Synthesis of 1,2-Dioxolanes by Annulation Reactions of Peroxycarbenium Ions with Alkenes

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Supporting Information

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General. Melting points were obtained using a Büchi 510 melting point apparatus and are reported uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature at 500 MHz and 400 MHz and 125 MHz and 100 MHz, respectively, using Bruker DRX 500 or DRX 400 spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. Infrared (IR) spectra were obtained using a MIDAC Prospect FT-IR spectrometer. High-resolution mass spectra were acquired on a VG Analytical 7070E or Fisons Autospec spectrometer, and were obtained by peak matching. Microanalyses were performed by Atlantic Microlab, Atlanta, GA. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on EM Reagents silica gel (SiO_2) 60 (230–400 mesh). As needed, reactions were performed under an atmosphere of nitrogen and flash chromatography was performed using Aldrich Davisil[®] silica gel (SiO_2) 60 (200–425 mesh) grade 633. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. THF, Et_2O , and CH_2Cl_2 were dried by filtration through alumina.¹

Caution: When handling organic peroxides minimize exposure to light, heat and metal salts.²⁻³ Furthermore, perform reactions in a small scale, and employ a safety shield.

I. Synthesis of the Peroxyketal and Silyl Peroxyketals

General Procedure for the Silyl Protection of Peroxyketals. Unless otherwise noted a solution of peroxyketal (1.0 equiv) and DMF (0.4 – 0.98 M) was treated with chlorosilane or trifluoromethanesulfonatesilane (2.2 – 3.0 equiv) and triethylamine (2.0 – 6.0 equiv). The reaction mixture was stirred for 10 min – 24 h at (– 40 °C – 25 °C) then added to ice-cold H_2O . The reaction mixture was stirred for 5 min and 100 mL of brine was added. The mixture was extracted with 4 x 100 mL of pentane. The organic layers were combined, dried over Na_2SO_4 , filtered, and the solvent was removed *in vacuo*. Purification by flash chromatography was performed using Davisil[®] silica gel.

Peroxyketal (11a).⁴ A solution of 4-*tert*-butylcyclohexanone **11** (5.00 g, 32.4 mmol), molecular sieves (5.00 g, 3 Å) and 150 mL of CH₂Cl₂, was treated with 185 mL of formic acid and H₂O₂ (45 mL, 1000 mmol, 50% H₂O). The reaction mixture was stirred vigorously for 3 min at ambient temperature then added to 50 mL of ice-cold H₂O. The layers were separated and the aqueous layer was extracted with 4 x 100 mL of CH₂Cl₂. The organic layers were combined and solvent was removed *in vacuo* to afford peroxyketal **11a** as a white powder (6.6 g, 99%): mp 83.0-84.0 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.27 (s, 2H), 2.30 (d, *J* = 13.4, 2H), 1.70 (d, *J* = 12.7, 2H), 1.43 (t, *J* = 13.5, 2H) 1.24 (m, 2H), 1.06 (s, 1H), 0.87 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 110.9, 47.7, 32.5, 29.9, 27.8, 23.6; IR (KBr) 3422, 2956 cm⁻¹; HRMS (CI/NH₃) *m/z* calcd for C₁₀H₁₉O₂ (M) 171.1380, found 171.1381. Anal. Calcd for C₁₀H₂₀O₄: C, 58.80; H, 9.87. Found: C, 59.03; H, 9.96.

Trimethylsilylperoxyketal (6). The standard silyl protection procedure was followed with **11a** (1.56 g, 7.64 mmol) in 88 mL of DMF with trimethylchlorosilane (2.15 mL, 16.8 mmol) and triethylamine (2.16 mL, 15.3 mmol).⁵ The solvent was removed *in vacuo* to afford **6** as a white solid (2.60 g, 98%): mp 54.0-55.0 °C; ¹H NMR (500 MHz, CDCl₃) δ 2.31 (m, 2H), 1.62 (m, 2H), 1.35 (m, 2H), 1.22 (m, 2H), 1.02 (m, 1H), 0.86 (s, 9H), 0.23 (s, 9H), 0.19 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 109.6, 47.7, 32.5, 30.7, 27.8, 23.7, -0.8, -1.0; IR (thin film) 2962, 2868, 1250 cm⁻¹; HRMS (ESI/Na) *m/z* calcd for C₁₆H₃₆O₄Si₂Na (M + Na) 371.2050, found 371.2058. Anal. Calcd for C₁₆H₃₆O₄Si₂: C, 55.12; H, 10.41. Found: C, 56.62; H, 10.44.

Trimethylsilylperoxyketal (7). The standard silyl protection procedure was followed with **11a** (0.50 g, 2.5 mmol) in 33 mL of DMF with triethylchlorosilane (0.91 mL, 5.4 mmol) and triethylamine (0.76 mL, 5.4 mmol). Purification by flash chromatography (hexanes) afforded **7** as a clear liquid (0.77 g, 73%): ¹H NMR (500 MHz, C₆D₆) δ 2.61 (m, 2H), 1.56 (m, 2H), 1.39 (m, 4H), 1.15 (t, *J* = 7.9, 9H), 1.11 (t, *J* = 7.9, 9H), 0.87 (m, 1H), 0.86 (q, *J* = 8.0, 6H), 0.83 (s, 9H), 0.80 (q, *J* = 8.1, 6H); ¹³C NMR (125 MHz, C₆D₆) δ 109.9, 48.1, 32.7, 31.4, 28.1, 24.4, 7.5, 4.80, 4.76; IR (thin film) 2951, 2874, 1448, 1238, 1012 cm⁻¹; HRMS (CI/NH₃) *m/z* calcd for C₂₀H₄₃O₄Si₂ (M – Et) 403.2700, found 403.2702. Anal. Calcd for C₂₂H₄₈O₄Si₂: C, 61.05; H, 11.18. Found: C, 61.23; H, 11.29.

tert-Butyldimethylsilylperoxyketal (8). The standard silyl protection procedure was followed with **11a** (1.50 g, 7.35 mmol) in 75 mL of DMF was cooled to -10°C . The mixture was treated with *tert*-butyldimethylsilyl trifluoromethanesulfonate (3.40 mL, 14.7 mmol) and triethylamine (2.10 mL, 14.7 mmol). Purification by flash chromatography (100:0 – 90:10 hexanes/EtOAc) afforded **8** as a clear viscous oil (1.7 g, 53%): ^1H NMR (500 MHz, CDCl_3) δ 2.30 (m, 2H), 1.63 (m, 2H), 1.35–1.22 (m, 4H), 1.02 (m, 1H), 0.96 (s, 9H), 0.93 (s, 9H), 0.86 (s, 9H), 0.18 (s, 6H), 0.15 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 109.4, 47.7, 32.5, 30.6, 27.8, 26.43, 26.36, 23.7, 18.6, 18.4, -5.36, -5.39; IR (thin film) 2954, 2858, 1445, 1250, 1061 cm^{-1} ; HRMS (ESI/Na) m/z calcd for $\text{C}_{22}\text{H}_{48}\text{O}_4\text{Si}_2\text{Na}$ ($M + \text{Na}$) 455.2989, found 455.2977. Anal. Calcd for $\text{C}_{22}\text{H}_{48}\text{O}_4\text{Si}_2$: C, 61.05; H, 11.18. Found: C, 61.32; H, 11.27.

Triisopropylsilylperoxyketal (9). The standard silyl protection procedure was followed with **11a** (1.00 g, 4.9 mmol) in 50 mL of DMF was cooled to -40°C . The mixture was treated with triisopropylsilyl trifluoromethanesulfonate (3.95 mL, 14.7 mmol) and triethylamine (4.20 mL, 29.4 mmol). Purification by flash chromatography (hexanes) afforded **9** as a clear liquid (1.10 g, 43%): ^1H NMR (500 MHz, CDCl_3) δ 2.35 (m, 2H), 1.64 (m, 2H), 1.35 (m, 2H), 1.28–1.17 (m, 9H), 1.13–1.10 (m, 36H), 0.86 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 109.1, 47.8, 32.6, 30.7, 27.9, 23.8, 18.3, 12.0; IR (thin film) 2945, 2867, 1465, 1255, 1061 cm^{-1} ; HRMS (ESI/Na) m/z calcd for $\text{C}_{28}\text{H}_{60}\text{O}_4\text{Si}_2\text{Na}$ ($M + \text{Na}$) 539.3928, found 539.3917. Anal. Calcd for $\text{C}_{28}\text{H}_{60}\text{O}_4\text{Si}_2$: C, 65.06; H, 11.70. Found: C, 65.52; H, 11.83.

Triethylsilylperoxyketal (7). A solution of 4-*tert*-butylcyclohexanone **11** (0.624 g, 4.05 mmol) in 6 mL of CH_2Cl_2 was treated with formic acid (4.5 mL, 120 mmol, 95–97%) and hydrogen peroxide (7.2 mL, 120 mmol, 50% H_2O). The reaction mixture was vigorously stirred for 10 min at ambient temperature then added to 50 mL CH_2Cl_2 and 50 mL of H_2O . The layers were separated and the aqueous layer was extracted with 3 x 50 mL of CH_2Cl_2 . The organic layers were combined and the solvent was removed *in vacuo* to afford a white solid (0.818 g, 99%). The unpurified product (0.818 g, 4.00 mmol), in 10 mL of DMF was treated with Et_3N (1.41 mL, 10.0 mmol), DMAP (0.0246 g, 0.200 mmol in 2 mL of DMF) and Et_3SiOTf (2.26 mL, 10.0 mmol). The reaction mixture was stirred for 18 h then added to 100 mL of ice-cold pentane/ H_2O (1:1). The organic layers were separated and the aqueous layer was extracted with 3 x 30 mL of pentane. The organic layers were combined, dried over Na_2SO_4 , filtered, and the solvent was removed *in vacuo*. Purification by flash chromatography (pentane) afforded **7** as a clear liquid (1.30 g, 75%): ^1H NMR (500 MHz, C_6D_6) δ 2.61 (m,

2H), 1.56 (m, 2H), 1.39 (m, 4H), 1.15 (t, $J = 7.9$, 9H), 1.11 (t, $J = 7.9$, 9H), 0.87 (m, 1H), 0.86 (q, $J = 8.0$, 6H), 0.83 (s, 9H), 0.80 (q, $J = 8.1$, 6H); ^{13}C NMR (125 MHz, C_6D_6) δ 109.9, 48.1, 32.7, 31.4, 28.1, 24.4, 7.53, 4.80, 4.76; IR (thin film) 2951, 2874, 1448, 1238, 1012 cm^{-1} ; HRMS (CI/ NH_3) m/z calcd for $\text{C}_{20}\text{H}_{43}\text{O}_4\text{Si}_2$ ($M - \text{Et}$) 403.2700, found 403.2702. Anal. Calcd for $\text{C}_{22}\text{H}_{48}\text{O}_4\text{Si}_2$: C, 61.05; H, 11.18. Found: C, 61.23; H, 11.29.

Triethylsilylperoxyketal (13). A solution of benzyloxyacetone **12** (1.00 g, 6.10 mmol) in 20 mL of CHCl_3 was treated with H_2O_2 (2.5 mL, 49 mmol, 50% H_2O) and trifluoroacetic acid (5.6 mL, 73 mmol, 99%). The reaction mixture was stirred for 5 min at ambient temperature then sat. aq. NaHCO_3 was added until the reaction mixture stopped bubbling. The reaction mixture was extracted with 6 x 50 mL of CH_2Cl_2 . The organic layers were combined and the solvent was removed *in vacuo* to afford a clear oil (1.30 g, ~90% product by ^1H NMR spectroscopy). The unpurified product (1.30 g, 5.46 mmol) in 28 mL of DMF was treated with Et_3SiOTf (3.94 mL, 17.5 mmol) and Et_3N (2.31 mL, 16.4 mmol). The reaction mixture was stirred for 4 h at room temperature then added to 100 mL of ice-cold pentane/ H_2O (1:1). The layers were separated and the aqueous layer was extracted with 4 x 50 mL of pentane. The organic layers were combined, dried over Na_2SO_4 , filtered, and the solvent was removed *in vacuo*. Purification by flash chromatography (100:0 – 60:40 pentane/ EtOAc) afforded **13** as a clear liquid (1.30 g, 54%): ^1H NMR (500 MHz, CDCl_3) δ 7.35–7.23 (m, 5H), 4.58 (s, 2H), 3.69 (s, 2H), 1.48 (s, 3H), 0.97 (m, 18H), 0.72 (m, 12H); ^{13}C NMR (125 MHz, CDCl_3) δ 138.7, 128.5, 127.69, 127.65, 110.8, 73.6, 70.7, 17.5, 6.9, 4.0; IR (thin film) 2955, 2878, 1456, 1240, 1006 cm^{-1} ; LRMS (ESI/ Na) m/z calcd for $\text{C}_{18}\text{H}_{40}\text{O}_4\text{Si}_2\text{Na}$ ($M + \text{Na}$) 465.25, found 465.25. Anal. Calcd for $\text{C}_{18}\text{H}_{40}\text{O}_4\text{Si}_2$: C, 59.68; H, 9.56. Found: C, 66.32; H, 7.71.

Triethylsilylperoxyketal (15). A solution of 3-methylcyclohexanone **14** (0.454 g, 4.05 mmol) in 6 mL of CH_2Cl_2 was treated with formic acid (4.5 mL, 120 mmol, 95–97%) and hydrogen peroxide (7.2 mL, 120 mmol, 50% H_2O). The reaction mixture was stirred for 10 min at ambient temperature then added to 50 mL of CH_2Cl_2 and 50 mL of H_2O . The layers were separated and the aqueous layer was extracted with 3 x 50 mL of CH_2Cl_2 . The organic layers were combined and solvent was removed *in vacuo* to afford a clear oil (0.455 g, ~95% product by ^1H NMR spectroscopy). The unpurified product (0.455 g, 2.81 mmol) in 12 mL of DMF was treated with Et_3N (1.79 mL, 12.7 mmol), DMAP (17.3 mg, 0.141 mmol in 2 mL of DMF) and Et_3SiOTf (2.15 mL, 12.7 mmol) at 0 $^\circ\text{C}$. The reaction mixture was stirred for 3 h from 0 $^\circ\text{C}$ – 25 $^\circ\text{C}$ then added to 100 mL of ice-cold pentane/ H_2O (1:1). The layers were separated and the aqueous layer was extracted with 3 x 30 mL of pentane. The organic layers were combined, dried over Na_2SO_4 , filtered, and the solvent removed *in vacuo*. Purification by flash chromatography (pentane) afforded **15** as a clear liquid (0.857 g, 54%): ^1H NMR (500 MHz, CDCl_3) δ 2.25 (m, 2H), 1.62 (m, 3H), 1.47 (m, $J = 13.4$, 3.6, 1H), 1.22 (m, $J = 13.5$, 4.4, 1H), 0.99 (m, 18H), 0.94 (m, 1H), 0.89 (d, $J = 6.5$, 3H), 0.85 (m, 1H), 0.71 (m, 12H); ^{13}C NMR (125 MHz, CDCl_3) δ 109.9, 38.7, 34.7, 30.1, 29.4, 22.7, 22.4, 7.0, 4.2, 4.1; IR (thin film) 2954, 2878, 1459, 1240, 1006 cm^{-1} ; HRMS (ESI/ Na) m/z calcd for $\text{C}_{19}\text{H}_{42}\text{O}_4\text{Si}_2\text{Na}$ ($M + \text{Na}$) 413.2519, found 413.2520. Anal. Calcd for $\text{C}_{19}\text{H}_{42}\text{O}_4\text{Si}_2$: C, 58.41; H, 10.84. Found: C, 58.69; H, 11.11.

Triethylsilylperoxyketal (17). A solution of 3-methylcyclohexanone **16** (0.398 g, 4.05 mmol) in 6 mL of CH₂Cl₂ was treated with formic acid (4.5 mL, 120 mmol, 95-97%) and hydrogen peroxide (7.2 mL, 120 mmol, 50% H₂O). The reaction mixture was stirred for 10 min at ambient temperature then added to 50 mL of CH₂Cl₂ and 50 mL of H₂O. The layers were separated and the aqueous layer was extracted with 3 x 50 mL of CH₂Cl₂. The organic layers were combined and the solvent was removed *in vacuo* to afford a clear oil (0.479 g, ~ 95% product by ¹H NMR spectroscopy). The unpurified product (0.479 g, 3.23 mmol) in 12 mL of DMF was treated with Et₃N (1.60 mL, 11.3 mmol), DMAP (0.0199 g, 0.162 mmol in 2 mL of DMF) and Et₃SiOTf (2.56 mL, 11.3 mmol). The reaction mixture was stirred for 4 h at room temperature then added to 100 mL of ice-cold pentane/H₂O (1:1). The layers were separated and the aqueous layer was extracted with 3 x 30 mL of pentane. The organic layers were combined, dried over Na₂SO₄, filtered, and the solvent was removed *in vacuo*. Purification by flash chromatography (pentane) **17** as a clear liquid (0.783 g, 51%): ¹H NMR (500 MHz, CDCl₃) δ 2.18 (m, 1H), 2.06 (m, 2H), 1.92 (m, 1H), 1.80 (m, 1H), 1.49 (dd, *J* = 10.0, 3.9, 1H), 1.29 (m, 1H), 1.02-0.98 (m, 21H), 0.75-0.72 (m, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 120.9, 42.0, 33.67, 33.55, 33.47, 20.0, 7.0, 4.1; IR (thin film) 2956, 2878, 1459, 1240, 1006 cm⁻¹; HRMS (ESI/Na) *m/z* calcd for C₁₈H₄₀O₄Si₂Na (M + Na) 399.2363, found 399.2379. Anal. Calcd for C₁₈H₄₀O₄Si₂: C, 57.39; H, 10.70. Found: C, 57.56; H, 10.78.

Triethylsilylperoxyketal (19). A solution of benzylacetone **18** (0.600 g, 4.05 mmol) in 6 mL of CH₂Cl₂ was treated with formic acid (4.5 mL, 120 mmol, 95-97%) and hydrogen peroxide (7.2 mL, 120 mmol, 50% H₂O). The reaction mixture was stirred for 10 min at ambient temperature then added to 50 mL of CH₂Cl₂ and 50 mL of H₂O. The layers were separated and the aqueous layer was extracted 3 x 50 mL with CH₂Cl₂. The organic layers were combined and the solvent was removed *in vacuo* to afford a clear oil (0.685 g, ~ 1:1 mixture of peroxyketal and benzylacetone as detected by ¹H NMR spectroscopy). The unpurified product (0.685 g, ~ 0.343 g of peroxyketal, 1.73 mmol), in 12 mL of DMF was treated with Et₃N (0.857 mL, 6.06 mmol), DMAP (0.0106 g, 0.086 mmol in 2 mL of DMF) and Et₃SiOTf (1.37 mL, 6.06 mmol) at 0 °C. The reaction mixture was stirred for 3 h from 0 °C – 25 °C then added to 100 mL of ice-cold pentane/H₂O (1:1). The layers were separated and the aqueous layer was extracted with 3 x 30 mL of pentane. The organic layers were combined, dried over Na₂SO₄, filtered, and the solvent was removed *in vacuo*. Purification by flash chromatography (pentane) afforded **19** as a clear liquid (0.857 g, 48%): ¹H NMR (500 MHz, CDCl₃) δ 7.25 (m, 3H), 7.18 (m, 2H), 2.70 (m, 2H), 2.03 (m, 2H), 1.41 (s, 3H), 0.99 (t, *J* = 4.6, 18H), 0.71 (q, *J* = 7.9, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 142.5, 128.59, 128.58, 126.0, 110.7, 36.3, 30.9, 19.1, 7.0, 4.1; IR (thin film) 2950, 2880, 1458, 1234, 1009 cm⁻¹; HRMS (CI/NH₃) *m/z* calcd for C₂₂H₄₆O₄Si₂N (M) 444.2965, found 444.2964. Anal. Calcd for C₂₂H₄₆O₄Si₂: C, 61.92; H, 9.92. Found: C, 62.02; H, 10.02.

II. Preparation of Alkenes

Alkenes **4**⁶, **28**⁷, and **26**⁸ were prepared according to literature procedures (see bibliography).

Benzhydryldimethyl-(2-methylallyl)silane (30a). Magnesium metal (0.930 g, 38.3 mmol, 50 mesh) was stirred vigorously for 16 h under N₂ then 17 mL of THF were added. The resultant gray suspension was treated with methallylchloride (0.900 mL, 9.20 mmol) dropwise at 0 °C – 25 °C. After 1 h, the reaction mixture was cooled to 0 °C and benzhydryldimethylchlorosilane⁷ (2.00 g, 7.67 mmol) was added dropwise. The reaction mixture was allowed to warm to ambient temperature and stirred for 3 days, followed by addition of HCl (1 M) at 0 °C. The reaction mixture was extracted with 3 x 100 mL of Et₂O. The organic layers were combined, dried over Na₂SO₄, filtered, and the solvent was removed *in vacuo*. Purification by flash chromatography (100:0 – 90:10 hexanes/EtOAc) afforded **30a** as a colorless oil (1.63 g, 76%): ¹H NMR (500 MHz, CDCl₃) δ 7.24 (m, 8H), 7.13 (m, 2H), 4.57 (s, 1H), 4.39 (s, 1H), 3.57 (s, 1H), 1.63 (s, 3H), 1.54 (s, 2H), 0.07 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 143.3, 142.8, 129.0, 128.6, 128.5, 125.3, 109.2, 45.4, 26.3, 25.4, -3.0; IR (thin film) 3066, 2955, 1633, 1488, 1244 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₉H₂₄Si (M) 280.1647, found 280.1643. Anal. Calcd for C₁₉H₂₄Si: C, 81.36; H, 8.62. Found: C, 81.34; H, 8.70.

Benzhydryldimethyl-(2,2,4-trimethylpent-4-enyl)silane (30). A solution of benzhydryldimethyl-(2-methylallyl)silane **30a** (0.100 g, 0.402 mmol) in 17 mL of CH₂Cl₂ was treated with SnCl₄ (0.4 mL, 1M in CH₂Cl₂) at –78 °C. The reaction mixture was allowed to warm to –3 °C over 22 h then added to 10 mL of ice-cold H₂O. The reaction mixture was extracted with 3 x 50 mL of CH₂Cl₂. The organic layers were combined, dried over Na₂SO₄, filtered, and the solvent was removed *in vacuo*. Purification by flash chromatography (100:0 – 90:10 hexanes/EtOAc) afforded **30** as a clear oil (0.035 g, 52%): ¹H NMR (500 MHz, CDCl₃) δ 7.26 (m, 8H), 7.15 (m, 2H), 4.82 (s, 1H), 4.56 (s, 1H), 3.50 (s, 1H), 1.92 (s, 2H), 1.66 (s, 3H), 0.95 (s, 6H), 0.74 (s, 2H), 0.16 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 146.9, 146.1, 131.9, 131.3, 128.1, 117.2, 56.7, 49.9, 37.5, 33.4, 33.1, 28.5, 2.6; IR (thin film) 3061, 2913, 1640, 1494, 1249 cm⁻¹; LRMS (ESI/Na) *m/z* calcd for C₂₃H₃₃Si (M + H) 336.24, found 337.50. Anal. Calcd for C₂₃H₃₂Si: C, 82.07; H, 9.58. Found: C, 82.03; H, 9.73.

III. Annulation Products Between Peroxycarbenium ions and Alkenes

General Procedure for the Annulation of Peroxycarbenium ions with Alkenes. Unless otherwise noted a solution of silyl peroxyketal (1.0 equiv) and alkene (3.0 equiv) in CH₂Cl₂ (0.16 M) was treated with SnCl₄ (2.0 equiv, 1.0 M solution in CH₂Cl₂) at –78 °C. The reaction mixture was allowed to warm to –3 °C over 2h – 24 h then added to ice-cold H₂O. The reaction mixture was extracted with CH₂Cl₂. The organic layers were combined, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. Purification by flash chromatography was performed using Davisil[®] silica gel.

3-(2-Benzyloxyethyl)-8-tert-butyl-3-methyl-1,2-dioxaspiro[4.5]decane (10). The standard annulation procedure was followed with silyl peroxyketal **7** (0.050 g, 0.116 mmol) and 2-methyl-4-(phenylmethoxy)-1-butene **4** (0.0613 g, 0.348 mmol) in 5 mL of CH₂Cl₂ and SnCl₄ (0.23 mL). Purification by flash chromatography (100:0 – 60:40 hexanes/EtOAc) afforded **10** as a clear liquid (0.0320 g, 80%): ¹H NMR (500 MHz, CDCl₃) δ 7.32 (m, 5H), 4.51 (d, *J* = 11.9, 1H), 4.47 (d, *J* = 11.9, 1H), 3.59 (m, 2H), 2.22 (d, *J* = 12.0, 1H), 2.01 (m, 4H), 1.91 (m, 1H), 1.58 (m, 2H), 1.40 (m, 2H), 1.32 (s, 3H), 1.29 (m, 2H), 0.95 (m, 1H), 0.83 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 138.3, 128.4, 127.7, 127.6, 84.5, 84.2, 73.1, 66.8, 57.6, 47.1, 38.9, 36.1, 35.9, 32.4, 27.5, 24.4, 23.8, 23.7; IR (thin film) 3031, 2941, 1454, 1110 cm⁻¹; HRMS (ESI/Na) *m/z* calcd for C₂₂H₃₄O₃Na (*M* + Na) 369.2406, found 369.2412. Anal. Calcd for C₂₂H₃₄O₃: C, 76.26; H, 9.89. Found: C, 76.50; H, 9.92.

3-(2-Benzyloxyethyl)-3,7-dimethyl-1,2-dioxaspiro[4.5]decane (20). The standard annulation procedure was followed with silyl peroxyketal **15** (0.050 g, 0.128 mmol) and 2-methyl-4-(phenylmethoxy)-1-butene **4** (0.068 g, 0.384 mmol) in 5 mL of CH₂Cl₂ and SnCl₄ (0.26 mL). Purification by flash chromatography (100:0 – 60:40 pentane/EtOAc) afforded **20** as a clear liquid (0.0280 g, 72%, d.r. 1:1): ¹H NMR (500 MHz, CDCl₃) δ 7.32 (m, 8H), 7.28 (m, 2H), 4.50 (m, 4H), 3.61 (m, 4H), 2.25 (t, *J* = 12.3, 2H), 2.06-1.91 (m, 10H), 1.67 (m, 4H), 1.56 (m, 4H), 1.34 (s, 3H), 1.33 (s, 3H), 1.29 (m, 2H), 1.06 (m, 2H), 0.87 (d, *J* = 5.3, 3H), 0.86 (d, *J* = 5.2, 3H), 0.80 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 138.6, 138.5, 128.6, 127.86, 127.77, 85.54, 85.53, 84.37, 84.36, 73.3, 67.0, 66.99, 58.37, 58.29, 44.5, 44.3, 39.2, 39.0, 35.4, 35.3, 34.1, 29.34, 29.28, 24.8, 24.5, 22.9, 22.8, 22.73, 22.72; IR (thin film) 3031, 2926, 2865, 1454 cm⁻¹; HRMS (ESI/Na) *m/z* calcd for C₁₉H₂₈O₃Na (*M* + Na) 327.1936, found 327.1937. Anal. Calcd for C₁₉H₂₈O₃: C, 74.96; H, 9.27. Found: C, 74.98; H, 9.47.

3-(2-Benzyloxyethyl)-3,5-dimethyl-5-phenethyl[1.2]dioxolane (21). The standard annulation procedure was followed with silyl peroxyketal **19** (0.50 g, 0.114 mmol) and 2-methyl-4-(phenylmethoxy)-1-butene **4** (0.060 mg, 0.342 mmol) in 5 mL of CH₂Cl₂ and SnCl₄ (0.23 mL). Purification by flash chromatography (100:0 – 60:40 pentane/EtOAc) afforded **21** as a clear liquid (0.0224 g, 57%, d.r. 1:1): ¹H NMR (500 MHz, CDCl₃) δ 7.36 (m, 8H), 7.30 (m, 6H), 7.21 (m, 6H), 4.52 (s, 2H), 4.50 (s, 2H), 3.62 (m, 4H),

2.71 (m, 4H), 2.44 (d, $J = 12.0$, 1H), 2.35 (d, $J = 12.1$, 1H), 2.22 (d, $J = 12.1$, 1H), 2.13 (d, $J = 12.1$, 1H), 2.00 (m, 6H), 1.85 (m, 2H), 1.42 (s, 3H), 1.389 (s, 3H), 1.386 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 142.26, 142.20, 138.52, 138.50, 128.64, 128.63, 128.61, 128.59, 128.50, 128.49, 127.87, 127.84, 127.81, 127.79, 126.1, 85.9, 85.2, 73.35, 73.32, 66.95, 66.94, 56.9, 56.8, 41.7, 41.4, 39.14, 39.06, 31.18, 31.13, 24.7, 24.5, 24.3, 24.0; IR (thin film) 3028, 2933, 2865, 1497 cm^{-1} ; HRMS (ESI/Na) m/z calcd for $\text{C}_{22}\text{H}_{28}\text{O}_3\text{Na}$ ($M + \text{Na}$) 363.1936, found 363.1945. Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{O}_3$: C, 77.61; H, 8.29. Found: C, 76.36; H, 8.27.

(8-tert-Butyl-1,2-dioxaspiro[4.5]dec-3-ylmethyl)-trimethylsilane (25).⁹ To a -78°C solution of silyl peroxyketal **6** (0.500 g, 1.16 mmol) and 40 mL of CH_2Cl_2 , was added allyltrimethylsilane **24** (1.88 mL, 11.6 mmol). After 5 min, SnCl_4 (4.6 mL) was slowly added to the reaction mixture. The reaction mixture was stirred for 24 h from -78°C to ambient temperature then 50 mL of H_2O were added. The reaction mixture was extracted with 3 x 20 mL of CH_2Cl_2 and the combined organic layers were concentrated *in vacuo*. Purification by flash chromatography (80:20 hexanes/ CH_2Cl_2) afforded **25** as a white solid (0.30 g, 92%): mp $73.0\text{--}74.0^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 4.33 (m, 1H), 2.32 (dd, $J = 11.6$, 6.9, 1H), 2.04 (m, $J = 9.8$, 2.9, 1H), 1.95 (m, $J = 10.5$, 3.1, 1H), 1.81 (dd, $J = 11.6$, 8.1, 1H), 1.55 (m, 4H), 1.36 (m, 2H), 1.21 (m, $J = 13.4$, 3.7, 1H), 1.07 (dd, $J = 14.0$, 5.5, 1H), 0.95 (m, 1H), 0.9–0.8 (m, 1H), 0.84 (s, 9H), 0.05 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 84.3, 79.4, 54.4, 47.2, 36.8, 36.2, 32.4, 27.6, 23.81, 23.78, 21.1, -1.0 ; IR (KBr) 2952, 1361, 1251, 861, 840 cm^{-1} ; HRMS (CI/NH_3) m/z calcd for $\text{C}_{16}\text{H}_{32}\text{O}_2\text{Si}$ (M) 284.2172, found 284.2166. Anal. Calcd for $\text{C}_{16}\text{H}_{32}\text{O}_2\text{Si}$: C, 67.54; H, 11.34. Found: C, 67.75; H, 11.34.

2-(8-tert-Butyl-1,2-dioxaspiro[4.5]dec-3-yl)-ethanol (27). The standard annulation procedure was followed with silyl peroxyketal **6** (0.0350 g, 0.0809 mmol) and triethyl-(3-methyl-but-3-enyloxy)-silane **26** (0.0490 g, 0.243 mmol) in 3.5 mL of CH_2Cl_2 and SnCl_4 (0.16 mL). Purification by flash chromatography (100:0 – 50:50 pentane/EtOAc) afforded **27** as a clear liquid (0.0159 g, 77%): ^1H NMR (500 MHz, CDCl_3) δ 3.78 (m, 2H), 2.22 (d, $J = 12$, 1H), 2.09 (m, 2H), 1.99 (m, 2H), 1.81 (ddd, $J = 14.4$, 5.5, 6.6, 2H), 1.61 (m, 2H), 1.48 (m, $J = 13.7$, 4.1, 1H), 1.39 (m, $J = 13.6$, 3.7, 1H), 1.36 (s, 3H), 1.31 (m, 2H), 0.96 (m, 1H), 0.88 (m, 1H), 0.83 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 85.3, 84.8, 59.3, 57.6, 47.1, 41.4, 36.1, 35.7, 32.4, 27.5, 24.4, 23.9, 23.7 cm^{-1} ; IR (thin film) 3339, 2942, 2868, 1442 cm^{-1} ; HRMS (ESI/Na) m/z calcd for $\text{C}_{15}\text{H}_{28}\text{O}_3\text{Na}$ ($M + \text{Na}$) 279.1936, found 279.1933. Anal. Calcd for $\text{C}_{15}\text{H}_{28}\text{O}_3$: C, 70.27; H, 11.01. Found: C, 69.59; H, 11.09.

Benzhydryl-(8-*tert*-butyl-1,2-dioxaspiro[4.5]dec-3-yl)methyl)-dimethylsilane (29). To a $-78\text{ }^{\circ}\text{C}$ solution of silyl peroxyketal **6** (2.0 g, 4.6 mmol) and 200 mL of CH_2Cl_2 , was added benzhydryldimethylsilane **28** (3.7 g, 13.9 mmol). After 5 min, SnCl_4 (4.6 mL) was slowly added to the reaction mixture. The reaction mixture was stirred for 22 h from $-78\text{ }^{\circ}\text{C}$ to ambient temperature then 100 mL of H_2O were added. The reaction mixture was extracted with 3 x 200 mL of CH_2Cl_2 and the combined organic layers were concentrated *in vacuo*. Purification by flash chromatography (80:20 hexanes/ CH_2Cl_2) afforded **29** as a white solid (1.4 g, 72%): mp $86.0\text{--}87.0\text{ }^{\circ}\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.25 (m, 8H), 7.14 (m, 2H), 4.21 (m, 1H), 3.57 (s, 1H), 2.21 (dd, $J = 6.9, 4.7$, 1H), 1.94 (m, 1H), 1.88 (m, 1H), 1.69 (dd, $J = 7.8, 3.8$, 1H), 1.58 (m, 2H), 1.44 (m, $J = 14, 4.4$, 1H), 1.33–1.25 (m, 3H), 1.17 (m, 1H), 1.05 (dd, $J = 14, 6.6$, 1H), 0.93 (m, 1H), 0.89 (s, 9H), 0.10 (s, 3H), 0.096 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 142.3, 128.8, 128.7, 128.44, 128.40, 125.4, 125.3, 84.3, 79.0, 54.5, 47.2, 45.3, 36.6, 36.1, 32.4, 27.5, 24.8, 23.7, 19.4, -2.5 , -2.6 ; IR (thin film) 3058, 2867, 1596, 1494, 1248 cm^{-1} ; HRMS (CI/ NH_3) m/z calcd for $\text{C}_{28}\text{H}_{41}\text{O}_2\text{Si}$ ($M + \text{H}$) 437.2876, found 437.2876. Anal. Calcd for $\text{C}_{28}\text{H}_{40}\text{O}_2\text{Si}$: C, 77.01; H, 9.23. Found: C, 77.22; H, 9.23.

2-(8-*tert*-Butyl-1,2-dioxaspiro[4.5]dec-3-yl)-ethanol (27). The standard annulation procedure was followed with silyl peroxyketal **27** (0.300 g, 0.696 mmol) and 3-Methyl-but-3-en-1-ol **32** (0.180 g, 2.09 mmol) in 30 mL of CH_2Cl_2 and SnCl_4 (1.4 mL). Purification by flash chromatography (100:0 – 50:50 pentane/ EtOAc) afforded **27** as a clear liquid (0.0840 g, 47%): Characterization data matched.

Benzhydryl-[3-(8-*tert*-butyl-3-methyl-1,2-dioxaspiro[4.5]dec-3-yl)-2,2-dimethylpropyl]dimethylsilane (31). The standard annulation procedure was followed with silyl peroxyketal **6** (0.0140 g, 0.0324 mmol) and benzhydryldimethyl-(2,2,4-trimethylpent-4-enyl)silane **30** (0.0100 g, 0.0324 mmol) in 1.5 mL of CH_2Cl_2 and SnCl_4 (0.032 mL). Purification by flash chromatography (100:0 – 80:20 pentane/ EtOAc) afforded **31** as a clear liquid (0.0090 g, 55%): ^1H NMR (500 MHz, CDCl_3) δ 7.23 (m, 8H), 7.12 (m, 2H), 3.48 (s, 1H), 1.96 (m, 4H), 1.69 (d, $J = 14.4$, 1H), 1.59 (m, 2H), 1.46 (m, 2H), 1.44 (m, $J = 13.6, 4.0$, 1H), 1.34 (m, 1H), 1.27 (s, 3H), 1.24 (m, 1H), 0.997 (s, 3H), 0.994 (s, 3H), 0.92 (m, 1H), 0.83 (s, 9H), 0.76 (m, 2H), 0.139 (s, 3H), 0.136 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.04, 143.02, 129.0, 128.4, 125.2, 86.5, 83.9, 60.5, 53.7, 47.2, 46.9, 36.4, 36.2, 34.3, 32.5, 32.0, 31.8, 31.4, 27.7, 25.9, 24.1, 23.9, -0.31 , -0.36 ; IR (thin film) 2951, 2868, 1597, 1250 cm^{-1} ; HRMS (ESI/ Na) m/z calcd for $\text{C}_{33}\text{H}_{50}\text{O}_2\text{SiNa}$ ($M + \text{Na}$) 529.3478, found 529.3475. Anal. Calcd for $\text{C}_{33}\text{H}_{50}\text{O}_2\text{Si}$: C, 78.20; H, 9.94. Found: C, 77.49; H, 9.83.

3-(8-*tert*-Butyl-3-methyl-1,2-dioxaspiro[4.5]dec-3-yl)-propionic acid ethyl ester (34). The standard annulation procedure was followed with silyl peroxyketal **6** (0.0500 g, 0.116 mmol) and 4-methyl-pent-4-enoic acid ethyl ester **33** (0.0493 g, 0.347 mmol) in 5 mL of CH₂Cl₂ and SnCl₄ (0.23 mL). Purification by flash chromatography (100:0 – 80:20 pentane/EtOAc) afforded **34** as a clear liquid (0.0124 g, 34%): ¹H NMR (500 MHz, CDCl₃) δ 4.13 (q, *J* = 7.2, 2H), 2.40 (m, 2H), 2.12 (d, *J* = 12.0, 1H), 2.08 (m, 2H), 2.05 (d, *J* = 12.0, 1H), 1.99 (m, 1H), 1.83 (ddd, *J* = 14.1, 10.6, 5.8, 1H), 1.60 (m, 2H), 1.46 (m, *J* = 13.6, 4.0, 1H), 1.34 (m, 2H), 1.29 (s, 3H), 1.25 (t, *J* = 7.1, 3H), 0.95 (m, 1H), 0.86 (m, 1H), 0.83 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 173.8, 84.7, 84.4, 60.7, 57.6, 47.3, 36.3, 36.0, 34.3, 32.6, 29.8, 27.7, 24.1, 23.9, 23.7, 14.4; IR (thin film) 2943, 2870, 1735, 1443 cm⁻¹; HRMS (ESI/Na) *m/z* calcd for C₁₈H₃₂O₄Na (*M* + Na) 335.2198, found 335.2201. Anal. Calcd for C₁₈H₃₂O₄: C, 69.19; H, 10.13 Found: C, 68.42; H, 10.45.

8-*tert*-Butyl-3-*p*-tolyl-1,2-dioxaspiro[4.5]decane (36). The standard annulation procedure was followed with silyl peroxyketal **6** (0.050 g, 0.116 mmol) and *p*-methylstyrene **35** (0.046 g, 0.348 mmol) in 5 mL of CH₂Cl₂ and SnCl₄ (0.23 mL). Purification by flash chromatography (100:0 – 80:20 hexanes/EtOAc) afforded **36** a clear liquid (0.0094 g, 28%): ¹H NMR (500 MHz, CDCl₃) δ 7.26 (d, *J* = 8.8, 2H), 7.15 (d, *J* = 7.9, 2H), 5.22 (t, *J* = 7.7, 1H), 2.67 (dd, *J* = 12.0, 7.8, 1H), 2.33 (s, 3H), 2.31 (dd, *J* = 12.0, 7.6, 1H), 2.10 (m, 2H), 1.64 (m, 2H), 1.50 (m, 2H), 1.36 (m, 1H), 0.97 (m, 2H), 0.85 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 138.5, 136.1, 129.5, 126.6, 84.9, 82.8, 54.8, 47.5, 36.4, 36.1, 32.6, 27.8, 24.2, 23.9, 21.4; IR (thin film) 2939, 1455, 1043 cm⁻¹; HRMS (ESI/Na) *m/z* calcd for C₁₉H₂₈O₂Na (*M* + Na) 311.1987, found 311.1992. Anal. Calcd for C₁₉H₂₈O₂: C, 79.12; H, 9.78. Found: C, 76.39; H, 9.77.

Benzhydryldimethyl-(5-methyl-5-phenethyl[1.2]dioxolan-3-ylmethyl)-silane (38). To a – 78 °C solution of silyl peroxyketal **19** (0.0500 g, 0.114 mmol) in 1 mL of CH₂Cl₂, was added benzhydryldimethylallylsilane **28** (0.0305 g, 0.114 mmol), and SnCl₄ (0.11 mL). The reaction mixture was allowed to warm to –5 °C over 2 h then added to 5 mL of ice-cold H₂O. The reaction mixture was extracted with 3 x 20 mL of CH₂Cl₂. The combined organic layers were concentrated *in vacuo*. Purification by flash chromatography (80:20 hexanes/CH₂Cl₂) afforded *trans*-**38** and *cis*-**38** as a clear liquid (0.0280 g, 57%, d.r. 2:1; major diastereomer isolated): IR (thin film) 3059, 2953, 1593, 1493, 1248 cm⁻¹; HRMS (CI/NH₃) *m/z* calcd for

$C_{28}H_{38}O_2NSi$ ($M + NH_4$) 448.2672, found 448.2661. Anal. Calcd for $C_{28}H_{34}O_2Si$: C, 78.09; H, 7.96. Found: C, 77.56; H, 8.00.

Major diastereomer (*trans*-38**).** 1H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 10H), 7.17 (m, 3H), 7.15 (m, 2H), 4.21 (m, 1H), 3.60 (s, 1H), 2.64 (m, 2H), 2.37 (dd, $J = 11.7, 7.0$, 1H), 1.85 (m, 2H), 1.73 (dd, $J = 11.7, 7.9$, 1H), 1.34 (s, 3H), 1.12 (dd, $J = 14.2, 6.2$, 1H), 0.86 (dd, $J = 14.2, 8.4$, 1H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 142.1, 129.0, 128.8, 128.63, 128.60, 128.58, 128.4, 126.1, 125.6, 125.5, 85.8, 79.9, 53.3, 45.6, 40.8, 30.9, 25.8, 19.5, -2.45, -2.47.

Minor diastereomer (*cis*-38**).** 1H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 10H), 7.17 (m, 3H), 7.15 (m, 2H), 4.28 (m, 1H), 3.60 (s, 1H), 2.64 (m, 2H), 2.29 (dd, $J = 11.7, 6.7$, 1H), 1.95 (m, $J = 8.6, 4.8$, 1H), 1.85 (m, 2H), 1.34 (s, 3H), 1.12 (dd, $J = 15.2, 6.2$, 1H), 0.86 (dd, $J = 14.3, 5.9$, 1H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, distinctive peaks) δ 85.6, 79.6, 53.7, 45.4, 42.4, 30.96, 23.6, 19.2.

2-(3,5-Dimethyl-5-phenethyl[1.2]dioxolan-3-yl)-ethanol (37**).** The standard annulation procedure was followed with silyl peroxyketal **19** (0.0500 g, 0.114 mmol) and triethyl-(3-methyl-but-3-enyloxy)-silane **26** (0.0685 g, 0.342 mmol) in 5 mL of CH_2Cl_2 and $SnCl_4$ (0.23 mL). Purification by flash chromatography (100:0 – 50:50 pentane/pentane) afforded **37** as a clear liquid (0.0192 g, 67%, d.r. 1:1): 1H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 4H), 7.18 (m, 6H), 3.77 (m, 4H), 2.67 (m, 4H), 2.32 (m, 4H), 2.16 (m, 2H), 2.00 (m, 4H), 1.83 (m, 4H), 1.38 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 141.9, 128.6, 128.41, 128.39, 126.07, 126.03, 86.14, 86.12, 86.0, 59.33, 59.31, 56.9, 56.8, 41.58, 41.56, 41.50, 41.16, 31.13, 30.99, 24.49, 24.34, 24.26, 23.6; IR (thin film) 3373, 3028, 2934, 1456 cm^{-1} ; HRMS (ESI/Na) m/z calcd for $C_{15}H_{22}O_3Na$ ($M + Na$) 273.1467, found 273.1470. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.70; H, 9.01.

IV. Oxidation of the Silane Moiety⁷

General Procedure for the oxidation of the silane moiety. To a solution of 1,2-dioxolane (1.0 equiv) in THF (1.0 M) was added $n-Bu_4NF$ (1.6 equiv, 1.0 M solution in THF) dropwise by syringe at 0 °C. The ice bath was removed and the reaction mixture was allowed to warm to ambient temperature. After 30 min, MeOH (53 equiv) was added to the reaction mixture followed by $KHCO_3$ (1.5 equiv) and H_2O_2 (10 equiv, 30% wt. H_2O). After 12 h – 24 h, the reaction mixture was diluted with CH_2Cl_2/H_2O (1:1), the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 . The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by flash chromatography was performed using Davisil[®] silica gel.

(8-*tert*-Butyl-1,2-dioxaspiro[4.5]dec-3-yl)-methanol (39). The standard oxidation procedure was followed with **29** (0.250 g, 0.570 mmol) in 5 mL of THF, *n*-Bu₄NF (0.9.2 mL), MeOH (1.30 mL), KHCO₃ (0.0860 g, 0.860 mmol) and H₂O₂ (0.72 mL, 5.7 mmol). Purification by flash chromatography (80:20 hexanes/EtOAc) afforded **39** as a white solid (0.0683 g, 52%): mp 58.0-59.0 °C; ¹H NMR (500 MHz, CDCl₃) δ 4.40 (dddd, *J* = 8.1, 7.3, 4.7, 3.3, 1H), 3.60 (m, 2H), 2.35 (dd, *J* = 12.0, 8.2, 1H), 2.09 (m, *J* = 7.1, 2.9, 1H), 2.01 (dd, *J* = 12, 4.8, 1H), 1.89 (m, 1H), 1.62 (m, 3H), 1.33 (m, 2H), 1.19 (m, 2H), 0.98 (m, 1H), 0.84 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 84.0, 81.0, 63.8, 47.4, 47.1, 35.5, 35.0, 32.4, 27.5, 24.3, 23.4; IR (thin film) 3316, 2938, 2862, 1451, 1039 cm⁻¹; HRMS (CI/NH₃) *m/z* calcd C₁₃H₂₄O₃ (M) 228.1725 found 228.1720. Anal. Calcd for C₁₃H₂₄O₃: C, 68.38; H, 10.59. Found: C, 68.60; H, 10.61.

3-(8-*tert*-Butyl-3-methyl-1,2-dioxaspiro[4.5]dec-3-yl)-2,2-dimethylpropan-1-ol (40). The standard oxidation procedure was followed with **31** (0.0650 g, 0.128 mmol) in 1.4 mL of THF, *n*-Bu₄NF (0.46 mL), MeOH (0.280 mL), KHCO₃ (0.0226 mg, 0.216 mmol) and H₂O₂ (0.083 mL, 1.4 mmol). Purification by flash chromatography (100:0 – 90:10 pentane/EtOAc) afforded **40** as white solid (0.0200 g, 52%): mp 79.5-80.5 °C; ¹H NMR (500 MHz, CDCl₃) δ 3.57 (dd, *J* = 11.3, 5.5, 1H), 3.21 (dd, *J* = 11.1, 8.9, 1H), 2.51 (dd, *J* = 8.5, 5.7, 1H), 2.10 (m, 3H), 1.97 (m, 2H), 1.59 (d, *J* = 12.4, 2H), 1.45 (m, 1H), 1.43 (s, 3H), 1.29 (m, 4H), 0.97 (s, 3H), 0.95 (s, 3H), 0.93 (m, 1H), 0.82 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 86.8, 84.5, 71.3, 61.8, 47.4, 47.2, 36.6, 36.3, 36.2, 32.6, 28.8, 27.7, 25.4, 25.3, 24.2, 23.9; IR (thin film) 3340, 2967, 2866, 1460, 1047 cm⁻¹; HRMS (ESI/Na) *m/z* calcd C₁₈H₃₄O₃Na (M + Na) 321.2406, found 321.2412. Anal. Calcd for C₁₈H₃₄O₃: C, 72.44; H, 11.48. Found: C, 72.71; H, 11.77.

(5-Methyl-5-phenethyl[1.2]dioxolan-3-yl)-methanol (41). The standard oxidation procedure was followed with **38** (0.280 g, 0.650 mmol) in 6 mL of THF, *n*-Bu₄NF (1.0 mL), MeOH (1.20 mL), KHCO₃ (0.0976 g, 0.975 mmol) and H₂O₂ (0.38 mL, 6.5 mmol). Purification by flash chromatography (100:0 – 90:10 pentane/EtOAc) afforded **41** as a clear liquid (0.0860 g, 60%, d.r. 2:1; mixture of diastereomers): ¹H NMR (500 MHz, CDCl₃) δ 7.27 (m, 4H), 7.19 (m, 6H), 4.46 (m, 1H), 4.41 (m, 1H), 3.65 (m, 4H), 2.69 (m, 4H), 2.52 (dd, *J* = 11.7, 8.3, 1H), 2.41 (dd, *J* = 12.0, 8.1, 1H), 2.31 (m, 2H), 2.16 (dd, *J* = 12.0, 5.4, 1H), 2.10 (dd, *J* = 12.2, 4.8, 1H), 1.93 (m, 2H), 1.83 (m, 2H), 1.40 (s, 3H), 1.37 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 142.0, 141.7, 128.6, 128.5, 128.4, 128.3, 126.1, 126.0, 85.4, 85.2, 81.9, 81.8, 63.7, 63.6, 47.0, 46.6, 41.1, 40.1, 31.2, 30.7, 24.2, 22.4; IR (thin film) 3406, 3017, 2946, 1455, cm⁻¹; HRMS (EI) *m/z* calcd C₁₃H₁₈O₃ (M) 222.1256, found 222.1253. Anal. Calcd for C₁₃H₁₈O₃: C, 70.24; H, 8.16. Found: C, 70.01; H, 8.25.

V. Oxidation of Hydroxyl Groups

(8-tert-Butyl-3-methyl-1,2-dioxaspiro[4.5]dec-3-yl)-acetic acid (42a). To a solution of **27** (0.0370 g, 0.144 mmol) in 1 mL of acetonitrile was added H_5IO_6 (0.0790 g, 0.346 mmol), $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ (0.001 g, 0.005 mmol), 1 mL of CCl_4 and 1 mL of H_2O .¹⁰ The reaction mixture was stirred for 1.5 h at ambient temperature then diluted with 10 mL of CH_2Cl_2 and 10 mL of H_2O . The layers were separated, and the aqueous layer was extracted with 3 x 10 mL of CH_2Cl_2 . The combined organic layers were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by celite-filtration afforded **42a** as a white solid (0.0339 g, 87%): mp 113–114 °C; ^1H NMR (500 MHz, CDCl_3) δ 12.1–9.6 (bs, 1H), 2.78 (d, $J = 14.9$, 1H), 2.72 (d, $J = 14.8$, 1H), 2.41 (d, $J = 12.4$, 1H), 2.12 (m, 2H), 1.94 (m, 1H), 1.61 (m, 2H), 1.53 (m, $J = 13.7$, 4.1, 1H), 1.46 (s, 3H), 1.34 (m, 2H), 1.24 (m, 1H), 0.96 (m, 1H), 0.84 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 176.42, 85.0, 83.2, 56.6, 47.0, 44.0, 36.0, 35.7, 32.4, 27.5, 24.0, 23.8, 23.5; IR (thin film) 2943, 2870, 1738 cm^{-1} ; HRMS (ESI/Na) m/z calcd $\text{C}_{15}\text{H}_{26}\text{O}_4\text{Na}$ ($M + \text{Na}$) 293.1729, found 293.1721.

(3,5-Dimethyl-5-phenethyl[1.2]dioxolan-3-yl)-acetic acid (43a). To a solution of **37** (0.0500 g, 0.199 mmol) in 1.3 mL of acetonitrile was added H_5IO_6 (0.109 g, 0.478 mmol), $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ (0.001 g, 0.007 mmol), 1.3 mL of CCl_4 and 2 mL of H_2O .¹⁰ The reaction mixture was stirred for 1.5 h at ambient temperature then diluted with 10 mL of CH_2Cl_2 and 10 mL of H_2O . The layers were separated, and the aqueous layer was extracted with 3 x 10 mL of CH_2Cl_2 . The combined organic layers were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by celite-filtration afforded **43a** as a clear oil (0.0380 g, 72%, d.r. 1:1; mixture of diastereomers): ^1H NMR (500 MHz, CDCl_3) δ 7.28 (m, 4H), 7.19 (m, 6H), 2.85–2.52 (m, 8H), 2.42–2.04 (m, 4H), 2.00–1.80 (m, 4H), 1.51 (s, 3H), 1.47 (s, 3H), 1.43 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 175.4, 141.9, 141.6, 128.49, 128.46, 128.31, 128.26, 126.0, 125.9, 86.3, 86.2, 83.9, 83.8, 55.9, 55.5, 43.92, 43.89, 41.7, 40.7, 31.0, 30.7, 24.7, 23.9, 23.6, 23.0; IR (thin film) 3028, 2936, 1718, 1454 cm^{-1} ; HRMS (ESI/Na) m/z calcd $\text{C}_{15}\text{H}_{20}\text{O}_4\text{Na}$ ($M + \text{Na}$) 287.1259, found 287.1253.

(8-tert-Butyl-3-methyl-1,2-dioxaspiro[4.5]dec-3-yl)-acetic acid methyl ester (42). To a solution of **42a** (0.0270 g, 0.0999 mmol) in 1 mL of hexanes and 1 mL of CH_3OH was added trimethylsilyl diazomethane (0.0950 mL, 0.190 mmol) at ambient temperature.¹¹ The reaction mixture was stirred for 20 min and acetic acid

was added dropwise until the yellow color disappeared. The solvent was removed *in vacuo* to afford **42** as a clear liquid (0.0270 g, 95%): ^1H NMR (500 MHz, CDCl_3) δ 3.67 (s, 3H), 2.72 (d, $J = 14.6$, 1H), 2.66 (d, $J = 14.6$, 1H), 2.42 (d, $J = 15.5$, 1H), 2.10 (m, 2H), 1.95 (m, 1H), 1.60 (m, 2H), 1.53 (m, $J = 13.5$, 4.2, 1H), 1.43 (s, 3H), 1.34 (m, 2H), 1.24 (m, 1H), 0.96 (m, 1H), 0.83 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.3, 85.1, 83.5, 56.7, 51.9, 47.2, 44.3, 36.2, 35.9, 32.6, 27.7, 24.2, 24.1, 23.7; IR (thin film) 2941, 2867, 2736, 2638, 1694 cm^{-1} ; HRMS (ESI/Na) m/z calcd $\text{C}_{16}\text{H}_{28}\text{O}_4\text{Na}$ ($M + \text{Na}$) 307.1885, found 307.1890. Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{O}_4$: C, 67.57; H, 9.92. Found: C, 67.57; H, 9.99.

(3,5-Dimethyl-5-phenethyl[1.2]dioxolan-3-yl)-acetic acid methyl ester (43). To a solution of **43a** (0.0160 g, 0.0605 mmol) in 0.5 mL of hexanes and 0.1 mL of CH_3OH was added trimethylsilyl diazomethane (0.0575 mL, 0.115 mmol) at ambient temperature.¹¹ The reaction mixture was stirred for 15 min and acetic acid was added dropwise until the yellow color disappeared. Solvent was removed *in vacuo* to afford **43** as a clear liquid (0.0142 g, 85%, d.r. 1:1; mixture of diastereomers): ^1H NMR (500 MHz, CDCl_3) δ 7.28 (m, 4H), 7.19 (m, 6H), 3.70 (s, 3H), 3.68 (s, 3H), 2.81-2.61 (m, 9H), 2.55 (d, $J = 12.5$, 1H), 2.27 (d, $J = 12.5$, 1H), 2.18 (d, $J = 12.5$, 1H), 2.06 (m, $J = 12.6$, 4.8, 1H), 1.96 (m, $J = 12.0$, 5.4, 1H), 1.86 (m, 2H), 1.48 (s, 3H), 1.44 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.1, 171.0, 142.0, 141.8, 128.46, 128.45, 128.31, 128.27, 126.0, 125.9, 86.2, 86.1, 84.1, 84.0, 55.7, 55.3, 51.8, 51.7, 44.1, 44.0, 41.7, 40.7, 31.0, 30.1, 24.6, 24.2, 23.9, 23.1; IR (thin film) 3028, 2953, 1735, 1455 cm^{-1} ; HRMS (ESI/Na) m/z calcd $\text{C}_{16}\text{H}_{22}\text{O}_4\text{Na}$ ($M + \text{Na}$) 301.1416, found 301.1416. Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_4$: C, 69.04; H, 7.97. Found: C, 69.16; H, 8.01.

VI. Stereochemical Proofs of Annulation Products

A. The Stereochemistry of **25** was determined by analysis of nOe data:

Relevant DPGSE-nOe data (mixing time 5.0 s): (the peaks in the NMR spectrum were assigned using $^1\text{H}/^1\text{H}$ COSY, $^1\text{H}/^{13}\text{C}$ HMQC, ^1H NMR chemical shifts, and ^1H NMR coupling constants)

(8-tert-Butyl-1,2-dioxaspiro[4.5]dec-3-ylmethyl)trimethylsilane (25)

nOe experiments were performed for **25** using a single diastereomer

H^{A} irradiated: H^{B} (10.8%)

Note: nOe between H^{A} and H^{B} suggests a 1,4-*cis* configuration. Coupling constants suggest H^{B} is in an axial position.

B. The Stereochemistry of *trans*-**38** was determined by analysis of nOe data:

Relevant DPGSE-nOe data (mixing time 5.0 s): (the peaks in the NMR spectrum were assigned using $^1\text{H}/^1\text{H}$ COSY, $^1\text{H}/^{13}\text{C}$ HMQC, and ^1H NMR chemical shifts)

Benzhydryl-dimethyl-(5-methyl-5-phenethyl[1.2]dioxolan-3-ylmethyl)silane (*trans*-38**)**

nOe experiments were performed for *trans*-**38** using a single diastereomer

H^{A} irradiated: H^{C} (4.3%)

H^{B} irradiated: Me (2.3%), H^{D} (1.7%)

Note: nOe between H^{B} and H^{D} and absence of nOe between H^{A} and H^{B} suggests a 1,3-*trans* configuration.

VII. X-Ray Crystallographic Data

X-ray Data Collection, Structure Solution and Refinement for **3-(8-*tert*-Butyl-3-methyl-1,2-dioxaspiro[4.5]dec-3-yl)-2,2-dimethylpropan-1-ol (40)**:

A colorless crystal of approximate dimensions 0.13 x 0.19 x 0.27 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART¹ program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ program. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/c$ which was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵ for neutral atoms were used throughout the analysis. Hydrogen atoms were either located from a difference-Fourier map and refined (x,y,z and U_{iso}) or were included using a riding model. The OH was disordered over three positions and included with site-occupancy = 1/3 at each position. Hydrogen atoms associated with C16, C17 and C18 were also included with partial site-occupancy consistent with the disordered model.

Final least-squares analysis yielded $wR2 = 0.1891$ and $Goof = 1.049$ for 337 variables refined against 3031 data ($0.85\text{\AA}$). As a comparison for refinement on F , $R1 = 0.0666$ for those 1912 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.

Definitions:

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

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

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

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

Table 1. Crystal data and structure refinement for **40**.

Identification code	kaw63 (Armando Ramirez)	
Empirical formula	$C_{18} H_{34} O_3$	
Formula weight	298.45	
Temperature	163(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 28.310(11)$ Å	$\alpha = 90^\circ$.
	$b = 6.229(2)$ Å	$\beta = 100.580(7)^\circ$.
	$c = 10.339(4)$ Å	$\gamma = 90^\circ$.
Volume	$1792.2(11)$ Å ³	
Z	4	
Density (calculated)	1.106 Mg/m ³	
Absorption coefficient	0.073 mm ⁻¹	
F(000)	664	
Crystal color	colorless	
Crystal size	0.27 x 0.19 x 0.13 mm ³	
Theta range for data collection	1.46 to 24.71°.	
Index ranges	$-33 \leq h \leq 33, -7 \leq k \leq 7, -12 \leq l \leq 12$	
Reflections collected	14089	
Independent reflections	3031 [R(int) = 0.0768]	
Completeness to theta = 24.71°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9906 and 0.9806	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3031 / 9 / 337	
Goodness-of-fit on F ²	1.049	
Final R indices [I > 2sigma(I) = 1912 data]	R1 = 0.0666, wR2 = 0.1615	
R indices (all data; 0.85Å)	R1 = 0.1155, wR2 = 0.1891	
Extinction coefficient	0.010(2)	
Largest diff. peak and hole	0.360 and -0.209 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **40**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	2526(1)	6780(4)	5601(2)	30(1)
O(2)	2015(1)	6345(4)	5170(2)	31(1)
C(1)	2659(1)	5354(5)	6721(3)	25(1)
C(2)	3095(1)	6401(5)	7562(3)	27(1)
C(3)	3534(1)	6388(5)	6897(3)	27(1)
C(4)	3665(1)	4101(5)	6529(3)	24(1)
C(5)	3230(1)	3144(6)	5626(3)	28(1)
C(6)	2781(1)	3145(5)	6252(4)	28(1)
C(7)	2209(1)	5307(6)	7364(3)	27(1)
C(8)	1819(1)	6448(5)	6377(3)	28(1)
C(9)	1777(2)	8809(6)	6739(4)	35(1)
C(10)	1346(1)	5249(5)	5963(4)	31(1)
C(11)	4146(1)	3944(5)	6025(3)	26(1)
C(12)	4131(2)	5247(6)	4750(4)	31(1)
C(13)	4556(1)	4748(7)	7060(4)	36(1)
C(14)	4249(2)	1580(6)	5739(4)	33(1)
C(15)	965(1)	5144(6)	6863(4)	37(1)
C(16)	1189(2)	4496(7)	8258(5)	45(1)
C(17)	600(2)	3420(7)	6285(6)	58(1)
C(18)	693(2)	7280(6)	6881(5)	50(1)
O(3)	806(3)	3939(12)	8960(8)	34(2)
O(4)	375(3)	3888(14)	5276(7)	27(2)
O(5)	496(3)	7903(11)	5366(7)	30(2)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **40**.

O(1)-C(1)	1.452(4)
O(1)-O(2)	1.461(3)
O(2)-C(8)	1.456(4)
C(1)-C(6)	1.520(4)
C(1)-C(2)	1.522(5)
C(1)-C(7)	1.540(5)
C(2)-C(3)	1.524(5)
C(3)-C(4)	1.537(4)
C(4)-C(5)	1.522(5)
C(4)-C(11)	1.547(5)
C(5)-C(6)	1.530(5)
C(7)-C(8)	1.534(5)
C(8)-C(10)	1.525(5)
C(8)-C(9)	1.528(5)
C(10)-C(15)	1.548(5)
C(11)-C(13)	1.514(5)
C(11)-C(14)	1.541(5)
C(11)-C(12)	1.542(5)
C(15)-C(16)	1.519(6)
C(15)-C(17)	1.533(6)
C(15)-C(18)	1.539(5)
C(16)-O(3)	1.453(8)
C(17)-O(4)	1.155(8)
C(18)-O(5)	1.611(9)
C(1)-O(1)-O(2)	103.1(2)
C(8)-O(2)-O(1)	104.0(2)
O(1)-C(1)-C(6)	109.9(3)
O(1)-C(1)-C(2)	104.9(2)
C(6)-C(1)-C(2)	111.2(3)
O(1)-C(1)-C(7)	104.1(3)
C(6)-C(1)-C(7)	112.0(3)
C(2)-C(1)-C(7)	114.3(3)
C(1)-C(2)-C(3)	112.6(3)

C(2)-C(3)-C(4)	111.7(3)
C(5)-C(4)-C(3)	108.1(3)
C(5)-C(4)-C(11)	115.5(3)
C(3)-C(4)-C(11)	114.2(3)
C(4)-C(5)-C(6)	112.5(3)
C(1)-C(6)-C(5)	113.0(3)
C(8)-C(7)-C(1)	104.8(3)
O(2)-C(8)-C(10)	101.0(3)
O(2)-C(8)-C(9)	108.1(3)
C(10)-C(8)-C(9)	115.8(3)
O(2)-C(8)-C(7)	102.1(2)
C(10)-C(8)-C(7)	116.6(3)
C(9)-C(8)-C(7)	111.2(3)
C(8)-C(10)-C(15)	121.7(3)
C(13)-C(11)-C(14)	107.6(3)
C(13)-C(11)-C(12)	109.0(3)
C(14)-C(11)-C(12)	108.3(3)
C(13)-C(11)-C(4)	110.5(3)
C(14)-C(11)-C(4)	109.6(3)
C(12)-C(11)-C(4)	111.6(3)
C(16)-C(15)-C(17)	108.5(3)
C(16)-C(15)-C(18)	109.9(4)
C(17)-C(15)-C(18)	107.9(3)
C(16)-C(15)-C(10)	111.5(3)
C(17)-C(15)-C(10)	106.8(3)
C(18)-C(15)-C(10)	112.0(3)
O(3)-C(16)-C(15)	108.6(5)
O(4)-C(17)-C(15)	113.3(5)
C(15)-C(18)-O(5)	106.3(4)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **40**. 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)	32(1)	33(1)	27(1)	13(1)	8(1)	1(1)
O(2)	33(1)	37(1)	24(1)	5(1)	7(1)	2(1)
C(1)	37(2)	20(2)	17(2)	4(1)	5(2)	0(1)
C(2)	37(2)	20(2)	26(2)	-3(2)	8(2)	0(2)
C(3)	37(2)	25(2)	22(2)	-7(2)	7(2)	-4(2)
C(4)	36(2)	19(2)	18(2)	2(1)	5(1)	1(1)
C(5)	34(2)	25(2)	25(2)	-7(2)	7(2)	-1(1)
C(6)	32(2)	23(2)	28(2)	-4(2)	6(2)	-5(2)
C(7)	35(2)	27(2)	22(2)	0(2)	10(2)	0(2)
C(8)	35(2)	25(2)	28(2)	4(1)	13(2)	1(2)
C(9)	43(3)	21(2)	44(2)	4(2)	16(2)	-2(2)
C(10)	37(2)	22(2)	34(2)	7(2)	9(2)	1(2)
C(11)	37(2)	20(2)	20(2)	1(1)	6(2)	2(1)
C(12)	42(2)	27(2)	29(2)	6(2)	14(2)	1(2)
C(13)	32(2)	40(2)	37(2)	-3(2)	5(2)	-4(2)
C(14)	45(2)	25(2)	32(2)	1(2)	13(2)	6(2)
C(15)	33(2)	25(2)	56(3)	15(2)	16(2)	4(2)
C(16)	46(3)	38(2)	57(3)	14(2)	29(2)	5(2)
C(17)	34(3)	33(2)	111(4)	19(3)	22(3)	-2(2)
C(18)	38(3)	34(2)	83(4)	18(2)	25(2)	8(2)
O(3)	49(5)	26(4)	35(4)	4(3)	25(4)	0(3)
O(4)	21(4)	25(4)	31(4)	-1(3)	-5(3)	7(3)
O(5)	27(4)	28(4)	33(4)	4(3)	0(4)	1(3)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **40**.

	x	y	z	U(eq)
H(3C)	732	5021	9366	52
H(4B)	139	4635	5390	41
H(5C)	405	6787	4936	45
H(2A)	3151(13)	5510(60)	8410(40)	43(10)
H(2B)	2985(12)	7910(60)	7760(30)	36(10)
H(3A)	3453(12)	7240(60)	6050(30)	31(9)
H(3B)	3806(13)	7090(60)	7510(40)	40(10)
H(4A)	3720(10)	3240(50)	7390(30)	19(8)
H(5A)	3296(12)	1620(60)	5370(30)	33(9)
H(5B)	3137(12)	4040(60)	4740(30)	35(10)
H(6A)	2470(13)	2570(60)	5650(40)	40(10)
H(6B)	2839(13)	2150(60)	7060(40)	39(10)
H(7A)	2264(12)	6030(60)	8190(40)	31(9)
H(7B)	2097(14)	3770(70)	7470(40)	52(11)
H(9A)	1702(13)	8990(60)	7620(40)	38(10)
H(9B)	2101(14)	9400(60)	6780(40)	39(10)
H(9C)	1541(15)	9640(70)	6080(40)	54(12)
H(10A)	1449(11)	3670(60)	5830(30)	30(9)
H(10B)	1190(11)	6000(50)	5070(30)	21(8)
H(12A)	3823(15)	4870(60)	4030(40)	51(12)
H(12B)	4442(13)	5170(50)	4480(30)	33(10)
H(12C)	4097(11)	6820(60)	4910(30)	23(8)
H(13A)	4540(12)	6240(70)	7230(40)	39(10)
H(13B)	4884(13)	4590(50)	6780(30)	31(9)
H(13C)	4594(14)	3990(70)	8000(40)	58(12)
H(14A)	4608(13)	1460(60)	5560(30)	36(10)
H(14B)	4228(13)	660(60)	6500(40)	45(11)
H(14C)	4032(13)	920(60)	4960(40)	39(10)
H(16A)	940(20)	4410(140)	8760(70)	54(5)
H(16B)	1339(13)	3130(30)	8260(40)	54(5)

H(16C)	1424(11)	5500(50)	8650(40)	54(5)
H(17A)	540(30)	3780(150)	5380(20)	54(5)
H(17B)	325(9)	3280(60)	6690(40)	54(5)
H(17C)	792(12)	2160(40)	6410(40)	54(5)
H(18A)	550(20)	7990(110)	6090(40)	54(5)
H(18B)	405(8)	7070(60)	7210(40)	54(5)
H(18C)	895(12)	8360(50)	7340(40)	54(5)

VIII. Bibliography

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A. HPLC trace and ^1H NMR spectra:

¹H spectrum

¹H spectrum