7)-C(9)-C(10)-C(11)	-22.4(5)
C(2)-C(1)-C(11)-C(10)	-171.4(4)
C(8)-C(1)-C(11)-C(10)	-2.3(6)
C(9)-C(10)-C(11)-C(1)	41.6(5)
C(7)-C(9)-C(12)-C(13)	159.9(3)
C(10)-C(9)-C(12)-C(13)	-74.0(4)
C(7)-C(9)-C(12)-C(17)	-20.9(5)
C(10)-C(9)-C(12)-C(17)	105.3(4)
C(17)-C(12)-C(13)-C(14)	0.3(6)
C(9)-C(12)-C(13)-C(14)	179.6(4)

C(12)-C(13)-C(14)-C(15)	0.8(7)
C(13)-C(14)-C(15)-C(16)	-1.4(7)
C(14)-C(15)-C(16)-C(17)	1.0(7)
C(15)-C(16)-C(17)-C(12)	0.1(7)
C(13)-C(12)-C(17)-C(16)	-0.7(6)
C(9)-C(12)-C(17)-C(16)	-180.0(4)

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