SUPPORTING INFORMATION FOR:

Substitution and Remote Protecting Group Influence on the Oxidation/Addition of α -Substituted 1,2-Anhydroglycosides: A Novel Entry into C-Ketosides

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Experimental protocols and spectroscopic data for compounds **11**, **15-23**, **31**, **32**.

General

NMR spectra were recorded on either Varian Inova-500 MHz or Varian VXR-500 MHz spectrometers. Chemical shifts were reported in δ , parts per million (ppm), relative to chloroform (7.24), benzene (7.16), dichloromethane (5.32), or acetone (2.04) as internal standards. Coupling constants, J , were reported in Hertz (Hz) and refer to apparent peak multiplicities and not true coupling constants. Mass spectra were recorded at the Mass Spectrometry Facility at the Department of Chemistry of the University of Utah at Salt Lake City on a Finnigan MAT 95 mass spectrometer. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. Solvents were purified according to the guidelines in *Purification of Common Laboratory Chemicals* (Perrin, Armarego, and Perrin: Oxford, 1966). (*i*-Pr)₂NEt was distilled from CaH₂. All other reagents were used without purification. Unless otherwise stated, all reactions were run under an atmosphere of dried nitrogen in flame-dried glassware. Concentration refers to removal of solvent under reduced pressure (house vacuum at ca. 20 mmHg). Characterization data for compounds **4** and **6-8** have been reported elsewhere¹.

2-Di-*tert*-butyl-6-methyl-8-(triisopropyl-silanyloxy)-4,4a,8,8a-tetrahydro-1,3,5-trioxa-2-sila-naphthalene (**11**). To slurry of glycal **29** and THF (0.053 mL) at 0°C was added *t*-BuLi (1.36 mL of a 1.7 M solution in pentane, 2.3 mmol). After stirring for 0.5 h the reaction mixture was cooled to -78°C and diluted with THF (0.90 mL); CH₃I (0.27 mL, 4.35 mmol) was then slowly added. After warming to rt, the reaction was quenched with aq. NH₄Cl (sat., 20 mL). The aqueous phase was extracted with 3:1 hexanes:ethyl acetate (3 X 10 mL), dried (Na₂SO₄), and concentrated. Flash chromatography (hexanes, then 100:1 hexanes:ethyl acetate) gave 105 mg (79%) of **11** as a colorless oil. $[\alpha]_D^{20} = -38.1^\circ$

¹ See Majumder, U.; Cox, J. M.; Rainier, J. D. *Org. Lett.* **2003**, 5, 913.

($c = 1.46$, THF); ^1H NMR (500 MHz, C_6D_6) δ 4.59 (s, 1 H), 4.51-4.54 (m, 1 H), 4.19 (dd, $J = 10.3, 4.9$ Hz, 1 H), 4.11 (dd, $J = 10.3, 6.8$ Hz, 1 H), 3.97 (dd, $J = 10.3$ Hz, 1 H), 3.79 (ddd, $J = 10.3, 10.3, 4.9$ Hz, 1 H), 1.60 (d, $J = 1.0$ Hz, 3 H), 1.23-1.21 (m, 21 H), 1.10 (s, 9 H), 1.08 (s, 9 H); ^{13}C NMR (125 MHz, C_6D_6) δ 151.3, 101.8, 78.5, 73.4, 72.5, 66.9, 28.0, 27.6, 23.3, 20.4, 19.5, 18.9, 18.8, 13.3; IR (neat) 2866, 1683, 1472, 1109; HRMS (CI) calcd for $\text{C}_{24}\text{H}_{49}\text{O}_4\text{Si}_2$ (MH^+) 457.3169, found 457.3188.

6-Allyl-2,2-di-*tert*-butyl-6-methyl-8-(triisopropyl-silanyloxy)-hexahydro-1,3,5-trioxa-2-sila-naphthalen-7-ol (**15**). To a solution of glycol **11** (0.018 g, 0.039 mmol) and CH_2Cl_2 (1 mL) at -78°C was added a solution of dimethyl dioxirane (0.59 mL of a 0.1 M solution in acetone, 0.06 mmol) dropwise. After 5 minutes, the reaction was warmed to 0°C and concentrated. The resulting anhydride was used in the subsequent coupling reaction without purification.

To a solution of the anhydride (0.039 mmol) from above and THF (2 mL) at -78°C was added propenylmagnesium bromide (0.20 mL of a 2.0 M solution in THF, 0.39 mmol) dropwise. After the addition was complete, the flask was placed in a -28°C freezer for 5 days. The reaction was quenched at -28°C with aq. NH_4Cl (sat., 20 mL). The mixture was extracted with 3:1 hexanes:ethyl acetate (3 X 10 mL), dried (Na_2SO_4), and concentrated. Flash chromatography (100:1 hexanes:ethyl acetate) gave 19 mg (93%) of *C*-ketoside **15** as a colorless oil. For characterization purposes, the alcohol was converted into the corresponding acetate.

To a solution of alcohol **15** (0.019 g, 0.036 mmol) and CH_2Cl_2 (0.5 mL) at rt was added acetic anhydride (0.034 mL, 0.36 mmol), (*i*-Pr) $_2\text{NEt}$ (0.063 mL, 0.36 mmol), and DMAP (ca. 0.005 g). After stirring overnight, the reaction was quenched with aq. NH_4Cl (sat., 5 mL). The mixture was extracted with CH_2Cl_2 (3 X 5 mL), dried (Na_2SO_4), and concentrated. Flash chromatography (50:1 hexanes:ethyl acetate) gave 21 mg (100%) of acetate **29** as a light yellow oil. $[\alpha]_D^{20} = -16.9^\circ$ ($c = 0.840$, THF); ^1H NMR (500 MHz, C_6D_6) 5.97 (dddd, $J = 18.6, 8.9, 8.9, 5.8$ Hz, 1 H), 5.15 (d, $J = 9.3$ Hz, 1 H), 5.11-5.08 (m, 2 H), 4.15-4.14 (dd, $J = 10.0, 4.6$ Hz, 1 H), 4.13 (dd, $J = 8.8, 8.8$ Hz, 1 H), 3.83 (dd, $J = 9.8, 9.8$ Hz, 1 H), 3.78 (dd, $J = 9.3, 9.3$ Hz, 1 H), 3.64 (ddd, $J = 9.8, 9.8, 4.9$ Hz, 1 H), 2.35 (dd, $J = 14.2, 5.9$ Hz, 1 H), 2.18 (dd, $J = 14.2, 8.3$ Hz, 1 H), 1.78 (s, 3H), 1.25-1.23 (m, 21 H), 1.15 (s, 3 H), 1.12 (s, 9 H), 1.11 (s, 9 H); ^{13}C NMR (125 MHz, C_6D_6) δ 168.8, 132.7, 128.4, 118.4, 79.7, 77.0, 76.3, 74.9, 69.0, 67.4, 45.1, 27.6, 27.2, 22.8, 20.8, 20.0,

18.6, 18.5, 17.0, 13.8; IR (neat) 2942, 2865, 1754, 1228, 1102, 828 cm^{-1} ; HRMS (CI) calcd for $\text{C}_{29}\text{H}_{57}\text{O}_6\text{Si}_2$ (MH^+) 557.3694, found 557.3717.

COSY summary: Cross peaks were observed between H(2) and H(3); H(3) and H(4); H(4) and H(5); H(5) and H(6); H(5) and H(6').

NOE summary: Enhancements were observed between H(5) and C(1) methyl; H(3) and C(1) methyl.

[2,2-Di-*tert*-butyl-8-(*tert*-butyl-diphenyl-silanyloxy)-4,4a,8,8a-tetrahydro-1,3,5-trioxa-2-sila-naphthalen-6-yl]-methanol **16**. To slurry of glucal derivative **30**¹ (2.1 g, 3.4 mmol) and THF (0.66 mL) at 0°C was added *t*-BuLi (21.3 mL of a 1.7 M solution in pentane, 32 mmol). After stirring for 0.5 h the reaction was cooled to -78°C, diluted with ether (14.3 mL), and then warmed to -30°C. HCHO gas was passed through the mixture until the color of the reaction turned from dark red to pale yellow. The reaction mixture was warmed to 0°C, stirred for 0.5 h, and then quenched with aq. NH_4Cl (sat., 40 mL). The aqueous phase was extracted with 3:1 hexanes:ethyl acetate (3 X 10 mL), dried (Na_2SO_4), and concentrated. Flash chromatography (hexanes, then 100:1 hexanes:ethyl acetate) gave 906 mg (41%) of the alcohol corresponding to **13** as a white solid (mp 44-46 °C). $[\alpha]_D^{20} = -18.94^\circ$ ($c = 1.985$, THF); ^1H NMR (500 MHz, C_6D_6) 7.96-7.94 (m, 2 H), 7.91-7.89 (m, 2 H), 7.30-7.24 (m, 6 H), 4.70-4.70 (m, 1 H), 4.58 (ddd, $J = 6.9, 3.1, 1.5$ Hz, 1 H), 4.31 (dd, $J = 10.3, 6.8$ Hz, 1 H), 4.1 (dd, $J = 10.3, 5.4$ Hz, 1 H), 3.96 (dd, $J = 10.3, 10.3$ Hz, 1 H), 3.68-3.57 (m, 3 H), 1.27 (s, 9 H), 1.12 (s, 9 H), 1.03 (s, 9 H), 0.93 (dd, $J = 6.8, 6.8$ Hz, 1 H); ^{13}C NMR (125 MHz, C_6D_6) δ 153.2, 136.4, 136.2, 134.9, 133.9, 129.9, 129.9, 128.4, 100.6, 77.8, 73.0, 72.4, 66.1, 61.7, 27.5, 27.1, 22.8, 19.9, 19.6; IR (neat) 3359 (broad), 2933, 2859, 1683, 1473, 1110, 826 cm^{-1} ; HRMS (CI) calcd for $\text{C}_{31}\text{H}_{47}\text{O}_5\text{Si}_2$ (MH^+) 555.2962, found 555.2961.

To a solution of the alcohol from above (0.162 g, 0.29 mmol), NaH (0.042 g, 1.74 mmol), tetrabutylammonium iodide (ca 0.015 g) and THF (5.4 mL) at 0 °C was added BnBr (0.21 mL, 1.7 mmol). The reaction mixture was warmed to rt, stirred overnight, and then quenched with water (20 mL). The aqueous phase was extracted with 3:1 hexanes:ethyl acetate (3 X 10 mL), dried (Na_2SO_4), and concentrated. Flash chromatography (hexanes then 10:1 hexanes:ethyl acetate) afforded 147 mg (79%) of benzyl ether **16** as a colorless oil. $[\alpha]_D^{20} = -16.90$ ($c = 0.84$, THF); ^1H NMR (500 MHz, C_6D_6) δ 7.96 (m, 2 H), 7.92-7.90 (m, 2 H), 7.31-7.08 (m, 11 H), 4.87 (d, $J = 2.0$ Hz, 1 H), 4.60 (dd, $J = 6.8, 1.5$ Hz, 1 H), 4.37-4.33 (m, 1 H), 4.32 (d, $J = 12.2$ Hz, 1 H), 4.27 (d, $J =$

12.2 Hz, 1 H), 4.13 (dd, $J = 10.3, 4.9$ Hz, 1 H), 3.98 (dd, $J = 10.3, 10.3$ Hz, 1 H), 3.78-3.74 (m, 1 H), 3.68-3.63 (m, 2 H), 1.28 (s, 9 H), 1.12 (s, 9 H), 1.03 (s, 9 H); ^{13}C NMR (125 MHz, C_6D_6) δ 151.6, 139.3, 137.1, 136.9, 135.6, 134.5, 130.6, 129.1, 129.0, 128.3, 103.0, 78.4, 73.7, 73.1, 73.0, 69.4, 66.9, 28.2, 27.8, 23.5, 20.5, 20.3; IR (neat) 2933, 2858, 1471, 1111, 825 cm^{-1} ; HRMS (CI) calcd for $\text{C}_{38}\text{H}_{53}\text{O}_5\text{Si}_2$ (MH $^{+}$) 645.3432, found 645.3421.

1a-Benzyloxymethyl-5,5-di-*tert*-butyl-7-(*tert*-butyl-diphenyl-silanyloxy)-hexahydro-1,2,4,6-tetraoxa-5-sila-cyclopropa[*b*]naphthalene (**17**). To a solution enol ether **16** (0.012 g, 0.019 mmol) and CH_2Cl_2 (1 mL) at -78°C was added dimethyl dioxirane (0.29 mL of an ca. 0.1 M solution in acetone, 0.03 mmole) dropwise. Following addition, the reaction was warmed to 0°C and concentrated. While **17** was generally used without purification, an analytical sample of **17** was prepared using flash chromatography (20:1 hexanes:ethyl acetate) to give 13 mg (100% yield) of **17** as a colorless oil. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.78-7.76 (m, 2 H), 7.74-7.72 (m, 2 H), 7.46-7.24 (m, 11 H), 4.50 (d, $J = 11.7$ Hz, 1 H), 4.46 (d, $J = 11.7$ Hz, 1 H), 4.13 (d, $J = 7.3$ Hz, 1 H), 4.05 (dd, $J = 10.3, 4.9$ Hz, 1 H), 3.92 (dd, $J = 10.3, 7.3$ Hz, 1 H), 3.85 (dd, $J = 10.3, 10.3$ Hz, 1 H), 3.68 (d, $J = 11.7$ Hz, 1 H), 3.58 (d, $J = 11.7$ Hz, 1 H), 3.58 (ddd, $J = 10.3, 10.0, 5.2$ Hz, 1 H), 2.93 (s, 1 H), 1.12 (s, 9 H), 1.04 (s, 9 H), 0.91 (s, 9 H); IR (film) 2934, 2859, 1472, 1112, 827, 701 cm^{-1} .

6-Allyl-6-benzyloxymethyl-2,2-di-*tert*-butyl-8-(*tert*-butyl-diphenyl-silanyloxy)-hexahydro-1,3,5-trioxa-2-sila-naphthalen-7-ol **18**. To a solution of glycal **16** (0.015 g, 0.023 mmol) and CH_2Cl_2 (1 mL) at 0°C was added a solution of dimethyl dioxirane (0.34 mL of a 0.1 M solution in acetone) dropwise. After 5 minutes, the reaction was concentrated to give anhydride **17** as a colorless oil. Anhydride **17** was used in the subsequent coupling chemistry without purification.

To a solution of **17** (0.023 mmol) and THF (1.5 mL) at -78°C was added propenylmagnesium bromide (0.12 mL of a 2.0 M solution in THF, 0.23 mmol) dropwise. After the addition was completed, the cooling bath was removed and the reaction mixture was stirred at rt for 2.5 h. The reaction was quenched with aq. NH₄Cl (sat., 20 ml), extracted with 3:1 hexanes:ethyl acetate (3 X 10 mL), dried (Na₂SO₄), and concentrated. Flash chromatography (10:1 hexanes:ethyl acetate) gave 15 mg (91%) of *C*-ketoside **18** as a colorless oil. $[\alpha]_D^{20} = +3.51^\circ$ (c = 0.74, THF); ¹H NMR (500 MHz, C₆D₆) δ 7.98 (m, 2 H), 7.9 (d, 2 H), 7.26-7.05 (m, 11 H), 5.95 (dddd, *J* = 17.4, 10.2, 7.3, 7.3 Hz, 1 H), 5.01 (d, *J* = 9.3 Hz, 1 H), 4.98 (d, *J* = 17.1 Hz, 1 H), 4.51 (dd, *J* = 8.8, 8.8 Hz, 1 H), 4.30 (dd, *J* = 9.8, 4.9 Hz, 1 H), 4.19 (ddd, *J* = 9.8, 9.8, 4.9 Hz, 1 H), 4.05-3.99 (m, 3 H), 3.93 (dd, *J* = 9.8, 9.8 Hz, 1 H), 3.76 (dd, *J* = 8.8, 6.3 Hz, 1 H), 3.54 (d, *J* = 10.7 Hz, 1 H), 3.38 (d, *J* = 10.7 Hz, 1 H), 2.40 (dd, *J* = 14.2, 6.8 Hz, 1 H), 2.26 (dd, *J* = 13.7, 7.8 Hz, 1 H), 1.75 (d, *J* = 5.9 Hz, 1 H), 1.29 (s, 9 H), 1.19 (s, 9 H), 1.11 (s, 9 H); ¹³C NMR (125 MHz, C₆D₆) δ 138.6, 137.2, 136.4, 136.1, 134.2, 134.1, 130.4, 130.3, 129.0, 129.0, 128.5, 128.1, 128.1, 118.5, 79.9, 79.6, 78.8, 76.9, 74.0, 73.8, 70.8, 68.4, 41.8, 28.2, 27.8, 27.8, 23.3, 20.6, 20.5; IR (neat) 3573, 2933, 2858, 1473, 1104, 827 cm⁻¹; HRMS (CI) calcd for C₄₁H₅₉O₆Si₂ (MH⁺) 703.3851, found 703.3821.

COSY summary: Cross peaks were observed between the OH and H(2); H(2) and H(3); H(3) and H(4); H(4) and H(5); H(5) and H(6); H(5) and H(6').

NOE summary: Enhancements were observed between H(3) and C(1) benzyloxy methylene; H(3) and H(5); H(5) and C(1) benzyloxy methylene.

6-Benzyloxymethyl-2,2-di-*tert*-butyl-8-(*tert*-butyl-diphenyl-silanyloxy)-6-prop-2-ynyl-hexahydro-1,3,5-trioxa-2-sila-naphthalen-7-ol (**19**). To a solution of anhydride **17** (0.022 mmol) and CH₂Cl₂ (1.0 mL) at -78°C was added propargylmagnesium bromide (0.22 mL of a 1.0 M solution in ether, 0.22 mmol). After the addition was completed, the cooling bath was removed. After 0.5 h, the reaction was quenched with aq. NH₄Cl (sat., 20 mL), extracted with 3:1 hexanes:ethyl acetate (3 X 10 mL), dried (Na₂SO₄), and concentrated. Flash chromatography (20:1 hexanes:ethyl acetate) gave 15 mg (99%) of *C*-ketoside **19** as a colorless oil. $[\alpha]_D^{20} = -2.94^\circ$ (c = 0.720, THF); ¹H NMR (500 MHz, CD₂Cl₂) δ 7.79 (m, 2 H), 7.73 (m, 2 H), 7.43-7.27 (m, 9 H), 7.14 (d, *J* = 6.8 Hz, 2 H), 4.29 (d, *J* = 12.2 Hz, 1 H), 4.23 (d, *J* = 12.2 Hz, 1 H), 4.08-4.04 (m, 2 H), 3.84 (dd, *J* = 8.8, 8.8 Hz, 1 H), 3.79-3.68 (m, 3 H), 3.50 (d, *J* = 10.8 Hz, 1 H), 3.39 (d, *J* = 10.8 Hz, 1 H), 2.53 (d, *J* =

17.1 Hz, 1 H), 2.38 (d, $J = 17.1$ Hz, 1 H), 2.01 (s, 1 H), 1.76 (d, $J = 5.9$ Hz, 1 H), 1.08 (s, 9 H), 1.07 (s, 9 H), 0.93 (s, 9 H); ^{13}C NMR (125 MHz, C_6D_6) δ 138.5, 137.2, 136.3, 136.0, 134.0, 130.4, 130.3, 129.0, 128.9, 128.5, 80.4, 79.6, 79.0, 78.5, 76.8, 74.0, 71.8, 71.7, 70.8, 68.2, 28.2, 27.8, 27.7, 27.7, 23.3, 20.6, 20.5; IR (neat) 3565, 3308, 2932, 2858, 1472, 1086, 826 cm^{-1} ; HRMS (CI) calcd for $\text{C}_{41}\text{H}_{57}\text{O}_6\text{Si}_2$ (MH^+) 701.3694, found 701.3738.

For characterization purposes, alcohol **19** was converted into the corresponding acetate.

To a solution of **19** (0.0097 g, 0.014 mmol) and CH_2Cl_2 (0.5 mL) at rt was added acetyl chloride (0.013 mL, 0.14 mmol), $(i\text{-Pr})_2\text{NEt}$ (0.029 mL, 0.14 mmol), and DMAP (ca 0.005 g). After stirring overnight, the reaction was quenched with aq. NH_4Cl (sat., 5 mL). The mixture was extracted with CH_2Cl_2 (3 X 5 mL), dried (Na_2SO_4), and concentrated. Flash chromatography (50:1 hexanes:ethyl acetate to 20:1 hexanes:ethyl acetate) gave 5 mg (56%) of the acetate corresponding to **19** as a white solid (mp 150-152 $^\circ\text{C}$). ^1H NMR (500 MHz, C_6D_6) 8.00-7.98 (m, 2 H), 7.77-7.75 (m, 2 H), 7.25-7.22 (m, 4 H), 7.18-6.99 (m, 7 H), 5.37 (d, $J = 9.3$ Hz, 1 H), 4.52 (dd, $J = 8.8$ Hz, 1 H), 4.21 (dd, $J = 9.8$, 4.4 Hz, 1 H), 4.15 (d, $J = 12.2$ Hz, 1 H), 4.10-4.00 (m, 2 H), 3.97 (d, $J = 12.7$ Hz, 1 H), 3.84 (dd, $J = 9.8$ Hz, 1 H), 3.48 (d, $J = 10.7$ Hz, 1 H), 3.43 (d, $J = 10.7$ Hz, 1 H), 2.47 (dd, $J = 2.2$ Hz, 2 H), 1.65 (dd, $J = 2.7$ Hz, 1 H), 1.19 (s, 9 H), 1.10 (s, 9 H), 1.07 (s, 3 H), 1.04 (s, 9 H).

COSY summary: Cross peaks were observed between the H(2) and H(3); H(3) and H(4); H(4) and H(5); H(5) and H(6); H(5) and H(6').

NOE summary: Enhancements were observed between H(2) and the propargylic methylene; H(3) and benzyloxy methylene; H(3) and H(5); H(5) and benzyloxy methylene.

2,2-Di-*tert*-butyl-8-(*tert*-butyl-diphenyl-silanyloxy)-6-methyl-6-vinyl-hexahydro-1,3,5-trioxa-2-sila-naphthalen-7-ol (**20**). To a solution of glycal **4** (0.023 g, 0.043 mmol) and CH_2Cl_2 (1 mL) at -78°C was added a solution of dimethyl dioxirane (0.65 mL of a 0.1 M solution in acetone, 0.06 mmol) dropwise. After 5 minutes, the reaction was warmed to 0°C and concentrated to give anhydride **5** as a colorless oil. Anhydride **5** was used in the subsequent coupling reaction without purification.

To a solution of **5** (0.043 mmol) and THF (2 mL) at -78°C was added vinylmagnesium bromide (0.43 mL of a 1.0 M solution in THF, 0.43 mmol) dropwise.

After the addition was completed, the cooling bath was removed and the temperature was allowed to slowly warm to rt. After stirring for 1.5 h, the reaction was quenched with aq. NH_4Cl (sat., 20 mL), extracted with 3:1 hexanes:ethyl acetate (3 X 10 mL), dried (Na_2SO_4), and concentrated. Flash chromatography (100:1 followed by 20:1 hexanes:ethyl acetate) gave 11 mg (45%) of *C*-ketoside **20** as a colorless oil. $[\alpha]_D^{20} = +37.36$ ($c = 0.61^\circ$, THF); ^1H NMR (500 MHz, C_6D_6) 7.95 (m, 2 H), 7.82 (m, 2 H), 7.26-7.18 (m, 6 H), 5.94 (dd, $J = 18.1, 11.2$ Hz, 1 H), 5.19 (dd, $J = 17.6, 1.5$ Hz, 1 H), 4.98 (dd, $J = 11.2, 1.5$ Hz, 1 H), 4.22 (dd, $J = 10.3, 4.9$ Hz, 1 H), 4.03 (dd, $J = 8.8, 8.8$ Hz, 1 H), 3.98 (dd, $J = 10.2, 10.2$ Hz, 1 H), 3.91 (dd, $J = 8.8, 8.8$ Hz, 1 H), 3.79 (ddd, $J = 9.8, 9.8, 4.9$ Hz, 1 H), 3.48 (dd, $J = 8.8, 3.4$ Hz, 1 H), 1.92 (d, $J = 3.4$ Hz, 1 H), 1.34 (s, 3 H), 1.27 (s, 9 H), 1.17 (s, 9 H), 1.07 (s, 9 H); ^{13}C NMR (125 MHz, C_6D_6) δ 137.6, 137.3, 136.1, 136.0, 133.3, 130.6, 130.5, 128.7, 128.5, 116.3, 79.8, 79.2, 79.2, 78.7, 70.0, 67.8, 28.9, 28.2, 27.8, 27.7, 23.3, 20.6, 20.4; IR (neat) 3575, 2933, 2859, 1473, 1092, 830 cm^{-1} ; HRMS (CI) calcd for $\text{C}_{33}\text{H}_{51}\text{O}_5\text{Si}_2$ (MH^+) 583.3275, found 583.3262.

COSY summary: Cross peaks were observed between the OH and H(2); H(2) and H(3); H(3) and H(4); H(4) and H(5); H(5) and H(6); H(5) and H(6')).

NOE summary: Enhancements were observed between H(2) and C(1) vinyl H's; H(5) and C(1) vinyl H's.

2,2-Di-*tert*-butyl-8-(*tert*-butyl-diphenyl-silanyloxy)-6-methyl-6-phenyl-hexahydro-1,3,5-trioxa-2-sila-naphthalen-7-ol (**21**). To a solution of anhydride **5** (0.038 mmol) and THF (2 mL) at -78°C was added phenylmagnesium bromide (0.38 mL of a 1.0 M solution in THF, 0.38 mmol) dropwise. After the addition was completed, the cooling bath was removed, the reaction mixture was stirred at rt for 1.5 hours, and the reaction was quenched with aq. NH_4Cl (sat., 20 mL). The mixture was extracted with 3:1 hexanes:ethyl acetate (3 X 10 mL), dried (Na_2SO_4), and concentrated. Flash chromatography (20:1 hexanes:ethyl acetate) gave 18 mg (75%) of *C*-ketoside **21** as a pale yellow oil. $[\alpha]_D^{20} = +11.30^\circ$ ($c = 0.69$, THF); ^1H NMR (500 MHz, C_6D_6) δ 7.97-7.95 (m, 2 H), 7.86 (m, 2 H), 7.48 (m, 2 H), 7.28-7.23 (m, 6 H), 7.04-6.99 (m, 3 H), 4.22 (dd, $J = 10.2, 5.4$ Hz, 1 H), 4.15 (dd, $J = 8.8, 8.8$ Hz, 1 H), 4.10 (dd, $J = 8.8, 8.8$ Hz, 1 H), 4.01 (dd, $J = 10.2, 10.2$ Hz, 1 H), 3.78 (dd, $J = 9.8, 3.9$ Hz, 1 H), 3.34 (ddd, $J = 9.8, 9.8, 4.6$ Hz, 1 H), 2.22 (d, $J = 3.9$ Hz, 1 H), 1.55 (s, 3 H), 1.26 (s, 9 H), 1.16 (s, 9 H), 0.87 (s, 9 H); ^{13}C NMR (125 MHz, C_6D_6) δ 143.2, 137.5, 136.0, 135.8, 132.9, 130.6, 130.4, 128.9, 128.9, 128.7, 128.5, 127.8, 127.5, 81.0, 80.5, 80.3, 77.8, 70.5, 67.7, 31.2, 28.1,

27.7, 27.5, 23.2, 20.6, 20.4; IR (neat) 3577, 2933, 2859, 1473, 1084, 828 cm^{-1} ; HRMS (CI) calcd for $\text{C}_{37}\text{H}_{53}\text{O}_5\text{Si}_2$ (MH^+) 633.3432, found 633.3416.

COSY summary: Cross peaks were observed between the OH and H(2); H(2) and H(3); H(3) and H(4); H(4) and H(5); H(5) and H(6); H(5) and H(6')).

NOE summary: Enhancements were observed between H(2) and C(1) methyl; H(5) and C(1) phenyl H's.

2,2-Di-*tert*-butyl-6-methyl-6-phenyl-8-(triisopropyl-silanyloxy)-hexahydro-1,3,5-trioxa-2-sila-naphthalen-7-ol (**22**). To a solution of glycal **11** (0.010 g, 0.032 mmol) and CH_2Cl_2 (1 mL) at -78°C was added a solution of dimethyl dioxirane (0.48 mL of a 0.1 M solution in acetone, 0.05 mmol) dropwise. After 5 minutes, the reaction was warmed to 0°C and concentrated. The anhydride was used in the subsequent coupling chemistry without purification.

To a solution of the anhydride from **11** (0.032 mmol) and THF (2 mL) at -78°C was added phenylmagnesium bromide (0.32 mL of a 1.0 M solution in THF, 0.32 mmol) dropwise. After the addition was completed, the cooling bath was removed, the reaction mixture was stirred at rt for 1.5 hours, and then quenched with aq. NH_4Cl (sat., 20 mL). The mixture was extracted with 3:1 hexanes:ethyl acetate (3 X 10 mL), dried (Na_2SO_4), and concentrated. Flash chromatography (50:1 hexanes:ethyl acetate) gave 13 mg (72%) of *C*-ketoside **22** as a white solid (mp $117\text{--}120^\circ\text{C}$). For characterization purposes, the alcohol was converted into the corresponding acetate.

To a solution of alcohol **22** (0.0083 g, 0.015 mmol) and CH_2Cl_2 (0.5 mL) at rt was added acetyl chloride (0.022 mL, 0.30 mmol), (*i*-Pr) $_2\text{NEt}$ (0.052 mL, 0.30 mmol), and DMAP (ca. 0.005 g). After stirring overnight, the reaction was quenched with aq. NH_4Cl (sat., 5 mL). The mixture was extracted with CH_2Cl_2 (3 X 5 mL), dried (Na_2SO_4), and concentrated. Flash chromatography (50:1 hexanes:ethyl acetate) gave 5 mg (31%) of the acetate corresponding to **22** as a colorless oil. $[\alpha]_D^{20} = +40.5^\circ$ ($c = 0.220$, THF); ^1H NMR (500 MHz, C_6D_6) 7.78 (m, 2 H), 7.22–7.16 (m, 2 H), 7.05 (m, 1 H), 5.54 (d, $J = 10.3$ Hz, 1 H), 4.34 (dd, $J = 9.8, 7.8$ Hz, 1 H), 4.19 (dd, $J = 10.3, 4.9$ Hz, 1 H), 3.91 (dd, $J = 10.2, 10.2$ Hz, 1 H), 3.88 (dd, $J = 9.7, 7.8$ Hz, 1 H), 3.46 (ddd, $J = 10.3, 10.3, 4.3$ Hz, 1 H), 1.84 (s, 3 H), 1.53 (s, 3 H), 1.28–1.24 (m, 21 H), 1.09 (s, 9 H), 0.89 (s, 9 H); (125 MHz, C_6D_6) δ 169.6, 143.6, 129.3, 127.5, 81.3, 80.7, 79.0, 75.5, 70.8, 67.6, 31.3, 28.1,

27.6, 23.3, 21.5, 20.6, 19.3, 19.1, 14.5; IR (neat) 2935, 2865, 1755, 1223, 1096 cm^{-1} ; HRMS (CI) calcd for $\text{C}_{32}\text{H}_{57}\text{O}_6\text{Si}_2$ (MH⁺) 593.3694, found 593.3686.

COSY summary: Cross peaks were observed between H(2) and H(3); H(3) and H(4); H(4) and H(5); H(5) and H(6); H(5) and H(6').

NOE summary: Enhancements were observed between H(3) and C(1) aryl H's; H(3) and H(5); H(5) and C(1) aryl H's; H(2) and C(1) methyl.

[2,2-Di-*tert*-butyl-7-(*tert*-butyl-dimethyl-silanyloxy)-8-(*tert*-butyl-diphenyl-silanyloxy)-6-methyl-hexahydro-1,3,5-trioxa-2-sila-naphthalen-6-yl]-acetic acid methyl ester (**24**). To a solution of anhydride **5** (0.033 mmol) and CH_2Cl_2 (1.0 mL) at 0°C was added a solution of silyl enol ether **23** (0.122 g, 0.66 mmol) and CH_2Cl_2 (0.25 mL) rapidly via cannula (0.25 mL rinse) followed by a solution of TBSOTf (0.017 mL, 0.073 mmol) and CH_2Cl_2 (0.5 mL, 0.25 mL rinse). The reaction mixture was placed in a -7°C freezer for 48 h and then quenched at 0°C with aq. NaHCO_3 (sat., 20 mL). The mixture was extracted with 3:1 hexanes:ethyl acetate (3 X 10 mL), dried (Na_2SO_4), and concentrated. Flash chromatography (100:1 hexanes:ethyl acetate) gave 18 mg (77%) of *C*-ketoside **24** as a colorless oil. $[\alpha]_{\text{D}}^{20} = -8.89^\circ$ ($c = 0.23$, THF); ^1H NMR (500 MHz, CDCl_3) δ 7.78 (m, 2 H), 7.67 (m, 2 H), 7.45-7.32 (m, 6 H), 4.25 (dd, $J = 10.3, 4.4$ Hz, 1 H), 4.10 (d, $J = 1.0$ Hz, 1 H), 4.05 (dd, $J = 9.8, 4.9$ Hz, 1 H), 3.98 (partially obscured ddd, $J = 10.3, 10.3, 4.6$ Hz, 1 H), 3.96 (dd, $J = 4.2, 1.2$ Hz, 1 H), 3.68 (dd, $J = 9.8, 9.8$ Hz, 1 H), 3.63 (s, 3 H), 2.99 (d, $J = 15.6$ Hz, 1 H), 2.88 (d, $J = 15.1$ Hz, 1 H), 1.32 (s, 3 H), 1.08 (s, 9 H), 0.89 (s, 9 H), 0.84 (s, 9 H), 0.74 (s, 9 H), -0.10 (s, 3 H), -0.42 (s, 3 H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.5, 136.9, 136.3, 134.1, 132.7, 130.1, 129.8, 127.8, 127.8, 81.5, 80.8, 77.0, 76.5, 68.0, 67.1, 51.5, 44.2, 27.4, 27.3, 27.0, 26.0, 24.7, 22.8, 20.0, 19.3, 18.1, -4.5, -5.2; IR (neat) 2933, 2859, 1741, 1471, 1110, 827; HRMS (CI) calcd for $\text{C}_{40}\text{H}_{67}\text{O}_7\text{Si}_3$ (MH⁺) 743.4195, found 743.4180.

To fully characterize **24**, we converted it into triol **32**. Not only did this resolve NMR signals that were overlapped in **24**, but it also relieved the gauche interactions between C(2) and C(3). As expected **32** adopts a chair conformer as exemplified by the large (9 Hz) coupling constants for the pyranyl protons.

To a solution of **24** (0.026 g, 0.035 mmol) and THF (1.75 mL) at 0 °C was added HF·pyridine (0.070 mL of a 1 M solution in THF, 0.07 mmol). After stirring for 6.5 h, the reaction was quenched with aq. NaHCO₃ (sat., 10 mL) at 0 °C. The mixture was extracted with 1:1 hexanes:ethyl acetate (3 x 10 mL), dried (Na₂SO₄), and concentrated. Flash chromatography (5:1 hexanes:ethyl acetate) gave 14.7 mg of **31** as a colorless oil. ¹H NMR (500 MHz, C₆D₆) δ 7.86-7.80 (m, 4 H), 7.26-7.18 (m, 6 H), 4.56 (dd, *J* = 3.4, 1.0 Hz, 1 H), 4.14 (dd, *J* = 3.4, 2.0 Hz, 1H), 3.99-3.95 (m, 1 H), 3.85 (ddd, *J* = 8.7, 4.9, 3.4 Hz, 1 H), 3.82-3.78 (m, 1 H), 3.70 (ddd, *J* = 11.7, 6.8, 4.9 Hz, 1 H), 3.43 (d, *J* = 15.1 Hz, 1 H), 3.31 (s, 3 H), 2.93 (d, *J* = 15.1 Hz, 1 H), 2.04 (dd, *J* = 6.4, 6.4 Hz, 1 H), 1.45 (s, 3 H), 1.45 (d, *J* = 7.3 Hz, 1 H), 1.2 (s, 9 H), 0.83 (s, 9 H), 0.09 (s, 3 H), -0.11 (s, 3 H).

To a solution of the diol from above (0.0082g, 0.014 mmol) and MeOH (1 mL) at rt was added p-toluenesulfonic acid monohydrate (0.032 g, 0.168 mmol) over 48 h. The reaction was cooled to 0°C and quenched by the slow addition of aq. NaHCO₃ (sat., 2 mL). The resulting mixture was extracted with 1:1 hexanes:ethyl acetate (5 x 2 mL), dried (Na₂SO₄), and concentrated. Flash chromatography (3:1 hexanes:ethyl acetate to 1:1 hexanes:ethyl acetate) gave 1.8 mg (27%) of **32** as a colorless oil. $[\alpha]_D^{20} = +15.0^\circ$ (*c* = 0.0470, THF); ¹H NMR (500 MHz, (CD₃)₂CO) δ 7.82-7.79 (m, 4 H), 7.44-7.37 (m, 6 H), 3.85 (dd, *J* = 9.1, 9.1 Hz, 1 H), 3.74 (d, *J* = 9.3 Hz, 1 H), 3.63 (dd, *J* = 11.5, 3.2 Hz, 1 H), 3.58 (s, 3 H), 3.53 (dd, *J* = 12.0, 5.2 Hz, 1 H), 3.51 (dd, *J* = 9.6, 9.6 Hz, 1 H), 3.29 (ddd, *J* = 8.8, 4.5, 4.5 Hz, 1 H), 2.52 (d, *J* = 2.0 Hz, 2 H), 1.11 (s, 3H), 1.07 (s, 9 H); ¹³C NMR (125 MHz, CDCl₃) δ 171.2, 135.9, 135.9, 133.6, 133.4, 130.4, 130.4, 128.4, 128.3, 78.0, 76.6, 75.2, 72.7, 72.0, 62.9, 51.8, 45.1, 27.3, 19.8, 17.2; IR (neat) 3435 (broad), 2930, 2858, 1725, 1431, 1113, 833 cm⁻¹.

COSY summary: Cross peaks were observed between H(2) and H(3); H(3) and H(4); H(4) and H(5); H(5) and H(6); H(5) and H(6').

NOE summary: Enhancements were observed between H(2) and CH₂ of methyl acetate; H(3) and H(5); H(3) and C(1) methyl; H(5) and C(1) methyl.