Allylation of Donor-Acceptor Cyclopropanes

Ming Yu and Brian L. Pagenkopf*

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712

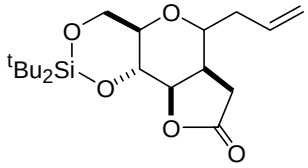
Supporting Information

Experimental Details

All reactions were run under an atmosphere of argon unless otherwise indicated. Flasks were oven or flamed-dried and allowed to cool in dry box or desiccator prior to use. Solvents and reagents were purified by standard methods.[1] The ^{1}H, ^{13}C, ^{31}F NMR data was obtained on a General Electric a Varian Unity Plus 300 or 400 spectrometer. For ^{1}H NMR, chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane and are, in all cases, referenced to the residual proton resonance peaks: δ 7.24 for $CHCl_3$. The ^{13}C NMR chemical shifts were reported in ppm relative to the center peak of the multiplet for deuterated solvents: δ 77.0 (t) for $CDCl_3$. ^{13}C and ^{19}F NMR spectra were routinely run with broadband ^{1}H decoupling. Chemical shifts for ^{19}F NMR are reported in ppm downfield from $CFCl_3$ as external standard. Coupling constants for all spectra are reported in Hertz (Hz). Infrared spectra were measured on a NEXUS 470 FT-IR spectrometer as thin films on sodium bromide plates and are recorded in units of cm^{-1}. HRMS (CI) were made with a VG analytical ZAB2-E instrument.

General Procedure

To a solution of the cyclopropane **1a** (250 mg, 0.76 mmol) in CH_2Cl_2 (5 mL) at rt was added $TiCl_4$ (82 μL, 1.7 eq). The mixture was stirred at rt for 1.0-1.5 h until TLC indicated complete consumption of starting material. To the dark brown solution was added allyltrimethylsilane (480 μL, 3.05 mmol, 4.0 eq). The resulting mixture was stirred for 2 h and then poured into saturated aqueous $NaHCO_3$ (10 mL). After stirring for 10 min the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 8 mL). The combined organic solution was washed with H_2O (2 × 4 mL), brine (5 mL) and dried ($MgSO_4$). After filtration through a small pad of celite, volatiles were removed under reduced pressure. Purification of the residue by flash chromatography on silica gel with 30:1 hexanes-EtOAc for elution gave the title products as colorless oils: **2a**(*β*) (44 mg, 16 %) and **2a** (*α*) (232 mg, 63%).



2a

4-Allyl-8,8-di-*tert*-butyl-hexahydro-1,5,7,9-tetraoxa-8-sila-cyclopenta[*a*]naphthalen-2-one (2a, Table 1, entry 1).

2a(*β*):

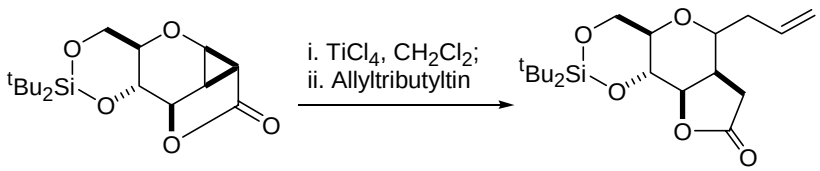
R_f 0.69 (25% EtOAc/hexanes);

IR (thin film) ν 1779, 1709, 1642 cm^{-1};

[1]Armarego, W.L.F.; Perrin, D. D. *Purification of Laboratory Chemicals*; 4th Ed.; Oxford ; Boston : Butterworth Heinemann, 1996.

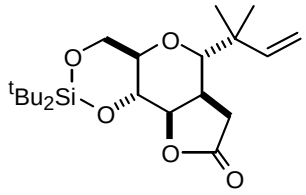
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84-5.70 (m, 1H), 5.19-5.12 (m, 2H), 4.49 (dd, *J* = 7.7, 7.7 Hz, 1H), 4.22 (ddd, *J* = 5.1, 5.1, 5.1 Hz, 1H), 3.90-3.76 (m, 3H), 3.32 (ddd, *J* = 10.2, 10.2, 5.1 Hz, 1H), 2.89-2.78 (m, H), 2.56 (dd, *J* = 16.9, 13.1 Hz, 1H), 2.45-2.37 (m, 2H), 2.10 (ddd, *J* = 14.6, 7.4, 7.4 Hz, 1H), 1.06 (s, 9H), 1.02 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 175.9, 133.1, 118.5, 82.9, 76.4, 75.7, 74.1, 66.5, 40.9, 37.9, 28.4, 27.6, 27.2, 23.0, 20.2;
HRMS m/z calcd for $C_{19}H_{33}O_5Si$ $[M+H]^+$ 369.2097, found: 369.2100.

2a(*α*):
R_f 0.62 (25% EtOAc/hexanes);
IR (thin film) ν 1783 cm^{-1};
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84-5.70 (m, 1H), 5.19-5.12 (m, 2H), 4.49 (dd, *J* = 7.7, 7.7 Hz, 1H), 4.22 (ddd, *J* = 5.1, 5.1, 5.1 Hz, 1H), 3.90-3.76 (m, 3H), 3.32 (ddd, *J* = 10.2, 10.2, 5.1 Hz, 1H), 2.89-2.78 (m, H), 2.56 (dd, *J* = 16.9, 13.1 Hz, 1H), 2.45-2.37 (m, 2H), 2.10 (ddd, *J* = 14.6, 7.4, 7.4 Hz, 1H), 1.06 (s, 9H), 1.02 (s, 9H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 175.4, 133.1, 118.4, 81.4, 75.9, 72.5, 66.8, 66.6, 38.8, 37.1, 32.0, 27.4, 27.0, 22.7, 19.9;
HRMS m/z calcd for $C_{19}H_{33}O_5Si$ $[M+H]^+$ 369.2097, found: 369.2096.



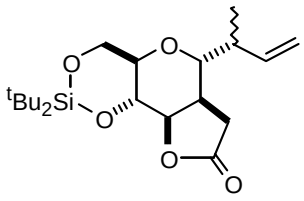
1a 2a(*α*)

(Table 1, entry 2)
The title compounds were prepared from **1a** according to the general procedure, except that 1.5 equivalents of alltyltributyltin was used (colorless syrups): **2a**(*β*): (20 mg, 11 %); **2a**(*α*): (156 mg, 76%).

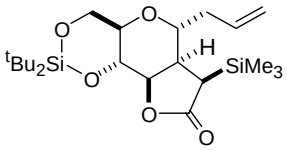


4-(1,1-Dimethyl-allyl)-8,8-di-*tert*-butyl-hexahydro-1,5,7,9-tetraoxa-8-sila-cyclopenta[*a*] naphthalen-2-one (Table 1, entry 3).
The title compound was prepared from **1a** according to the general procedure, except that 3.0 equivalents of prenyltrimethylsilane was used. Purification by flash chromatography on silica gel with 15:1 hexanes-EtOAc for elution gave the title compound as colorless syrup (68 mg, 78%).
R_f 0.65 (25% EtOAc/hexanes);
IR (thin film) ν 1765 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (dd, *J* = 17.6, 10.4 Hz, 1H), 5.09-5.05 (m, 2H), 4.52 (dd, *J* = 8.6, 8.6 Hz, 1H), 4.09-4.06 (m, 1H), 3.91 (dd, *J* = 8.9, 8.9 Hz, 1H), 3.74-3.70 (m, 2H), 3.45 (d, *J* = 4.8 Hz, 1H), 2.98-2.90 (m, 2H), 1.00 (s, 9H), 0.99 (s, 3H), 0.94 (s, 9H), 0.93 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 144.2, 113.9, 82.2, 81.3, 75.1, 68.9, 66.6, 41.8, 35.7, 33.9, 27.3, 26.9, 26.0, 22.7, 22.6, 19.9;
HRMS m/z calcd for $C_{21}H_{37}O_5Si$ $[M+H]^+$ 397.2410, found: 397.2394.

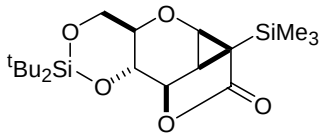


4-(1-Methyl-allyl)-8,8-di-*tert*-butyl-hexahydro-1,5,7,9-tetraoxa-8-sila-cyclopenta[*a*] naphthalen-2-one (Table 1, entry 4).
The title compounds were prepared from **1a** according to the general procedure, except that 3.5 equivalents of crotyltrimethylsilane was used. Purification by flash chromatography on silica gel with 15:1 hexanes-EtOAc for elution gave the title compounds as colorless syrup: A (41 mg, 40%), B (39 mg, 39%).
Diastereomer A:
R_f 0.64 (15% EtOAc/hexanes);
IR (thin film) ν 1761 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56 (ddddd, *J* = 10.1, 10.1, 10.1, 10.1, 1.4 Hz, 1H), 5.15-5.08 (m, 2H), 4.45 (dd, *J* = 7.9, 7.9 Hz, 1H), 4.10 (ddd, *J* = 10.0, 5.0, 1.8 Hz, 1H), 3.87-3.78 (m, 2H), 3.48 (dd, *J* = 10.0, 1.4 Hz, 1H), 3.44-3.37 (m, 1H), 3.01-2.94 (m, 1H), 2.59-2.43 (m, 3H), 1.02 (d, *J* = 6.3 Hz, 3H), 1.01 (s, 9H), 0.98 (s, 9H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 140.1, 117.1, 81.2, 76.8, 75.7, 66.7, 66.6, 40.0, 37.1, 32.4, 27.4, 26.9, 22.7, 19.9, 16.6;
HRMS submitted.



2b(α)

Diastereomer B:
R_f 0.64 (15% EtOAc/hexanes);
IR (thin film) ν 1768 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75-5.66 (m, 1H), 5.08-5.00 (m, 2H), 4.52 (dd, *J* = 7.7, 7.7 Hz, 1H), 4.03 (dd, *J* = 10.0, 5.0 Hz, 1H), 3.96 (d, *J* = 10.4, 7.8 Hz, 1H), 3.75 (dd, *J* = 10.1, 10.1 Hz, 1H), 3.55-3.47 (m, 2H), 2.86 (dddd, *J* = 9.2, 9.2, 9.2, 4.8 Hz, 1H), 2.57(dd, *J* = 16.8, 8.8 Hz, 1H), 2.47 (d, *J* = 18.0, 10.0 Hz, 1H), 2.46-2.37 (m, 1H), 1.05 (d, *J* = 6.5 Hz, 3H), 1.01 (s, 9H), 0.96 (s, 9H);
^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 139.0, 115.8, 82.1, 76.5, 75.7, 67.0, 66.6, 40.4, 37.2, 30.9, 27.3, 27.0, 22.6, 19.9, 18.0;
HRMS submitted.



1b

6,6-Di-*tert*-butyl-2a-trimethylsilanyl-hexahydro-1,3,5,7,-tetraoxa-6-sila benzo[*g*]cyclopropa [*cd*] inden-2-one (1b, table 1, entry 5).

To a solution of cyclopropane **1a** (350 mg, 1.1 mmol) in THF (6 mL) at –78 °C was added trimethyl chlorosilane (191 μL, 1.5 mmol, 1.4 eq) followed by LDA (275 μL × 0.8 M, 2.2 mmol, 2.0 eq). After stirring at –78 °C for 5 min saturated aqueous $NaHCO_3$ solution (5mL) was added to the reaction solution. The resulting mixture was allowed to warm to room temperature and the organic layer was separated and the aqueous layer was extracted with Et_2O (2 × 3 mL). The combined organic layers were washed with H_2O (2 × 2 mL), brine (3 mL) and dried ($MgSO_4$). After filtration through a small pad of celite, volatiles were removed under reduced pressure. Purification of the residual oil by flash chromatography on silica gel with 50:1 hexanes-EtOAc for elution afforded the title compound as a colorless needles (409 mg, 96%).

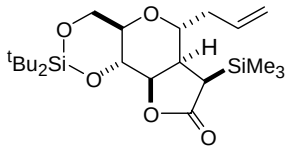
R_f 0.64 (20% EtOAc/hexanes);

IR (thin film) ν 1759, 1713 cm^{-1};

^1H NMR (300 MHz, $CDCl_3$) δ 4.85 (d, *J* = 6.1 Hz, 1H), 4.28 (dd, *J* = 9.5, 5.4 Hz, 1H), 4.17 (d, *J* = 5.4 Hz, 1H), 3.97 (d, *J* = 9.5 Hz, 1H), 3.82 (dd, *J* = 10.8, 9.5 Hz, 1H), 3.51 (ddd, *J* = 9.5, 5.4, 5.4, 5.4 Hz, 1H), 2.44 (dd, *J* = 5.8, 5.8 Hz, 1H), 1.05 (s, 9H), 1.01 (s, 9H), 0.14 (s, 9 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 173.2, 77.7, 76.3, 74.3, 66.9, 62.5, 28.3, 27.3, 27.1, 26.2, 22.5, 20.1, -3.2;

HRMS m/z calcd for $C_{19}H_{35}O_5Si$ $[M+H]^+$ 399.2023, found: 399.2024.



2b(α)

4-Allyl-8,8-di-*tert*-butyl-3-trimethylsilanyl-hexahydro-1,5,7,9-tetraoxa-8-sila-cyclopenta[*a*] naphthalen-2-one (2b(*α*)), table 1, entry 5).

The title compound was prepared from **1b** according to the general procedure. Purification by flash chromatography on silica gel with 15:1 hexanes-EtOAc for elution gave the title compound as colorless syrup (68 mg, 72%).

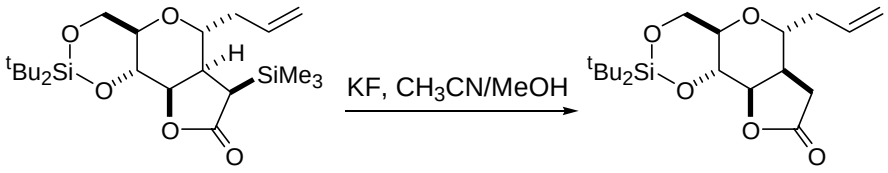
R_f 0.52 (25% EtOAc/hexanes);

IR (thin film) ν 1751 cm^{-1};

^1H NMR (300 MHz, $CDCl_3$) δ 5.83-5.69 (m, 1H), 5.18 (s, 1H), 5.13 (dd, *J* = 7.4, 1.5 Hz, 1H), 4.52 (dd, *J* = 8.3, 8.3 Hz, 1H), 4.18-4.08 (m, 2H), 3.88 (ddd, *J* = 11.2, 11.2, 8.2 Hz, 1H), 3.55 (ddd, *J* = 10.2, 10.2, 5.1 Hz, 1H), 3.09 (dd, *J* = 11.0, 8.5 Hz, 1H), 2.58 (ddd, *J* = 14.8, 7.4, 7.4 Hz, 1H), 2.37 (d, *J* = 11.0 Hz, 1H), 2.3**X** (ddd, *J* = 14.0, 7.0, 7.0 Hz, 1H), 1.05 (s, 9H), 1.02 (s, 9H), 0.28 (s, 9 H);

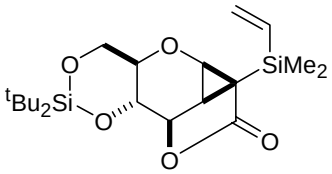
^{13}C NMR (75 MHz, $CDCl_3$) δ 178.5, 133.8, 118.4, 79.9, 75.8, 71.8, 67.0, 66.1, 42.3, 37.4, 35.7, 27.6, 27.2, 22.7, 20.2, 0.0;

HRMS m/z calcd for $C_{22}H_{41}O_5Si_2$ $[M+H]^+$ 441.2493, found: 441.2493.



2b(*α*) **2a(*α*)**

To a solution of **2b(*α*)** (310 mg, 0.70 mmol) in CH_3CN (4 mL) and MeOH (2 mL) was added KF (204 mg, 3.5 mmol, 5.0 eq). The mixture was stirred at rt for 30 min. The organic solvent was removed under reduced pressure and the residue was dissolved in EtOAc (10 mL). The resulting solution was washed with H_2O (2 × 2 mL), brine (3 mL) and dried ($MgSO_4$). After filtration through a small pad of celite, volatiles were removed under reduced pressure. Purification of the residual oil by flash chromatography on silica gel with 30:1 hexanes-EtOAc for elution afforded the title compound as colorless oil (251 mg, 97%).



6,6-Di-*tert*-butyl-2a-(dimethyl-vinyl-silanyl)-hexahydro-1,3,5,7-tetraoxa-6-sila-benzo[g] cyclopropa[*cd*]inden-2-one (table 1, entry 6).

The title compound was prepared from **1a** according to the procedure described above for the preparation of **1b**, except that 1.6 equivalents of vinyldimethylchlorosilane was used. Purification by flash chromatography on silica gel with 50:1 hexanes-EtOAc for elution gave the title compound as an oily solid (1.71 g, 97%).

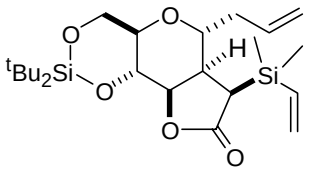
R_f 0.55 (25% EtOAc/hexanes);

IR (thin film) ν 1761 cm^{-1};

^1H NMR (300 MHz, $CDCl_3$) δ 6.10-5.96 (m, 2H), 5.88 (dd, *J* = 18.4, 5.6 Hz, 1H), 4.85 (d, *J* = 5.9 Hz, 1H), 4.28 (dd, *J* = 9.5, 5.4 Hz, 1H), 4.16 (d, *J* = 5.4 Hz, 1H), 3.96 (d, *J* = 9.5 Hz, 1H), 3.81 (dd, *J* = 10.2, 10.2 Hz, 1H), 3.49 (ddd, *J* = 10.2, 10.2, 5.4 Hz, 1H), 2.45 (dd, *J* = 5.6, 5.6 Hz, 1H), 1.04 (s, 9H), 1.00 (s, 9H), 0.27 (s, 3 H), 0.24 (s, 3 H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 135.3, 134.5, 78.0, 76.5, 74.6, 67.2, 62.8, 28.0, 27.6, 27.4, 26.5, 22.8, 20.4, -4.6, -4.7;

HRMS m/z calcd for $C_{20}H_{35}O_5Si_2$ $[M+H]^+$ 411.2023, found: 411.2022.



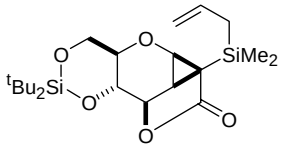
4-Allyl-8,8-di-*tert*-butyl-3-(dimethyl-vinyl-silanyl)-hexahydro-1,5,7,9-tetraoxa-8-sila-cyclopenta[*a*]naphthalen-2-one (table 1, entry 6)

The title compound was prepared from the starting cyclopropane according to the general procedure. Purification by flash chromatography on silica gel with 30:1 hexanes-EtOAc for elution gave the title compound as white solid (156 mg, 70%).

R_f 0.50 (25% EtOAc/hexanes);

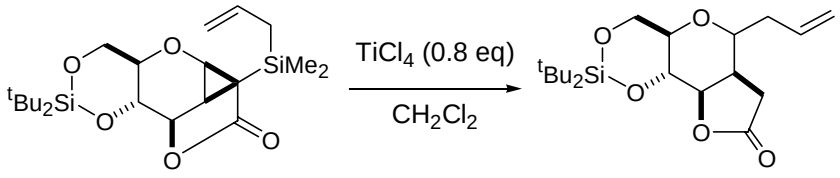
IR (thin film) ν 1758 cm^{-1};

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.25 (dd, *J* = 20.0, 14.6 Hz, 1H), 6.07 (dd, *J* = 14.6, 3.8 Hz, 1H), 5.82 (dd, *J* = 20.0, 3.8 Hz, 1H), 5.81-5.67 (m, 1H), 5.16 (s, 1H), 5.12 (d, *J* = 8.2 Hz, 1H), 4.49 (dd, *J* = 8.2, 8.2 Hz, 1H), 4.16 (dd, *J* = 7.7, 7.7 Hz, 1H), 4.07 (dd, *J* = 10.0, 5.1 Hz, 1H), 3.95 (dd, *J* = 9.1, 9.1 Hz, 1H), 3.84 (dd, *J* = 10.0, 10.0 Hz, 1H), 3.52 (ddd, *J* = 10.0, 10.0, 5.1 Hz, 1H), 3.06 (dd, *J* = 10.7, 8.6 Hz, 1H), 2.55 (ddd, *J* = 14.7, 7.7, 7.7 Hz, 1H), 2.40 (d, *J* = 11.0 Hz, 1H), 2.31 (ddd, *J* = 14.3, 7.0, 7.0 Hz, 1H), 1.04 (s, 9H), 1.00 (s, 9H), 0.37 (s, 3 H), 0.35 (s, 3 H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 178.2, 136.5, 135.0, 133.8, 118.4, 80.1, 75.6, 71.6, 66.9, 66.2, 42.2, 37.4, 35.5, 27.6, 27.3, 22.7, 20.2, -1.7, -2.4;
HRMS m/z calcd for $C_{23}H_{41}O_5Si_2$ $[M+H]^+$ 453.2493, found: 453.2498.



2a-(Allyl-dimethyl-silanyl)-6,6-di-*tert*-butyl-hexahydro-1,3,5,7,-tetraoxa-6-sila-benzo[*g*] cyclopropa[*cd*]inden-2-one (table 1, entry 7).

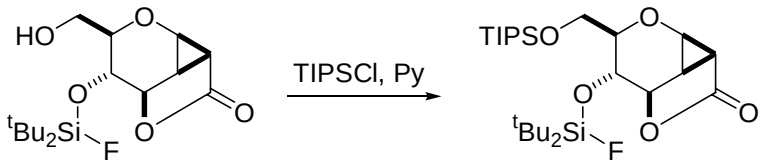
The title compound was prepared from **1a** according to the procedure described above for the preparation of **1b**, except that 1.6 equivalents of allyldimethylchlorosilane was used. Purification by flash chromatography on silica gel with 50:1 hexanes-EtOAc for elution gave the title compound as colorless oil (178 mg, 93%).
R_f 0.73 (25% EtOAc/hexanes);
IR (thin film) ν 1759, 1627 cm^{-1};
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85-5.70 (m, 1H), 4.96-4.89 (m, 2H), 4.28 (dd, *J* = 9.5, 5.4 Hz, 1H), 4.17 (d, *J* = 5.4 Hz, 1H), 3.96 (d, *J* = 9.5 Hz, 1H), 3.81 (dd, *J* = 10.8, 9.9 Hz, 1H), 3.50 (ddd, *J* = 10.8, 9.5, 5.4 Hz, 1H), 2.45 (dd, *J* = 5.8, 5.8 Hz, 1H), 1.73 (dd, *J* = 8.0, 1.0 Hz, 1H), 1.04 (s, 9H), 1.00 (s, 9H), 0.14 (s, 3H), 0.07 (s, 3H);
^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 133.6, 114.6, 78.0, 76.6, 74.6, 67.2, 62.6, 27.8, 27.6, 27.4, 26.4, 22.7, 21.6, 20.4, -4.8, -4.9;
HRMS m/z calcd for $C_{21}H_{37}O_5Si_2$ $[M+H]^+$ 425.2180, found: 425.2178.



2a

(table 1, entry 7).

To a solution of starting cyclopropane (130 mg, 0.31 mmol) in CH_2Cl_2 (7 mL) at rt was added $TiCl_4$ (27 μL, 0.25 mmol, 0.8 eq). The mixture was stirred at rt for 3.5 h until TLC indicated complete consumption of starting material. The reaction solution was then poured into saturated aqueous $NaHCO_3$ (10 mL). After stirring for 10 min the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 6 mL). The combined organic solution was washed with H_2O (2 × 4 mL), brine (5 mL) and dried ($MgSO_4$). After filtration through a small pad of celite, volatiles were removed under reduced pressure. Purification of the residue by flash chromatography on silica gel with 30:1 hexanes-EtOAc for elution gave the title products as colorless oils: **2a**(*β*) (22 mg, 19 %) and **2a**(*α*) (65 mg, 58%).



5-Di-*tert*-butyl-fluoro-silanyloxy)-4-triisopropylsilanyloxymethyl-hexahydro-1,3-dioxa-cyclopropa[*cd*]inden-2-one (table 1, entry 8).

To a rt solution of the alcohol[2] (189 mg, 0.54 mmol) in CH_2Cl_2 (3.0 mL) were added pyridine (0.25 mL, 3.1 mmol) and triisopropylsilyl chloride (115 µL, 0.82 mmol, 1.5 eq). The reaction mixture was stirred at rt for 20 h and then poured into saturated aqueous NH_4Cl solution (4 mL) with vigorous stirring. After 10 min the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layers were washed with H_2O (2 × 3 mL), brine (3 mL) and dried ($MgSO_4$). After filtration through celite, volatiles were removed under reduced pressure. Purification of the residual oil by flash chromatography on silica gel using 20:1 hexanes-EtOAc for elution provided the title compound as a foamy solid (240 mg, 88%).

R_f 0.75 (50% EtOAc/hexanes);

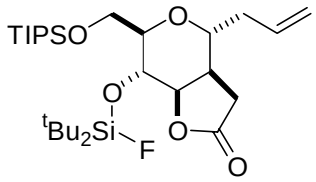
IR (thin film) ν 1783 cm^{-1};

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.84 (dd, *J* = 6.2, 2.0 Hz, 1H), 4.24 (dd, *J* = 6.2, 2.0 Hz, 1H), 4.14 (dd, *J* = 6.0, 6.0 Hz, 1H), 3.90 (dd, *J* = 11.6, 2.4 Hz, 1H), 3.76 (dd, *J* = 11.6, 6.0 Hz, 1H), 3.44 (ddd, *J* = 6.0, 6.0, 2.4 Hz, 1H), 2.48 (ddd, *J* = 5.8, 5.8, 5.8 Hz, 1H), 2.28 (dd, *J* = 6.2, 6.2 Hz, 1H), 1.04-1.00 (m, 39H);

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4,81.8, 76.3, 67.1, 63.5, 54.5, 26.83, 26.80, 26.5, 20.9, 20.05 (d, *J* = 14.5 Hz), 20.02 (d, *J* = 14.5 Hz), 17.8, 11.8;

^{19}F NMR (300 MHz, $CDCl_3$) δ -159.3;

HRMS m/z calcd for $C_{25}H_{48}O_5FSi_2$ $[M+H]^+$ 508.3024, found: 508.3014.



4-Allyl-7-(di-*tert*-butyl-fluoro-silanyloxy)-6-triisopropylsilanyloxymethyl-terahydro-furo[3,2,-*c*] pyran-2-one (table 1, entry 8).

The title compound was prepared from the starting cyclopropane according to the general procedure. Purification by flash chromatography on silica gel with 30:1 hexanes-EtOAc for elution gave the title compound as colorless oil (142 mg, 65%).

R_f 0.74 (25% EtOAc/hexanes);

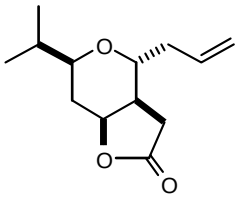
IR (thin film) ν 1716 cm^{-1};

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87-5.73 (m, 1H), 5.15-5.03 (m, 2H), 4.56 (dd, *J* = 8.8, 8.8 Hz, 1H), 4.38 (dd, *J* = 8.8, 8.8 Hz, 1H), 3.96 (dd, *J* = 14.0, 6.0 Hz, 1H), 3.87 (dd, *J* = 14.4, 6.4 Hz, 1H), 3.75-3.62 (m, 2H), 2.65-2.44 (m, 2H), 2.44-2.23(m, 3H), 1.07-1.02 (m, 39H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 133.5, 118.0, 81.3, 75.8, 71.6, 68.0, 62.3, 37.9, 37.8, 32.5, 27.0, 26.9 (d, *J* = 15.3 Hz), 20.2 (d, *J* = 15.3 Hz), 18.0, 17.9, 11.9;

---

[2] Yu, M.; Lynch, V.; Pagenkopf, B. L. *Org. Lett.* **2001**, *3*, 2563-2566.

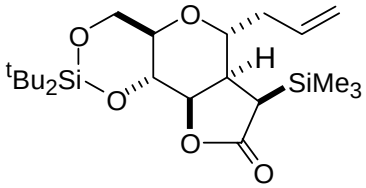
^{19}F NMR (300 MHz, $CDCl_3$) δ -157.8;
HRMS m/z calcd for $C_{28}H_{54}O_5FSi_2$ $[M+H]^+$ 545.3491, found: 545.3494.



4- Allyl-6-isopropyl-tetrahydro-furo[3,2-*c*]pyran-2-one (table 1, entry 9)
The title compound was prepared from the starting cyclopropane[3] according to the general procedure. Purification by flash chromatography on silica gel with 20:1 hexanes-EtOAc for elution gave the title compound as colorless oil (32 mg, 60%).
R_f 0.52 (33% EtOAc/hexanes);
IR (thin film) ν 1759 cm^{-1};
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85-5.75 (m, 1H), 5.11-5.07 (m, 2H), 4.73 (ddd, *J* = 9.4, 6.4, 6.4 Hz, 1H), 3.70 (ddd, *J* = 8.2, 5.4, 5.4 Hz, 1H), 3.32 (ddd, *J* = 9.6, 7.8, 4.0 Hz, 1H), 2.56-2.42 (m, 2H), 2.38-2.30 (m, 1H), 2.27-2.20 (m, 1H), 2.07 (ddd, *J* = 13.7, 5.8, 4.1 Hz, 1H), 1.78 (dddd, *J* = 6.8, 6.8, 6.8, 6.8, 6.8 Hz, 1H), 1.67-1.51 (m, 2H), 0.86 (dd, *J* = 6.7, 6.7 Hz, 6H);;
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 134.0, 117.7, 76.3, 74.1, 71.7, 38.0, 37.9, 31.8, 31.7, 29.7, 18.7, 18.5;
HRMS m/z calcd for $C_{13}H_{21}O_3$ $[M+H]^+$ 225.1491, found: 225.1491.

[3]Yu, M and Pagenkopf, B. L. *J. Am. Chem. Soc.* **2003**, *125*, 8122-8123.

Crystallographic
Material
For



2b(α)

In this experimental section, the compound **1** stands for **2b(*α*)** in the manuscript.

Table 1. Crystallographic Data for **1**.

Table 2. Fractional coordinates and equivalent isotropic thermal parameters ($Å^2$) for the non-hydrogen atoms of **1**.

Table 3. Bond Lengths (Å) and Angles (^{o}) for the non-hydrogen atoms of **1**.

Table 4. Anisotropic thermal parameters for the non-hydrogen atoms of **1**.

Table 5. Fractional coordinates and isotropic thermal parameters ($Å^2$) for the hydrogen atoms of **1**.

Table 6. Torsion Angles (^{o}) for the non-hydrogen atoms of **1**.

Figure 1. View of **1** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 30% probability level. Hydrogen atoms are drawn to an arbitrary size. The methyl group hydrogen atoms have been omitted for clarity.

Figure 2. Unit cell packing diagram for **1**. The view is approximately down the **a** axis.

X-ray Experimental for $C_{22}H_{40}O_5Si_2$: Crystals grew as colorless by slow evaporation from acetone and $CDCl_3$. The data crystal was cut from a large, hexagonal plate and had approximate dimensions; 0.30x0.23x0.08 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 568 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 92 seconds per frame. The data were collected at –120 °C using a Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.**Error! Bookmark not defined.** The structure was solved by direct methods using SIR92**Error! Bookmark not defined.** and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.**Error! Bookmark not defined.** Most of the hydrogen atom positions were observed in a ΔF map and refined using isotropic displacement parameters. Some of the methyl hydrogen atoms did not refine well. Subsequently, the hydrogen atoms on the methyl carbon atoms were calculated in ideal positions with isotropic displacement parameters set to 1.5xUeq of the

attached atom. The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0532*P)^2 + (0.6297*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.108, with R(F) equal to 0.0423 and a goodness of fit, S, = 1.01. Definitions used for calculating $R(F)$,$R_w(F^2)$ and the goodness of fit, S, are given below.[5] The data were checked for secondary extinction effects but no correction was necessary. The absolute configuration was assigned by internal comparison and confirmed by the method of Flack.**Error! Bookmark not defined.** The Flack x parameter refined to 0.0(1) for the reported configuration and 1.0(1) for the inverted configuration. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).**Error! Bookmark not defined.** All figures were generated using SHELXTL/PC.**Error! Bookmark not defined.** Tables of positional and thermal parameters, bond lengths and angles, torsion angles, figures and lists of observed and calculated structure factors are located in tables 1 through 7.

Table 1. Crystal data and structure refinement for 1.

Empirical formula	C22 H40 O5 Si2	
Formula weight	440.72	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21	
Unit cell dimensions	a = 8.7099(1) Å	α= 90°.
	b = 8.5749(1) Å	β= 99.110(1)°.
	c = 17.4951(3) Å	γ = 90°.
Volume	1290.17(3) $Å^3$	
Z	2	
Density (calculated)	1.134 Mg/m^3	
Absorption coefficient	0.164 mm^{-1}	
F(000)	480	
Crystal size	0.30 x 0.23 x 0.08 mm	
Theta range for data collection	3.07 to 27.49°.	
Index ranges	-11<=h<=11, -10<=k<=11, -22<=l<=22	
Reflections collected	5756	
Independent reflections	5756 [R(int) = 0.0000]	
Completeness to theta = 27.49°	99.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5756 / 1 / 351	
Goodness-of-fit on F^2	1.011	
Final R indices [I>2sigma(I)]	R1 = 0.0423, wR2 = 0.1034	
R indices (all data)	R1 = 0.0494, wR2 = 0.1083	
Absolute structure parameter	0.00(10)	
Largest diff. peak and hole	0.543 and -0.372 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si1	3829(1)	2114(1)	3427(1)	28(1)
O2	2603(2)	2154(2)	2600(1)	32(1)
C3	2375(2)	3544(2)	2148(1)	25(1)
C4	941(3)	3351(3)	1538(1)	29(1)
O5	1315(2)	2385(2)	913(1)	34(1)
C6	1560(3)	3286(3)	302(1)	30(1)
C7	1249(3)	4976(3)	452(1)	28(1)
C8	352(2)	4887(3)	1142(1)	28(1)
C9	427(2)	6261(3)	1704(1)	29(1)
O10	1907(2)	6315(2)	2202(1)	27(1)
C11	2200(3)	4941(2)	2666(1)	26(1)
C12	3686(3)	5256(3)	3233(1)	32(1)
O13	4126(2)	3929(2)	3706(1)	36(1)
C14	5722(3)	1247(4)	3241(2)	44(1)
C15	5461(5)	-227(5)	2751(3)	102(2)
C16	6524(4)	2481(6)	2777(2)	77(1)
C17	6861(3)	936(4)	3978(2)	55(1)
C18	2826(3)	1112(4)	4165(1)	47(1)
C19	2768(6)	-690(5)	4013(2)	81(1)
C20	1235(4)	1853(8)	4125(2)	113(2)
C21	3722(3)	1370(4)	4985(1)	52(1)
O22	1968(2)	2688(2)	-253(1)	42(1)
Si23	3061(1)	6242(1)	394(1)	31(1)
C24	3253(4)	6154(4)	-654(2)	48(1)
C25	2749(4)	8288(3)	679(2)	42(1)
C26	4894(3)	5491(4)	970(2)	44(1)
C27	-952(3)	6206(4)	2150(1)	40(1)
C28	-779(3)	7311(4)	2825(2)	49(1)
C29	-875(4)	6908(6)	3543(2)	65(1)

Table 3. Bond lengths [Å] and angles [°] for 1.

Si1-O13	1.6395(16)	C16-H16C	0.96
Si1-O2	1.6566(14)	C17-H17A	0.96
Si1-C18	1.877(3)	C17-H17B	0.96
Si1-C14	1.883(3)	C17-H17C	0.96
O2-C3	1.427(2)	C18-C20	1.516(5)
C3-C4	1.518(3)	C18-C21	1.537(3)
C3-C11	1.524(3)	C18-C19	1.568(5)
C3-H3	0.99(2)	C19-H19A	0.96
C4-O5	1.450(3)	C19-H19B	0.96
C4-C8	1.539(3)	C19-H19C	0.96
C4-H4	0.94(3)	C20-H20A	0.96
O5-C6	1.362(3)	C20-H20B	0.96
C6-O22	1.201(3)	C20-H20C	0.96
C6-C7	1.505(3)	C21-H21A	0.96
C7-C8	1.540(3)	C21-H21B	0.96
C7-Si23	1.932(2)	C21-H21C	0.96
C7-H7	0.97(3)	Si23-C25	1.855(3)
C8-C9	1.530(3)	Si23-C26	1.862(3)
C8-H8	0.93(3)	Si23-C24	1.869(3)
C9-O10	1.438(2)	C24-H24A	0.96(3)
C9-C27	1.534(3)	C24-H24B	0.98(5)
C9-H9	0.98(3)	C24-H24C	0.97(4)
O10-C11	1.432(3)	C25-H25A	0.87(4)
C11-C12	1.525(3)	C25-H25B	0.97(3)
C11-H11	0.97(3)	C25-H25C	0.98(3)
C12-O13	1.423(3)	C26-H26A	0.99(4)
C12-H12A	1.00(3)	C26-H26B	1.03(3)
C12-H12B	0.99(3)	C26-H26C	1.09(4)
C14-C17	1.520(4)	C27-C28	1.502(4)
C14-C15	1.525(5)	C27-H27A	0.98(3)
C14-C16	1.564(5)	C27-H27B	1.00(3)
C15-H15A	0.96	C28-C29	1.319(5)
C15-H15B	0.96	C28-H28	1.03(4)
C15-H15C	0.96	C29-H29A	0.95(4)
C16-H16A	0.96	C29-H29B	1.05(3)
C16-H16B	0.96		

O13-Si1-O2	106.84(8)	C3-C4-H4	110.5(15)
O13-Si1-C18	107.37(12)	C8-C4-H4	111.1(16)
O2-Si1-C18	107.70(10)	C6-O5-C4	110.50(17)
O13-Si1-C14	108.94(12)	O22-C6-O5	119.7(2)
O2-Si1-C14	108.57(10)	O22-C6-C7	129.5(2)
C18-Si1-C14	116.98(13)	O5-C6-C7	110.77(18)
C3-O2-Si1	121.00(12)	C6-C7-C8	102.50(18)
O2-C3-C4	108.98(17)	C6-C7-Si23	111.15(15)
O2-C3-C11	110.19(16)	C8-C7-Si23	126.05(15)
C4-C3-C11	110.81(17)	C6-C7-H7	107.1(17)
O2-C3-H3	109.3(14)	C8-C7-H7	107.6(15)
C4-C3-H3	109.0(13)	Si23-C7-H7	101.3(16)
C11-C3-H3	108.5(14)	C9-C8-C4	113.10(17)
O5-C4-C3	109.57(18)	C9-C8-C7	119.38(19)
O5-C4-C8	104.32(17)	C4-C8-C7	102.79(18)
C3-C4-C8	113.70(17)	C9-C8-H8	109.3(17)
O5-C4-H4	107.3(16)	C4-C8-H8	103.6(17)

C7-C8-H8	107.4(16)	H19B-C19-H19C	109.5
O10-C9-C8	110.94(17)	C18-C20-H20A	108.5
O10-C9-C27	113.09(17)	C18-C20-H20B	112.1
C8-C9-C27	110.3(2)	H20A-C20-H20B	109.5
O10-C9-H9	105.3(13)	C18-C20-H20C	107.8
C8-C9-H9	110.9(14)	H20A-C20-H20C	109.5
C27-C9-H9	106.2(14)	H20B-C20-H20C	109.5
C11-O10-C9	112.29(16)	C18-C21-H21A	109.3
O10-C11-C3	109.56(16)	C18-C21-H21B	109.3
O10-C11-C12	106.23(17)	H21A-C21-H21B	109.5
C3-C11-C12	111.79(18)	C18-C21-H21C	109.8
O10-C11-H11	109.0(15)	H21A-C21-H21C	109.5
C3-C11-H11	108.8(15)	H21B-C21-H21C	109.5
C12-C11-H11	111.4(15)	C25-Si23-C26	109.38(14)
O13-C12-C11	111.01(18)	C25-Si23-C24	109.96(15)
O13-C12-H12A	110.3(17)	C26-Si23-C24	108.31(14)
C11-C12-H12A	107.7(16)	C25-Si23-C7	111.21(12)
O13-C12-H12B	110.0(19)	C26-Si23-C7	114.55(11)
C11-C12-H12B	111.0(18)	C24-Si23-C7	103.20(12)
H12A-C12-H12B	107(2)	Si23-C24-H24A	107.2(18)
C12-O13-Si1	124.82(13)	Si23-C24-H24B	109(2)
C17-C14-C15	110.5(3)	H24A-C24-H24B	109(3)
C17-C14-C16	105.9(3)	Si23-C24-H24C	109(2)
C15-C14-C16	107.9(3)	H24A-C24-H24C	110(3)
C17-C14-Si1	113.24(19)	H24B-C24-H24C	112(3)
C15-C14-Si1	111.6(2)	Si23-C25-H25A	108(3)
C16-C14-Si1	107.3(2)	Si23-C25-H25B	114.6(18)
C14-C15-H15A	108.9	H25A-C25-H25B	110(3)
C14-C15-H15B	111.7	Si23-C25-H25C	115(2)
H15A-C15-H15B	109.5	H25A-C25-H25C	108(3)
C14-C15-H15C	107.9	H25B-C25-H25C	102(3)
H15A-C15-H15C	109.5	Si23-C26-H26A	106(2)
H15B-C15-H15C	109.5	Si23-C26-H26B	112.2(19)
C14-C16-H16A	109.7	H26A-C26-H26B	104(3)
C14-C16-H16B	109.4	Si23-C26-H26C	112.6(18)
H16A-C16-H16B	109.5	H26A-C26-H26C	112(3)
C14-C16-H16C	109.3	H26B-C26-H26C	110(3)
H16A-C16-H16C	109.5	C28-C27-C9	113.0(2)
H16B-C16-H16C	109.5	C28-C27-H27A	108.5(18)
C14-C17-H17A	109.3	C9-C27-H27A	114.3(18)
C14-C17-H17B	109.6	C28-C27-H27B	110.0(15)
H17A-C17-H17B	109.5	C9-C27-H27B	104.2(14)
C14-C17-H17C	109.5	H27A-C27-H27B	107(2)
H17A-C17-H17C	109.5	C29-C28-C27	124.8(4)
H17B-C17-H17C	109.5	C29-C28-H28	123(2)
C20-C18-C21	107.9(3)	C27-C28-H28	112(2)
C20-C18-C19	113.6(4)	C28-C29-H29A	116(2)
C21-C18-C19	107.4(3)	C28-C29-H29B	125.5(19)
C20-C18-Si1	107.4(2)	H29A-C29-H29B	118(3)
C21-C18-Si1	110.7(2)		
C19-C18-Si1	109.9(2)		
C18-C19-H19A	109.4		
C18-C19-H19B	109.5		
H19A-C19-H19B	109.5		
C18-C19-H19C	109.5		
H19A-C19-H19C	109.5		

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 1. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si1	34(1)	22(1)	25(1)	2(1)	-5(1)	-1(1)
O2	44(1)	20(1)	27(1)	1(1)	-8(1)	-3(1)
C3	27(1)	22(1)	24(1)	2(1)	-3(1)	0(1)
C4	30(1)	28(1)	25(1)	-4(1)	-3(1)	-5(1)
O5	45(1)	26(1)	27(1)	-4(1)	-6(1)	-1(1)
C6	28(1)	32(1)	26(1)	-3(1)	-7(1)	-2(1)
C7	29(1)	30(1)	23(1)	1(1)	-4(1)	2(1)
C8	23(1)	33(1)	25(1)	-2(1)	-3(1)	-2(1)
C9	26(1)	30(1)	28(1)	1(1)	-4(1)	7(1)
O10	29(1)	22(1)	28(1)	-1(1)	-5(1)	2(1)
C11	30(1)	22(1)	25(1)	0(1)	-3(1)	2(1)
C12	40(1)	21(1)	31(1)	-3(1)	-10(1)	1(1)
O13	45(1)	23(1)	33(1)	-1(1)	-15(1)	1(1)
C14	47(1)	39(1)	42(1)	-2(1)	-3(1)	13(1)
C15	65(2)	84(3)	143(4)	-63(3)	-23(3)	32(2)
C16	61(2)	108(3)	67(2)	32(2)	28(2)	25(2)
C17	36(1)	68(2)	57(2)	15(2)	-3(1)	2(1)
C18	50(1)	54(2)	33(1)	12(1)	-4(1)	-12(1)
C19	111(3)	56(2)	72(2)	16(2)	-2(2)	-37(2)
C20	35(2)	240(7)	65(2)	72(3)	12(1)	13(3)
C21	59(2)	66(2)	30(1)	7(1)	0(1)	13(2)
O22	50(1)	42(1)	32(1)	-10(1)	1(1)	2(1)
Si23	31(1)	31(1)	29(1)	4(1)	1(1)	-2(1)
C24	54(2)	56(2)	37(1)	7(1)	12(1)	1(2)
C25	48(2)	31(1)	47(2)	3(1)	3(1)	-7(1)
C26	30(1)	53(2)	47(2)	13(1)	3(1)	0(1)
C27	29(1)	55(2)	37(1)	-1(1)	2(1)	9(1)
C28	43(1)	57(2)	49(2)	-7(1)	10(1)	15(1)
C29	60(2)	89(3)	49(2)	-15(2)	19(1)	9(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 1.

	x	y	z	U(eq)
H15A	6451	-630	2670	153
H15B	4915	-1009	2994	153
H15C	4861	53	2261	153
H16A	7497	2078	2672	115
H16B	5859	2706	2298	115
H16C	6705	3419	3078	115
H17A	7799	498	3846	82
H17B	7097	1895	4255	82
H17C	6407	214	4298	82
H19A	2253	-1194	4391	122
H19B	2207	-893	3504	122
H19C	3807	-1088	4049	122
H20A	705	1356	4501	169
H20B	1301	2953	4225	169
H20C	670	1674	3616	169
H21A	3186	853	5352	79
H21B	4750	945	5017	79
H21C	3789	2466	5099	79
H3	3290(30)	3720(30)	1890(13)	22(6)
H4	150(30)	2840(30)	1747(14)	29(6)
H7	540(30)	5350(30)	10(16)	35(7)
H8	-680(30)	4680(30)	944(15)	36(7)
H9	340(30)	7260(30)	1423(13)	27(6)
H11	1320(30)	4760(30)	2936(14)	28(6)
H12A	3490(30)	6170(40)	3561(16)	45(7)
H12B	4550(40)	5560(40)	2955(18)	52(9)
H24A	4250(40)	6600(40)	-705(17)	50(8)
H24B	3240(50)	5060(50)	-820(20)	77(12)
H24C	2420(40)	6750(50)	-950(20)	76(12)
H25A	3530(50)	8840(50)	570(20)	74(12)
H25B	1770(40)	8740(40)	438(17)	42(8)
H25C	2700(40)	8440(40)	1230(20)	55(9)
H26A	5750(50)	6100(50)	800(20)	77(11)
H26B	4980(40)	5750(40)	1550(20)	64(10)
H26C	5050(40)	4250(50)	891(19)	65(10)
H27A	-1180(30)	5170(40)	2334(17)	45(8)
H27B	-1870(30)	6510(30)	1758(14)	33(6)
H28	-560(40)	8430(50)	2660(20)	64(10)
H29A	-1240(50)	5880(50)	3610(20)	71(12)
H29B	-740(40)	7670(40)	4019(19)	59(9)

Table 6. Torsion angles [°] for 1.

O13-Si1-O2-C3	18.95(18)
C18-Si1-O2-C3	134.04(18)
C14-Si1-O2-C3	-98.40(18)
Si1-O2-C3-C4	-166.75(14)
Si1-O2-C3-C11	-45.0(2)
O2-C3-C4-O5	-77.3(2)
C11-C3-C4-O5	161.28(17)
O2-C3-C4-C8	166.41(17)
C11-C3-C4-C8	45.0(2)
C3-C4-O5-C6	-100.4(2)
C8-C4-O5-C6	21.7(2)
C4-O5-C6-O22	175.9(2)
C4-O5-C6-C7	-4.2(2)
O22-C6-C7-C8	164.9(2)
O5-C6-C7-C8	-15.1(2)
O22-C6-C7-Si23	-58.1(3)
O5-C6-C7-Si23	122.00(16)
O5-C4-C8-C9	-159.78(17)
C3-C4-C8-C9	-40.5(3)
O5-C4-C8-C7	-29.7(2)
C3-C4-C8-C7	89.6(2)
C6-C7-C8-C9	152.82(18)
Si23-C7-C8-C9	24.6(3)
C6-C7-C8-C4	26.7(2)
Si23-C7-C8-C4	-101.5(2)
C4-C8-C9-O10	46.7(2)
C7-C8-C9-O10	-74.4(2)
C4-C8-C9-C27	-79.3(2)
C7-C8-C9-C27	159.57(19)
C8-C9-O10-C11	-61.0(2)
C27-C9-O10-C11	63.5(3)
C9-O10-C11-C3	66.5(2)
C9-O10-C11-C12	-172.59(17)
O2-C3-C11-O10	-177.61(16)
C4-C3-C11-O10	-56.9(2)
O2-C3-C11-C12	64.9(2)
C4-C3-C11-C12	-174.39(19)
O10-C11-C12-O13	-177.49(19)
C3-C11-C12-O13	-58.0(3)
C11-C12-O13-Si1	32.8(3)
O2-Si1-O13-C12	-12.8(2)
C18-Si1-O13-C12	-128.1(2)
C14-Si1-O13-C12	104.3(2)
O13-Si1-C14-C17	72.3(2)
O2-Si1-C14-C17	-171.7(2)
C18-Si1-C14-C17	-49.6(3)
O13-Si1-C14-C15	-162.3(3)
O2-Si1-C14-C15	-46.3(3)
C18-Si1-C14-C15	75.8(3)
O13-Si1-C14-C16	-44.2(2)
O2-Si1-C14-C16	71.8(2)
C18-Si1-C14-C16	-166.2(2)
O13-Si1-C18-C20	65.8(3)
O2-Si1-C18-C20	-48.9(3)
C14-Si1-C18-C20	-171.4(3)

O13-Si1-C18-C21	-51.7(2)
O2-Si1-C18-C21	-166.5(2)
C14-Si1-C18-C21	71.0(3)
O13-Si1-C18-C19	-170.2(2)
O2-Si1-C18-C19	75.1(2)
C14-Si1-C18-C19	-47.4(3)
C6-C7-Si23-C25	-174.06(16)
C8-C7-Si23-C25	-49.4(2)
C6-C7-Si23-C26	-49.4(2)
C8-C7-Si23-C26	75.2(2)
C6-C7-Si23-C24	68.09(19)
C8-C7-Si23-C24	-167.3(2)
O10-C9-C27-C28	43.1(3)
C8-C9-C27-C28	167.9(2)
C9-C27-C28-C29	-125.9(3)

Figure 1a. Displacement ellipsoids are scaled to the 50% probability level. Hydrogen atoms are drawn to an arbitrary size. The methyl group hydrogen atoms have been omitted for clarity.

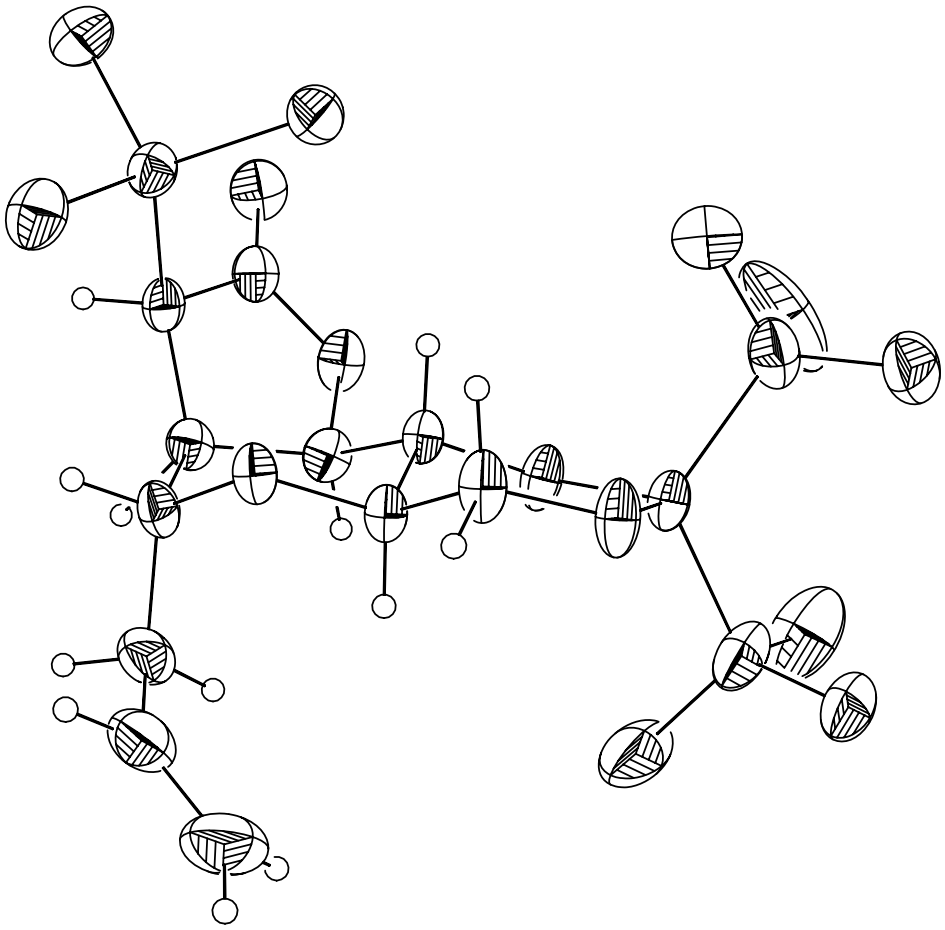


Figure 1b. Displacement ellipsoids are scaled to the 50% probability level. Hydrogen atoms are drawn to an arbitrary size. The methyl group hydrogen atoms have been omitted for clarity.

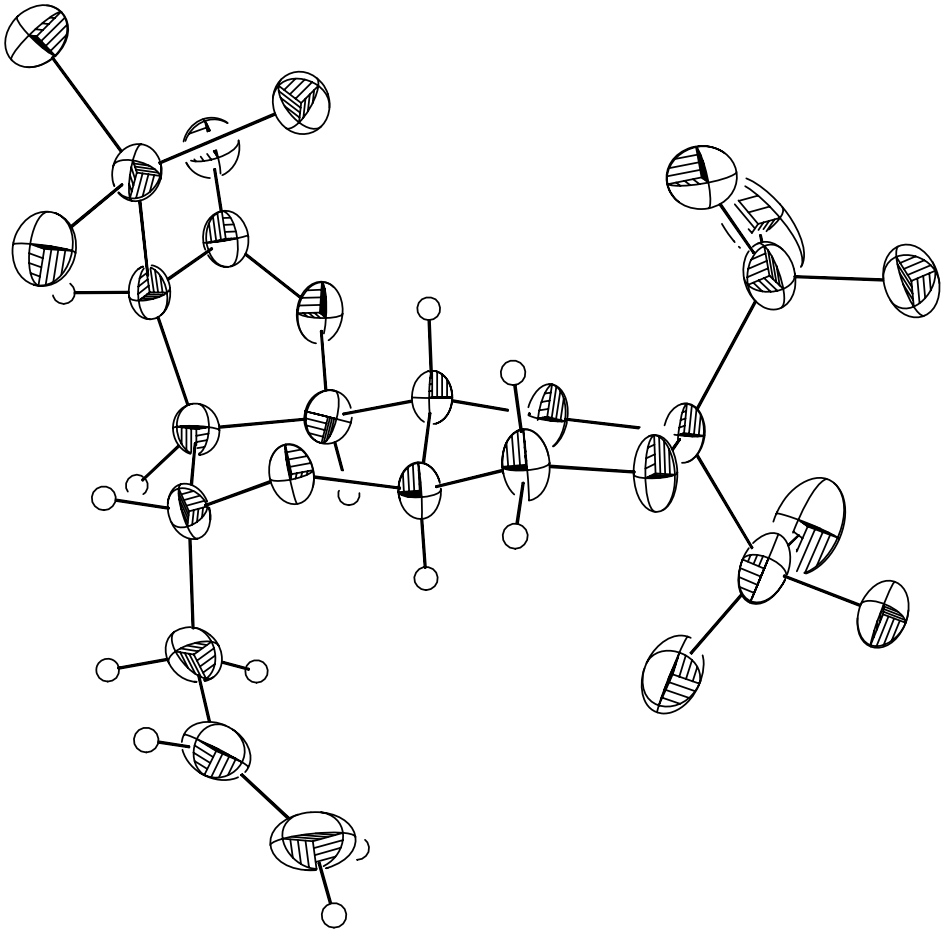


Figure 2. Unit cell packing diagram for **1**. The view is approximately down the **a** axis.