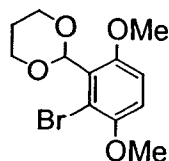


Experimental section

General Information: ^1H NMR spectra were recorded on a 400 MHz spectrometer at ambient temperature with CDCl_3 as the solvent unless otherwise stated. ^{13}C NMR spectra were recorded on a 75.0 MHz spectrometer at ambient temperature. Chemical shifts are reported in parts per million relative to chloroform (^1H , δ 7.24; ^{13}C , δ 77.0). Data for ^1H NMR are reported as follows: chemical shift, integration, multiplicity (app = apparent, par obsc = partially obscure, ovrlp = overlapping, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constants. All ^{13}C NMR spectra were recorded with complete proton decoupling. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR spectrophotometer. Low and high-resolution mass spectra were obtained in the Boston University Mass Spectrometry Laboratory using a Finnegan MAT-90 spectrometer. Optical rotations were recorded on an AUTOPOL III digital polarimeter at 589 nm, and are recorded as $[\alpha]_D$ (concentration in grams/100 mL solvent). Chiral HPLC analysis was performed on an Agilent 1100 series (Regis reversible HPLC column (R,R) whelk-O1, 25 cm x 4.0 mm). X-ray crystal structure analyses were performed by Dr. Emil Lobkovsky (Department of Chemistry and Chemical Biology, Cornell University). Analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F plates. Flash chromatography was performed using 200-400 mesh silica gel (Sorbent Tech. Inc.). Yields refer to chromatographically and spectroscopically pure materials, unless otherwise stated. Ph_3COOH was prepared according to the literature procedure.^{S1} All other reagents were used as supplied by Sigma-Aldrich, Fluka, and Strem Chemicals. Methylene chloride, toluene, hexane, and benzene were distilled from calcium hydride; tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone ketyl prior to use. All reactions were carried out in oven-dried glassware under argon atmosphere unless otherwise noted.

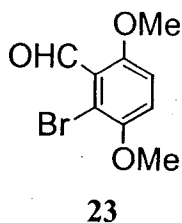


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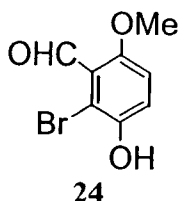
2-(2-bromo-3,5-dimethoxyphenyl)-1,3-dioxane 58. 2-(2,5-dimethoxyphenyl)-1,3-dioxane **22** (3.0 g, 13.4 mmol) was dissolved in 90 mL of hexane and the reaction was cooled to $-25\text{ }^\circ\text{C}$. To the cooled solution was added 30 mL of freshly distilled benzene followed by dropwise addition of *n*-BuLi (2.2 M, 9.0 mL, 19.8 mmol). After 10 h, $\text{BrCF}_2\text{CF}_2\text{Br}$ (3 mL, 25 mmol) in 30 mL THF was added and the reaction was warmed up to rt and stirred for 0.5 h.

After solvent evaporation, the mixture was subjected to silica gel chromatography (20 % EtOAc in hexane) providing 2.84 g (9.5 mmol, 70 %) of 2-(6-bromo-2,5-dimethoxyphenyl)-1,3-dioxane **58** as a light yellow solid. mp $105\text{--}106\text{ }^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 6.82 (s, 2H), 6.18 (s, 1H), 4.27–4.23 (m, 2H), 3.97–3.91 (m, 2H), 3.79 (s, 3H), 3.78 (s, 3H), 2.40–2.20 (m, 1H), 1.38–1.35 (d, 1H, $J = 13.6\text{ Hz}$); ^{13}C NMR (75.0 MHz, CDCl_3) δ 152.9, 151.1, 127.3, 114.2, 113.5, 112.4, 99.8, 67.9, 57.3, 25.9; IR (neat) ν_{max} 2963, 2845, 1479, 1260, 1105 cm^{-1} ; CIHRMS M^+ calculated for $\text{C}_{12}\text{H}_{15}\text{BrO}_4$: 302.0154, found: 302.0191.

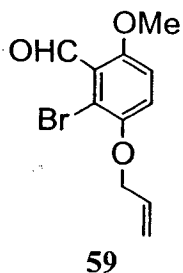
^{S1} Bissing, D. E.; Matuszac, C. A.; McEwen, W. E. *J. Am. Chem. Soc.* **1964**, *86*, 3824.



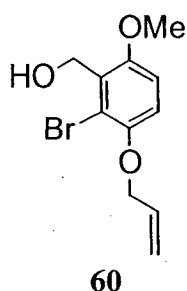
2-Bromo-3,5-dimethoxybenzaldehyde 23. To a solution of 2-(6-bromo-2,5-dimethoxyphenyl)-1,3-dioxane **58** (3.0 g, 9.9 mmol) in 60 mL of THF was added 50 mL of 11 M HCl and the reaction was stirred at rt for 10 min. The mixture was extracted with Et₂O, washed with sat. brine, dried over MgSO₄, filtered, and the solvent removed *in vacuo* to afford 2.4 g (9.9 mmol, 100 %) of **23** as a light yellow solid which was adequately pure for characterization and used directly in the next step. mp 97-98 °C; ¹H NMR (400 MHz, CDCl₃) δ 10.39 (s, 1H), 7.05 (d, 1H, *J* = 9.0 Hz), 6.91 (d, 1H, *J* = 9.0 Hz), 3.87 (s, 3H), 3.85 (s, 3H); ¹³C NMR (75.0 MHz, CDCl₃) δ 190.9, 155.7, 150.8, 125.3, 117.4, 114.9, 111.8, 57.4, 56.8; IR (neat) ν_{max} 1696, 1479, 1264, 1032, 806 cm⁻¹; CIHRMS [M+H]⁺ calculated for C₉H₁₀BrO₃: 244.9815, found: 244.9787.



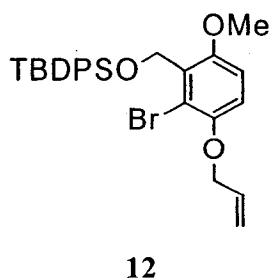
2-Bromo-3-hydroxy-6-methoxybenzaldehyde 24. To a round-bottomed flask containing **23** (2.9 g, 11.8 mmol) was added 75 mL of conc. H₂SO₄. After the flask was sealed with a glass stopper and Teflon tape, the mixture was stirred at 70 °C for 14 h. The reaction mixture was transferred dropwise onto 150 g of ice. After the quenched reaction was cooled to rt, the mixture was extracted with 3 × 200 mL Et₂O. The organic extracts were combined, dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification on silica gel (12 % to 25 % EtOAc in hexane) provided 1.42 g (6.1 mmol, 52 %) of **24** as brown crystals. mp 102-104 °C; ¹H NMR (400 MHz, CDCl₃) δ 10.38 (s, 1H), 7.21 (d, 1H, *J* = 8.8 Hz), 6.92 (d, 1H, *J* = 8.8 Hz), 5.72 (s, 1H), 3.87 (s, 3H); ¹³C NMR (75.0 MHz, CDCl₃) δ 189.6, 157.1, 147.5, 123.2, 121.3, 113.0, 110.4, 57.0; IR (neat) ν_{max} 3328, 1680, 1566, 1296, 1264, 1189, 1030, 815 cm⁻¹; CIHRMS M⁺ calculated for C₈H₇BrO₃: 229.9579, found: 229.9558.



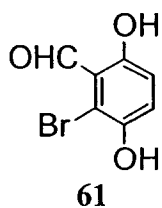
2-Bromo-6-methoxy-3-(2-propenyloxy)benzaldehyde 59. 2-Bromo-3-hydroxy-6-methoxy benzaldehyde **24** (1.33 g, 5.76 mmol) was dissolved in 30 mL of DMF and K₂CO₃ (2.35 g, 17 mmol) and allyl bromide (0.74 g, 6.12 mmol) were added consecutively. After 3 h, the reaction was quenched by addition of 100 mL of water. The aqueous layer was extracted with Et₂O (3 × 100 mL), the organic extracts combined, washed with sat. brine, dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude 2-bromo-6-methoxy-3-(2-propenyloxy)benzaldehyde **59** (1.50 g, 5.54 mmol, 96 % yield, light yellow solid) was found to be analytically pure and used directly in the next step. mp 78-81 °C; ¹H NMR (400 MHz, CDCl₃) δ 10.39 (s, 1H), 7.05 (d, 1H, *J* = 8.8 Hz), 6.88 (d, 1H, *J* = 8.8 Hz), 6.05-6.00 (m, 1H), 5.45 (d, 1H, *J* = 16.8 Hz), 5.30 (d, 1H, *J* = 10.4 Hz), 4.56 (d, 2H, *J* = 8.8 Hz), 3.58 (s, 3H); ¹³C NMR (75.0 MHz, CDCl₃) δ 191.0, 156.0, 149.7, 132.8, 125.1, 119.7, 118.2, 116.0, 111.6, 71.3, 56.8; IR (neat) ν_{max} 3421, 1694, 1273, 1032, 803 cm⁻¹; CIHRMS [M+H]⁺ calculated for C₁₁H₁₂BrO₃: 270.9972, found: 270.9952.



2-Bromo-6-methoxy-3-(2-propenyloxy)benzenemethanol 60. 2-Bromo-6-methoxy-3-(2-propenyloxy)benzaldehyde **59** (1.87 g, 6.90 mmol) was dissolved in 30 mL of EtOH, and 313 mg (8.27 mmol) of NaBH₄ was added. The reaction mixture was stirred at rt for 30 min, diluted with water, and glacial AcOH added dropwise until no further bubbling was observed. The mixture was extracted with Et₂O, the organic extracts were combined, washed with brine, dried over MgSO₄, and concentrated *in vacuo*. The alcohol product 2-Bromo-6-methoxy-3-(2-propenyloxy)benzenemethanol **60** (1.90 g, 6.90 mmol, 100 % yield, pale yellow solid) was adequately pure for characterization and used directly in the next step. mp 40-45 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.81 (d, 1H, *J* = 8.8 Hz), 6.77 (d, 1H, *J* = 8.8 Hz), 6.07-6.00 (m, 1H), 5.45 (d, 1H, *J* = 17.2 Hz), 5.27 (d, 1H, *J* = 10.4 Hz), 4.89 (d, 1H, *J* = 7.2 Hz), 4.53 (m, 1H), 3.81 (s, 3H), 2.45 (t, 1H, *J* = 7.2 Hz); ¹³C NMR (75.0 MHz, CDCl₃) δ 153.2, 149.7, 133.2, 130.3, 117.9, 116.4, 114.2, 110.3, 71.0, 60.8, 56.5; IR (neat) ν_{max} 3421, 2937, 1477, 1262, 1035 cm⁻¹; CIHRMS [M+H]⁺ calculated for C₁₁H₁₄BrO₃: 273.0128, found: 273.0097.

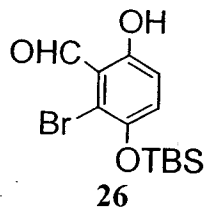


[[2-Bromo-6-methoxy-3-(2-propenyloxy)phenyl]methoxy] (1,1-dimethyl-ethyl)diphenylsilane 12. 2-Bromo-6-methoxy-3-(2-propenyloxy)benzenemethanol **60** (1.82 g, 6.66 mmol) in 20 mL of DMF was added 2.1 mL (8.08 mmol) of TBDPSCI and 1.15 g (16.91 mmol) of imidazole. The reaction was stirred at rt for 2.5 h, then 50 mL of water was added and the mixture was extracted with Et₂O. The organic extracts were combined, washed with brine, dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification on silica gel (25 % CH₂Cl₂ in hexane) gave 3.2 g (6.26 mmol, 94 %) of **12** as a white solid. mp 95-98 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.76-7.73 (m, 4H), 7.40-7.33 (m, 6H), 6.81 (d, 1H, *J* = 8.8 Hz), 6.70 (d, 1H, *J* = 8.8 Hz), 6.20-6.00 (m, 1H), 5.47 (d, 1H, *J* = 17.6 Hz), 5.28 (d, 1H, *J* = 10.4 Hz), 4.90 (s, 2H), 4.54 (m, 2H), 3.63 (s, 3H), 1.01 (s, 9H); ¹³C NMR (75.0 MHz, CDCl₃) δ 153.4, 149.8, 136.0, 134.4, 133.5, 130.3, 129.6, 127.6, 118.0, 117.7, 114.5, 110.4, 71.7, 61.0, 56.3, 27.1, 19.7; IR (neat) ν_{max} 2931, 2856, 1478, 1262, 1042 cm⁻¹; CIHRMS M⁺ calculated for C₂₇H₃₁BrO₃Si: 510.1226, found: 510.1234.

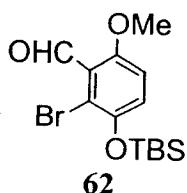


2-Bromo-3,5-dihydroxybenzaldehyde 61. To a solution of 2,5-dihydroxybenzaldehyde (5.0 g, 36.2 mmol) in 170 mL of CHCl₃ was added Br₂ (1.94 mL, 37.7 mmol) in 120 mL of CHCl₃ dropwise over 1.5 h. After addition, the reaction was stirred for an additional 1.5 h. The CHCl₃ solution was then washed with 8 × 100 mL sat. Na₂S₂O₃ to thoroughly remove excess Br₂. The organic phase was dried over MgSO₄, filtered, and solvent removed *in vacuo* to afford 7.4 g (34.3 mmol, 94 %) of 2-bromo-3,5-dihydroxybenzaldehyde **61** as a yellow solid, which was adequately pure for characterization and used directly in the next step. mp 123-125 °C ¹H NMR (400 MHz, CDCl₃) δ 11.63 (s, 1H), 10.24 (s, 1H), 7.21 (d, 1H, *J* = 9.2 Hz), 6.89 (d, 1H, *J* = 9.2 Hz), 5.39 (s, 1H); ¹³C NMR (75.0 MHz, CDCl₃) δ 197.1, 158.5, 145.8,

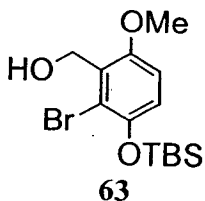
125.7, 118.8, 116.7, 112.1; IR (thin film) ν_{max} 3281, 1634, 1457, 1286, 1170 cm^{-1} ; CIHRMS M^+ calculated for $\text{C}_7\text{H}_5\text{BrO}_3$: 215.9438, found: 215.9422.



2-Bromo-3-[(1,1-dimethylethyl)dimethylsilyl]oxy]-6-hydroxybenzaldehyde 26. 2-Bromo-3,5-dihydroxybenzaldehyde **61** (7.4 g, 34.3 mmol) was dissolved in 140 mL of CH_2Cl_2 , then imidazole (3.5 g, 51.5 mmol) and TBDMSCl (7 g, 46.4 mmol) was added and the mixture was stirred at rt for 15 min. The salt formed was filtered and the solution was directly concentrated for chromatography. Purification on silica gel (10 % EtOAc in hexane) provided 10.64 g (32.2 mmol, 94 %) of **26** as a yellow solid. mp 42-45 °C. ^1H NMR (400 MHz, CDCl_3) δ 11.96 (s, 1H), 10.33 (s, 1H), 7.04 (d, 1H, $J = 9.2$ Hz), 6.81 (d, 1H, $J = 9.2$ Hz), 1.02 (s, 9H), 0.21 (s, 1H); ^{13}C NMR (75.0 MHz, CDCl_3) δ 198.4, 158.6, 145.9, 129.3, 118.7, 118.2, 117.8, 26.0, 18.6, -3.9; IR (thin film) ν_{max} 2928, 2857, 1654, 1471, 1255, 1175, 1003 cm^{-1} ; CIHRMS M^+ calculated for $\text{C}_{13}\text{H}_{19}\text{BrO}_3\text{Si}$: 330.0287, found: 330.0292.

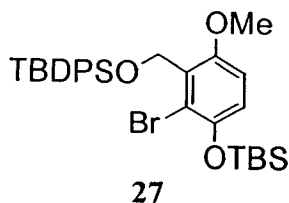


2-Bromo-3-[(1,1-dimethylethyl)dimethylsilyl]oxy]-6-methoxybenzaldehyde 62. Compound **26** (3.3 g, 10 mmol) in 30 mL of THF was added to NaH (600 mg, 15 mmol) (60 % in mineral oil, prewashed with 2 x 30 mL hexane). The mixture was stirred for 0.5 h, then MeI (1.87 mL, 30 mmol) and 15 drops of DMA were added. The reaction was kept at 65°C for 6 h. After cooling to rt, the crude reaction mixture was filtered, concentrated, and subjected to silica gel chromatography (10 % EtOAc in hexane) to afford 2.48 g (7.2 mmol, 72 %) of 2-bromo-3-[(1,1-dimethylethyl)dimethylsilyl]oxy]-6-methoxybenzaldehyde **62** as a pale yellow solid. mp 67-69 °C. ^1H NMR (400 MHz, CDCl_3) δ 10.36 (s, 1H), 7.00 (d, 1H, $J = 8.8$ Hz), 6.82 (d, 1H, $J = 8.8$ Hz), 3.84 (s, 3H), 1.02 (s, 3H), 0.21 (s, 1H); ^{13}C NMR (75.0 MHz, CDCl_3) δ 191.1, 156.0, 147.3, 125.0, 124.7, 118.0, 111.8, 56.8, 26.0, 18.6, -4.0; IR (thin film) ν_{max} 2949, 2930, 2859, 1695, 1471, 1258, 1047 cm^{-1} ; CIHRMS $[M+H]^+$ calculated for $\text{C}_{13}\text{H}_{21}\text{BrO}_3\text{Si}$: 345.0522, found: 345.0497.

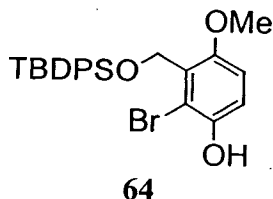


2-Bromo-3-[(1,1-dimethylethyl)dimethylsilyl]oxy]-6-methoxybenzenemethanol 63. 2-Bromo-3-[(1,1-dimethylethyl)dimethylsilyl]oxy]-6-methoxybenzaldehyde **62** (7.16 g, 20.8 mmol) was dissolved in 70 mL of EtOH and 828 mg (21.8 mmol) of NaBH_4 was added at 0°C. The reaction mixture was stirred for 30 min, diluted with water, and glacial AcOH added dropwise until no further bubbling was observed. The mixture was extracted with EtOAc. The organic extracts were combined, washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo*. The alcohol product 2-Bromo-3-[(1,1-dimethylethyl)dimethylsilyl]oxy]-6-methoxybenzenemethanol **63** (7.20 g, 20.8 mmol, 100 %, light yellow solid) was analytically pure and used directly in the next step. mp 56-58°C. ^1H NMR (400 MHz, CDCl_3) δ 6.78 (d, 1H, $J = 8.8$ Hz), 6.71 (d, 1H, $J = 8.8$ Hz), 4.87 (s, 2H), 3.80 (s, 3H), 1.02 (s, 9H), 0.20 (s, 6H); ^{13}C NMR (75.0 MHz, CDCl_3) δ 152.6, 146.9, 130.0, 119.2, 118.7, 110.4, 61.0, 56.4, 26.0, 18.5, -4.1; IR (thin

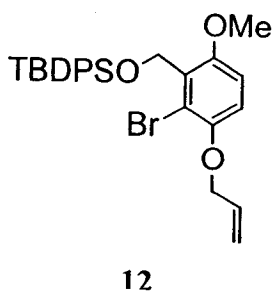
film) ν_{max} 3288, 2930, 2858, 1473, 1253, 1046, 1001 cm^{-1} ; CIHRMS M^+ calculated for $\text{C}_{14}\text{H}_{23}\text{BrO}_3\text{Si}$: 346.0600, found: 346.0635.



[[2-Bromo-3-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]-6-methoxyphenyl] methoxy(1,1-dimethylethyl)diphenylsilane 27. 2-Bromo-3-[[[(1,1-dimethylethyl)dimethylsilyl]oxy]-6-methoxybenzene-methanol **63** (7.2 g, 20.8 mmol) in 70 mL of DMF was added 6.48 mL (24.9 mmol) of TBDPSCl and 3.1 g (45.6 mmol) of imidazole. The reaction was stirred at rt for 2 h, then 150 mL water was added and the mixture extracted with EtOAc. The organic extracts were combined, washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo*. Purification on silica gel (15 % CH_2Cl_2 in hexane) provided 11.3 g (19.3 mmol, 93 %) of **27** as a white solid. mp 69-71 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.76-7.74 (m, 4H), 7.40-7.35 (m, 6H), 6.78 (d, 1H, $J = 8.8\text{Hz}$), 6.64 (d, 1H, $J = 8.8\text{Hz}$), 4.88 (s, 2H), 3.62 (s, 3H), 1.04 (s, 9H), 1.02 (s, 9H), 0.22 (s, 6H); ^{13}C NMR (75.0 MHz, CDCl_3) δ 153.1, 146.8, 136.0, 134.3, 130.0, 129.6, 127.6, 120.3, 119.4, 110.4, 60.8, 56.2, 27.2, 26.1, 19.7, 18.6, -4.0; IR (thin film) ν_{max} 3071, 2931, 2857, 1476, 1257, 1112, 1045 cm^{-1} ; CIHRMS $[M+H]^+$ calculated for $\text{C}_{30}\text{H}_{42}\text{BrO}_3\text{Si}_2$: 585.1857, found: 585.1861.

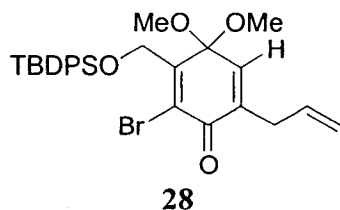


2-Bromo-3-[[[(1,1-dimethylethyl)diphenylsilyl]oxy]-4-methoxyphenol 64. **27** (3.74 g, 6.40 mmol) was dissolved in 15 mL of THF at 0 $^\circ\text{C}$, TBAF (1M in THF, 6.4 mL, 6.4 mmol) was added. The reaction was stirred for 10 min before being quenched with 15 mL of sat. NH_4Cl . The layers were separated. The aqueous layer was extracted with Et_2O . The combined organic layers were washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo*. The phenol product 2-bromo-3-[[[(1,1-dimethylethyl)diphenylsilyl]oxy]methyl]-4-methoxyphenol **64** was analytically pure for characterization and used directly in the next step. mp 55-57 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) 7.75-7.73 (m, 4H), 7.44-7.37 (m, 6H), 6.94 (d, 1H, $J = 8.8\text{Hz}$), 6.74 (d, 1H, $J = 8.8\text{Hz}$), 4.86 (s, 2H), 3.62 (s, 3H), 1.04 (s, 9H); ^{13}C NMR (75.0 MHz, CDCl_3) δ 152.4, 146.8, 136.0, 134.1, 129.7, 128.8, 127.7, 115.2, 115.0, 111.9, 60.5, 56.5, 27.0, 19.6; IR (thin film) ν_{max} 3517, 2932, 2856, 1428, 1263, 1112, 1043 cm^{-1} ; CIHRMS $[M+H]^+$ calculated for $\text{C}_{24}\text{H}_{27}\text{BrO}_3\text{Si}$: 471.0992, found: 471.1010.



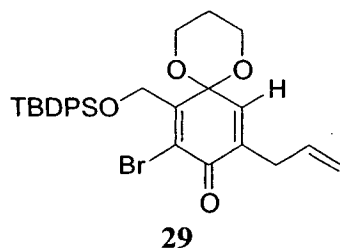
[[2-Bromo-6-methoxy-3-(2-propenyloxy)phenyl]methoxy(1,1-diethylethyl)diphenylsilane 12. 2-Bromo-3-[[[(1,1-dimethylethyl)diphenylsilyl]oxy]methyl]-4-methoxyphenol 10.2 g (21.7 mmol) was dissolved in 50 mL of DMF and K_2CO_3 (7.5 g, 54.3 mmol, 2.5 equiv.) and allyl bromide (2.25 mL, 15.2 mmol, 1.2 equiv.) were added consecutively. After stirring at rt for 150 min, the reaction was quenched by addition of water. The aqueous layer was extracted with Et_2O (3 \times 100 mL), the organic extracts combined, washed with sat. brine, dried over MgSO_4 , filtered, and concentrated *in vacuo*. Purification on silica gel (25 % CH_2Cl_2 in hexane)

afforded [[2-bromo-6-methoxy-3-(2-propenyloxy)phenyl]methoxy](1,1-dimethyl-ethyl)diphenylsilane **12** (10.8 g, 21.2 mmol, 97% yield) as a white solid. mp 95-98 °C. ^1H and ^{13}C NMR, IR and Mass Spectroscopy are identical with **12** made from the alternative route (see page S4).



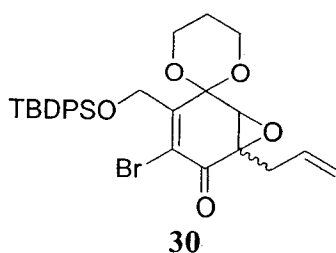
2-Bromo-3-[[[(1,1-dimethylethyl)diphenylsilyl]oxy]methyl]-4,4-dimethoxy-6-(2-propenyl)-2,5-cyclohexadien-1-one 28. Compound **12** (2.0 g, 3.91 mmol) was weighed into a Schlenk flask, sealed under high vacuum, and placed in a 180 °C oil bath for 2 h. The heating for the bath was removed, and the reaction mixture was cooled gradually to 50 °C. MeOH (10 mL) and a stir bar were then added. After the brown oil had dissolved, 1.3 g (4.03 mmol) of $\text{PhI}(\text{OAc})_2$ was added

and the mixture was stirred at rt for 20 min. The reaction mixture was quenched with 1 M NaHCO_3 and extracted with Et_2O . The organic extracts were combined, washed with brine, dried over MgSO_4 , filtered and concentrated *in vacuo*. Purification on silica gel (30 % CH_2Cl_2 in hexane) provided 1.48 g (2.74 mmol, 70 %) of **28** as a pale yellow solid. mp 94-96 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.78-7.76 (m, 4H), 7.44-7.37 (m, 6H), 6.48 (s, 1H), 5.48-5.76 (m, 1H), 5.17-5.12 (m, 2H), 4.42 (s, 2H), 3.22 (s, 6H), 3.15 (d, 2H, J = 6.8 Hz), 1.05 (s, 9H); ^{13}C NMR (75.0 MHz, CDCl_3) δ 178.6, 153.6, 140.7, 140.0, 136.1, 134.2, 133.2, 130.6, 128.0, 118.4, 97.7, 61.0, 51.9, 34.0, 27.1, 19.8; IR (neat) ν_{max} 2933, 1675, 1427, 1113, 1075 cm^{-1} ; CIHRMS $[\text{M}+\text{H}-\text{C}_4\text{H}_9]^+$ calculated for $\text{C}_{28}\text{H}_{25}\text{BrO}_4\text{Si}$: 484.0705, found: 484.0740.

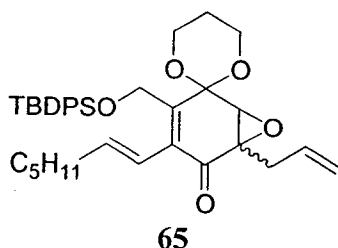


8-Bromo-7-[[[(1,1-dimethylethyl)diphenylsilyl]oxy]methyl]-10-(2-propenyl)-1,5-dioxaspiro[5.5] undeca-7,10-dien-9-one 29. A mixture of **28** (1.4 g, 2.59 mmol) and PPTS (98 mg, 0.39 mmol) were placed in a round-bottomed flask fitted with a water condenser to which were added 15 mL of benzene and 0.5 mL (6.57 mmol) of 1,3-propanediol. After stirring at 80 °C for 20 min, pH 7 buffer was added at rt and the reaction mixture

was extracted with Et_2O . The organic extracts were combined, washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo*. Purification on silica gel (6 % EtOAc in hexane) provided 1.29 g (2.34 mmol, 90 %) of **29** as a white solid. mp 118-121 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.80-7.77 (m, 4H), 7.44-7.35 (m, 6H), 7.31 (s, 1H), 5.86-5.79 (m, 1H), 5.17-5.12 (m, 2H), 4.56 (s, 2H), 4.14-4.08 (m, 2H), 3.86-3.82 (m, 2H), 3.14-3.12 (d, 2H, J = 6.8 Hz), 1.91-1.83 (m, 1H), 1.39 (d, 1H, J = 10.8 Hz), 1.04 (s, 9H); ^{13}C NMR (75.0 MHz, CDCl_3) δ 178.5, 153.3, 136.1, 135.7, 134.3, 133.8, 133.0, 129.8, 129.4, 127.8, 118.5, 92.7, 61.5, 61.3, 34.1, 27.1, 24.8, 19.6; IR (neat) ν_{max} 2959, 2931, 1674, 1241, 1113, 1086 cm^{-1} ; CIHRMS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{29}\text{H}_{34}\text{BrO}_4\text{Si}$: 553.1411, found: 553.1399.



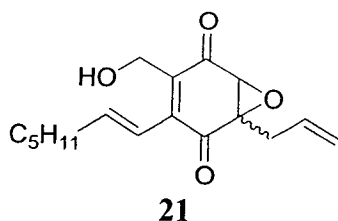
4'-Bromo-3'--[[[(1,1-dimethylethyl)diphenylsilyl]oxy]methyl]-6'-(2-propenyl)-spiro[1,3-dioxane-2,2'-[7]oxabicyclo[4.1.0]hept[3]en]-5'-one 30. Ph_3COOH (468 mg, 1.70 mmol) was dissolved in 12 mL of THF at -78°C , then 2.52 mL (1.26 mmol) of 0.5 M KHMDS in toluene was added. After 10 min, dienone **29** (300 mg, 0.54 mmol) in 12 mL of THF was added dropwise over 15 min. The yellow solution formed was slowly warmed to -20°C over 6 h during which time the yellow color faded. After addition of 100 mL of water, the mixture was warmed to rt and extracted with Et_2O . The organic extracts were combined, washed with brine, dried over MgSO_4 , filtered and concentrated *in vacuo*. Purification on silica gel (4–20 % EtOAc in hexane) provided 250 mg (0.44 mmol, 81 %) of epoxide **30** as a white solid. mp $115\text{--}117^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.76–7.73 (m, 4H), 7.42–7.35 (m, 6H), 5.79–5.69 (m, 1H), 5.20–5.15 (m, 2H), 4.53 (d, 1H, $J = 10.8$ Hz), 4.47 (d, 1H, $J = 10.8$ Hz), 4.24–4.16 (m, 2H), 4.19 (s, 1H), 3.92–3.89 (m, 2H), 2.88 (dd, 1H, $J = 7.6, 15.2$ Hz), 2.62 (dd, 1H, $J = 7.6, 15.2$ Hz), 1.89–1.77 (m, 1H), 1.43 (d, 1H, $J = 13.2$ Hz), 1.04 (s, 9H); ^{13}C NMR (75.0 MHz, CDCl_3) δ 187.1, 151.1, 136.1, 133.8, 131.2, 129.9, 127.8, 119.6, 94.6, 62.0, 61.2, 59.3, 54.7, 32.9, 27.0, 24.4, 19.7; IR (neat) ν_{max} 2931, 1700, 1141, 1112, 1075, 1008 cm^{-1} ; CIHRMS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{29}\text{H}_{34}\text{BrO}_5\text{Si}$: 569.1361, found: 569.1402.



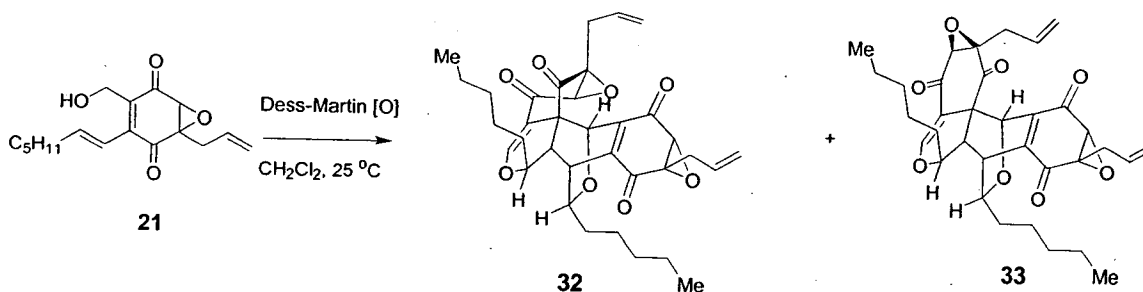
3'--[[[(1,1-Dimethylethyl)diphenylsilyl]oxy]methyl]-4'-(1E)-1-heptenyl-6'-(2-propenyl)-spiro[1,3-dioxane-2,2'-[7]oxabicyclo[4.1.0]hept[3]en]-5'-one 65. $\text{Pd}(\text{PPh}_3)_4$ (32 mg, 0.028 mmol) was placed in a 10 mL Schlenk flask. Next 160 mg (0.28 mmol) of epoxide **30** dissolved in 8 mL of degassed toluene was added, followed by addition of 270 μL (0.7 mmol) of *E*-tributyl-1-heptenyl-stannane.^{S2} The mixture was stirred at 110°C for 4 h, then cooled to rt, concentrated, and directly subjected to silica gel chromatography (7 % EtOAc in hexane) to afford 162 mg (0.28 mmol, 98 %) of 3'--[[[(1,1-Dimethylethyl)diphenylsilyl]oxy]methyl]-4'-(1E)-1-heptenyl-6'-(2-propenyl)-spiro[1,3-dioxane-2,2'-[7]oxabicyclo[4.1.0]hept[3]en]-5'-one **65** as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.73–7.70 (m, 4H), 7.41–7.36 (m, 6H), 6.39–6.28 (m, 2H), 5.82–5.72 (m, 1H), 5.18–5.12 (m, 2H), 4.46 (d, 1H, $J = 11.6$ Hz), 4.43 (d, 1H, $J = 11.6$ Hz), 4.18 (s, 1H), 4.22–4.08 (m, 2H), 3.84–3.80 (m, 2H), 2.84 (dd, 1H, $J = 7.6, 15.2$ Hz), 2.59 (dd, 1H, $J = 7.6, 15.2$ Hz), 2.10 (m, 2H), 1.76 (m, 1H), 1.37 (m, 3H), 1.30–1.24 (m, 4H), 1.04 (s, 9H), 0.86 (t, 3H, $J = 6.8$ Hz); ^{13}C NMR (75.0 MHz, CDCl_3) δ 194.9, 144.5, 140.0, 136.1, 134.0, 132.0, 129.7, 127.7, 121.9, 119.1, 94.2, 6.8, 60.6, 59.7, 59.1, 54.5, 34.3, 32.6, 31.7, 28.9, 27.1, 24.5, 22.7, 19.6, 14.4; IR (neat) ν_{max} 2929, 1678,

^{S2} (a) Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1988**, *341*, 293. (b) Zweifel, G.; Miller, J. A. *Organic Reactions*, Vol. 32, John Wiley & Sons, New York, 1984, p. 430.

1428, 1145, 1112, 999 cm^{-1} ; CIHRMS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{36}\text{H}_{47}\text{O}_5\text{Si}$: 587.3195, found: 587.3247.



3-(1E)-1-Heptenyl-4-(hydroxymethyl)-1-(2-propenyl)-7-oxabicyclo[4.1.0]hept-3-ene-2,5-dione 21. Enone **58** (120 mg, 0.20 mmol) was dissolved in 5 mL of CH_3CN , followed by addition of 2.5 mL 48 % aqueous HF. The mixture was stirred at rt for 7 h, then quenched with sat. NaHCO_3 until no further bubbling was observed. The aqueous solution was extracted with Et_2O , and the organic extracts were combined, washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo*. Purification on silica gel (25 % EtOAc in hexane) provided 45 mg (0.16 mmol, 76 %) of quinone monoepoxide **21** as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 6.50-6.46 (m, 1H), 6.29 (d, 1H, $J = 16$ Hz), 5.74-5.63 (m, 1H), 5.19 (m, 2H), 4.53 (d, 1H, $J = 12.8$ Hz), 4.40 (d, 1H, $J = 12.8$ Hz), 3.68 (s, 1H), 2.84 (dd, 1H, $J = 7.6, 15.2$ Hz), 2.72 (dd, 1H, $J = 7.6, 15.2$ Hz), 2.35 (t, 1H, $J = 6.0$ Hz), 2.21 (m, 2H), 1.48-1.40 (m, 2H), 1.34-1.22 (m, 4H), 0.88 (t, 3H, $J = 6.8$ Hz); ^{13}C NMR (75.0 MHz, CDCl_3) δ 195.0, 193.8, 147.4, 142.6, 136.8, 130.4, 120.9, 120.4, 61.5, 57.9, 57.6, 34.6, 31.7, 31.6, 28.5, 22.6, 14.2; IR (neat) ν_{max} 3446, 2929, 1683, 1653, 1301, 1001 cm^{-1} ; CIHRMS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{23}\text{O}_4$: 291.1598, found: 291.1601.



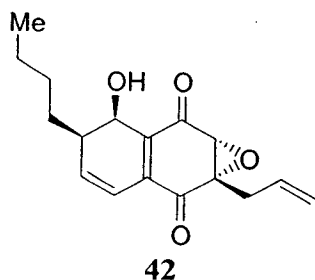
Model Dimers 32 and 33. Quinone monoepoxide **21** (25 mg, 0.086 mmol) was dissolved in 3 mL of CH_2Cl_2 and 40 mg (0.095 mmol) of Dess-Martin periodinane^{S3} was added. After stirring at rt for 1h, the reaction mixture was neutralized with sat. $\text{NaHCO}_3/\text{Na}_2\text{S}_2\text{O}_3$ and extracted with Et_2O . The organic extracts were combined, washed with brine, dried over MgSO_4 , filtered and concentrated *in vacuo*. Crude ^1H NMR analysis showed pyran monomers : dimer **32** : dimer **33** in a 8:3:3 ratio. The mixture was allowed to stand on a silica gel column for 1h, then eluted and purified by flash chromatography (4 % EtOAc in hexane) to afford 6.4 mg (0.011 mmol, 26 %) of **32** as a yellow oil and 11.6 mg (0.02 mmol, 46 %) of **33** as a yellow solid.

Torreyanic acid-type dimer 32. ^1H NMR (400 MHz, CDCl_3) δ 7.85 (s, 1H), 5.68 (s, 1H), 5.72-5.58 (m, 2H), 5.21-5.10 (m, 4H), 4.32 (m, 1H), 4.13 (m, 1H), 3.68 (s, 1H), 3.64

^{S3} (a) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155. (b) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277. For two improved procedures for the preparation of Dess Martin Periodinane, see: (c) Ireland, R. E.; Liu, J. *J. Org. Chem.* **1993**, *58*, 2899. (d) Meyers, S. D.; Schreiber, S. L. *J. Org. Chem.* **1994**, *59*, 7459.

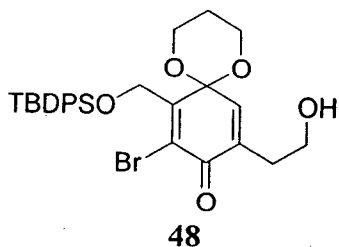
(s, 1H), 3.28 (s, 1H), 2.90 (dd, 1H, $J = 8.0, 15.2$ Hz), 2.79-2.67 (m, 2H), 2.65 (s, 1H), 2.51 (dd, 1H, $J = 6.4, 15.2$ Hz), 1.23-1.10 (m, 16H), 0.83 (m, 6H); ^{13}C NMR (75.0 MHz, CDCl_3) δ 200.9, 189.0, 188.8, 188.2, 159.1, 145.5, 143.5, 130.4, 129.9, 129.8, 120.7, 120.2, 112.8, 82.1, 78.2, 71.9, 70.2, 64.6, 63.6, 62.7, 57.9, 50.4, 39.4, 37.2, 35.1, 33.3, 32.4, 31.7, 31.3, 30.0, 25.6, 25.1, 22.7, 14.1; IR (neat) ν_{max} 2931, 2859, 1715, 1688, 1587, 1304, 1209, 924 cm^{-1} ; CILRMS: m/z 577 (9, $[\text{M}+\text{H}]^+$), 288 (63, $[\text{M}/2]^+$), 217 (100, $[\text{M}/2-\text{C}_5\text{H}_{11}]^+$); CIHRMS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{34}\text{H}_{41}\text{O}_8$: 577.2803, found: 577.2733.

Dimer 33. ^1H NMR (400 MHz, CDCl_3) δ 7.43 (s, 1H), 5.74-5.58 (m, 2H), 5.25-5.19 (m, 4H), 4.56 (s, 1H), 4.30 (m, 1H), 4.17 (m, 1H), 3.64 (s, 1H), 3.56 (s, 1H), 3.30 (s, 1H), 2.95-2.88 (m, 2H), 2.81-2.67 (m, 2H), 2.39 (s, 1H), 1.23-1.10 (m, 16H), 0.83 (m, 6H); ^{13}C NMR (75.0 MHz, CDCl_3) δ 199.1, 191.4, 188.7, 188.3, 152.6, 145.3, 142.3, 129.7, 121.0, 120.8, 110.6, 80.9, 71.9, 68.8, 64.5, 62.5, 59.7, 57.9, 57.5, 51.3, 39.3, 38.4, 37.4, 35.2, 32.9, 31.7, 31.5, 31.2, 31.0, 29.9, 25.6, 25.0, 22.6, 14.1; IR (neat) ν_{max} 2931, 1717, 1688, 1616, 1207, 1126, 923 cm^{-1} ; EILRMS: m/z 577 (1, $[\text{M}+\text{H}]^+$), 288 (71, $[\text{M}/2]^+$), 217 (100, $[\text{M}/2-\text{C}_5\text{H}_{11}]^+$); CIHRMS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{34}\text{H}_{41}\text{O}_8$: 577.2803, found: 577.2801.



Compound 42. Dimer 33 (4.0 mg, 0.0069 mmol) in 1 mL of toluene was heated at 105° for 9 h. The reaction mixture was concentrated and purified by flash column chromatography (16.7 % EtOAc in hexane) to afford 2.1 mg (0.007 mmol, 53 %) of 42 as a pale yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 6.63 (dd, 1H, $J = 2.8, 5.6$ Hz), 6.32 (d, 1H, $J = 9.6$ Hz), 5.69 (m, 1H), 5.19 (m, 3H), 4.58 (app t, 1H, $J = 5.2$ Hz), 3.73 (s, 1H), 2.90 (dd, 1H, $J = 7.6, 15.2$ Hz), 2.69 (dd, 1H, $J = 6.0, 15.2$ Hz), 2.42 (m, 1H),

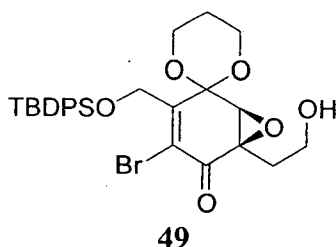
1.88 (d, 1H, $J = 5.2$ Hz), 1.85-1.34 (m, 6H), 0.93 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (75.0 MHz, CDCl_3) δ 194.1, 191.8, 143.1, 136.8, 134.7, 130.4, 120.7, 118.5, 62.7, 62.1, 58.6, 40.0, 31.9, 29.5, 28.0, 22.8, 14.2; IR (neat) ν_{max} 3441, 2927, 2857, 1693, 1664 cm^{-1} ; CIHRMS $[\text{M}]^+$ calculated for $\text{C}_{17}\text{H}_{20}\text{O}_4$: 288.1362, found: 288.1376.



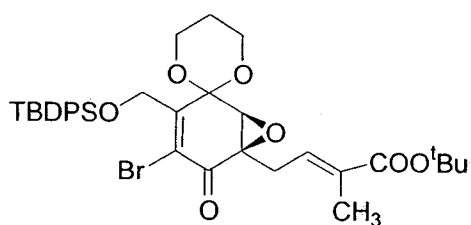
Alcohol 48. 29 (750 mg, 1.36 mmol) was dissolved in 7 mL of THF and 7 mL of water, 75 μL (0.015 mmol, 1.1 % equiv) of OsO_4 (0.2 M in toluene, prepared by dissolving 500 mg of OsO_4 in 20 mL of toluene) and 638 mg (2.98 mmol, 2.2 eq) NaIO_4 was added. The reaction was stirred at rt for 1.5 h. The reaction was quenched with addition of 20 mL of sat. $\text{Na}_2\text{S}_2\text{O}_3$ and the mixture was extracted with EtOAc. The organic extracts were combined, washed with water, dried over

MgSO_4 , filtered and concentrated *in vacuo*. Purification on silica gel (50 % EtOAc in hexane) provided 465 mg (0.84 mmol, 62 %) of an aldehyde intermediate. ^1H NMR (400 MHz, CDCl_3) δ 9.71 (s, 1H), 7.78 (d, 4H, $J = 7.6$ Hz), 7.53 (s, 1H), 7.41 (m, 6H), 4.57 (s, 2H), 4.09 (m, 2H), 3.85 (m, 2H), 3.46 (s, 2H), 1.87 (m, 1H), 1.39 (d, 1H, $J = 13.2$ Hz), 1.05 (s, 9H); ^{13}C NMR (75.0 MHz, CDCl_3) δ 197.3, 178.2, 154.3, 136.8, 136.0, 133.7, 129.8, 129.3, 128.3, 127.7, 92.4, 61.4, 44.4, 27.0, 24.6, 19.6, 14.4; IR (neat) ν_{max} 3071,

2959, 2932, 2858, 1729, 1670, 1471, 1428, 1380, 1243, 1112, 989 cm^{-1} ; CIHRMS M^+ calculated for $\text{C}_{28}\text{H}_{31}\text{BrO}_6\text{Si}$: 555.1204, found: 555.1178. To the aldehyde (700 mg, 1.26 mmol) in 11 mL of THF was added 1 mL of MeOH and 1 mL of H_2O . The mixture was cooled to 0 °C and 44 mg (1.52 mmol, 1.2 equiv) of $\text{BH}_3\cdot\text{BuNH}_2$ was added. The reaction was stirred at 0 °C for 20 min and then quenched with 10 mL of 1N HCl. The aqueous layer was extracted with EtOAc. The organic extracts were combined, washed with water, dried over MgSO_4 , filtered and concentrated *in vacuo*. Purification on silica gel (50 % EtOAc in hexane) provided 535 mg (0.96 mmol, 76 %) of alcohol **48**. ^1H NMR (400 MHz, CDCl_3) δ 7.79 (dd, 4H, J = 6.4, 0.8 Hz), 7.48 (s, 1H), 7.39 (m, 6H), 4.56 (s, 2H), 4.13 (m, 2H), 3.84 (dd, 2H, J = 4.8, 12 Hz), 3.75 (t, 2H, J = 6.0 Hz), 2.61 (t, 2H, J = 6.0 Hz), 2.15 (br s, 1H), 1.87 (m, 1H), 1.39 (d, 1H, J = 13.6 Hz), 1.05 (s, 9H); ^{13}C NMR (75.0 MHz, CDCl_3) δ 179.2, 153.8, 136.1, 135.2, 133.9, 133.8, 129.8, 129.2, 127.8, 92.5, 61.5, 61.3, 61.2, 34.1, 27.1, 24.8, 19.7; IR (neat) ν_{max} 3448, 3070, 3049, 2958, 2932, 2858, 1737, 1672, 1471, 1428, 1376, 1243, 1112, 986 cm^{-1} ; CIHRMS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{28}\text{H}_{34}\text{BrO}_5\text{Si}$: 557.1361, found: 557.1376.

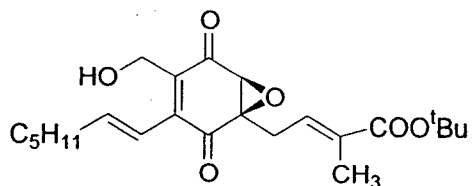


Epoxide 49. To 240 mg (0.869 mmol, 6.0 equiv) of Ph_3COOH and 150 mg of 4Å MS in 4 mL of toluene was added 720 μL (0.720 mmol, 5.0 equiv) of 1.0 M NaHMDS in THF at rt. After 10 min, 67.2 mg (0.287 mmol, 2 equiv) of *L*-DIPT in 1 mL of toluene was added, the mixture was stirred for 15 min at rt. The reaction mixture was cooled to -78 °C, 80 mg (0.144 mmol) of **48** in 3 mL of toluene was added, and the reaction was stirred at -40 °C for 50 h. The reaction was quenched with water and the mixture extracted with EtOAc. The combined organic layers were washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo*. Purification on silica gel (50 % EtOAc in hexane) provided 75 mg (0.131 mmol, 91%) of epoxide **49** as a foamy solid. ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, 4H, J = 6.8 Hz), 7.40 (m, 6H), 4.54 (d, 1H, J = 10.8 Hz), 4.49 (d, 1H, J = 10.8 Hz), 4.45 (s, 1H), 4.25 (m, 2H), 3.91 (m, 2H), 3.79 (br s, 2H), 2.38 (dt, 1H, J = 5.2, 14.8 Hz), 2.09 (m, 1H), 1.97 (br s, 1H), 1.86 (m, 1H), 1.43 (d, 1H, J = 13.6 Hz), 1.05 (s, 9H). ^{13}C NMR (75.0 MHz, CDCl_3) δ 187.8, 151.2, 136.0, 133.6, 129.8, 127.7, 126.7, 94.6, 62.0, 61.2, 61.6, 58.6, 58.5, 56.2, 32.1, 27.0, 24.4, 19.6; IR (neat) ν_{max} 3422, 2931, 2858, 1699, 1472, 1428, 1244, 1142, 1109, 1078, 1007 cm^{-1} ; CIHRMS $[\text{M}]^+$ calculated for $\text{C}_{28}\text{H}_{33}\text{BrO}_6\text{Si}$: 572.1230, found: 572.1276. $[\alpha]_{\text{D}}^{23} = +45.6^\circ$ (c = 1.0, CHCl_3). After the alcohol **49** was converted to the corresponding acetate (Ac_2O , Et_3N , cat DMAP), the ee was determined to be 91 % using a Regis chiral HPLC column (R,R) whelk-O1 (25 cm x 4.0 mm (10 % isopropanol in hexane, retention time 30.0 min (major enantiomer) and 32.1 min (minor enantiomer)).

**50**

Enoate 50. To epoxide **49** (240 mg, 0.42 mmol) in 20 mL of CH₂Cl₂ was added 330 mg (0.78 mmol, 1.8 equiv) of Dess-Martin periodinane. After stirring at rt for 35 min, the reaction mixture was neutralized with 1:1 sat. NaHCO₃/Na₂S₂O₃. The aqueous layer was washed with 2 × 30 mL CH₂Cl₂, and the combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo* to

afford a foamy solid. The crude aldehyde was used in the next step directly by redissolving in 15 mL of CH₂Cl₂ and cooling to -78 °C. of *tert*-Butyl 2-(triphenyl phosphoranylidene) propionate (240 mg, 0.62 mmol, 1.5 eq)^{S4} in 5 mL of CH₂Cl₂ was added dropwise. The reaction mixture was slowly warmed to 5 °C over 4 h. Then 20 mL sat. NH₄Cl was added and the reaction was stirred at rt for 5 min. The organic layer was separated and 2 × 20 mL CH₂Cl₂ was used to further extract the aqueous layer. The organic extracts were combined, washed with brine, dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification on silica gel (17 % EtOAc in hexane) provided 270 mg (0.395 mmol, 94 %) of enoate **50**. ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, 4H, *J* = 7.6 Hz), 7.42-7.39 (m, 6H), 6.51 (t, 1H, *J* = 8.0 Hz), 4.52 (d, 1H, *J* = 10.8 Hz), 4.47 (d, 1H, *J* = 10.8 Hz), 4.18 (m, 2H), 4.16 (s, 1H), 3.91 (m, 2H), 2.94 (dd, 1H, *J* = 8.0, 16.0 Hz), 2.80 (dd, 1H, *J* = 8.0, 16.0 Hz), 1.85 (s, 3H), 1.82 (m, ovrlp, 1H), 1.47 (s, 9H), 1.45 (d, ovrlp, 1H), 1.04 (s, 9H); ¹³C NMR (75.0MHz, CDCl₃) δ 186.9, 167.0, 151.2, 136.0, 133.5, 132.1, 129.8, 127.7, 126.6, 94.5, 80.7, 62.0, 61.2, 60.3, 59.1, 55.1, 29.9, 28.3, 27.0, 24.3, 19.6, 13.1; IR(neat) ν_{max} 2931, 2858, 1701, 1142, 1113 cm⁻¹; CIHRMS [M+H]⁺ calculated for C₃₅H₄₄BrO₇Si: 683.2041, found: 683.2114. [α]_D²³ = + 30.1° (c = 1.0, CHCl₃).

**9**

Quinone monoepoxide 9. Pd(PPh₃)₄ (100 mg, 0.087 mmol, 0.2 equiv) was placed in a Schlenk flask, then 300 mg (0.44 mmol) of enoate **50** dissolved in 6 mL of degassed toluene was added, followed by addition of 340 mg (0.88 mmol, 2 equiv) of *E*-tributyl-1-heptenylstannane. The mixture was stirred at 110 °C for 2 h, cooled to rt, concentrated and directly

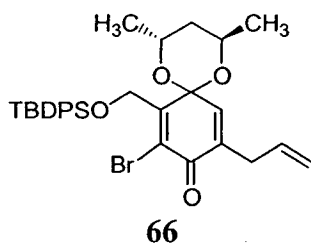
subjected to silica gel chromatography (17 % EtOAc in hexane) providing 280 mg (0.40 mmol, 91 %) of the α-heptenyl enone as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.70 (m, 4H), 7.43-7.34 (m, 6H), 6.54 (t, 1H, *J* = 8.0 Hz), 6.31 (m, 2H), 4.45 (d, 1H, *J* = 11.2 Hz), 4.42 (d, 1H, 11.2Hz), 4.14 (m, ovrlp, 2H), 4.13 (s, 1H), 3.82 (m, 2H), 2.90 (dd, 1H, *J* = 8.0, 16.0 Hz), 2.76 (dd, 1H, *J* = 8.0, 16.0 Hz), 1.84 (s, 3H), 1.74 (m, 1H), 1.46 (s, 9H), 1.39-1.24 (m, ovrlp, 7H), 1.03 (s, 9H), 0.86 (t, 3H, *J* = 7.2Hz); ¹³C NMR (75.0

^{S4} (a) Stotter, P. L.; Hill, K. A. *Tetrahedron Lett.* **1975**, *21*, 1679. (b) Shing, T. K. M.; Yang, J. *J. Org. Chem.* **1995**, *60*, 5785. In order to achieve satisfactory results, the Ph₃P=C(Me)CO₂^tBu was recrystallized from hexane/CH₂Cl₂ (10:1) and the following ¹H NMR differed slightly from that reported in reference 51b: ¹H NMR (400 MHz, CDCl₃) δ 0.93 (s, 9H), 1.54 (d, 3H, *J* = 13.6 Hz), 7.7 – 7.4 (m, 15H).

MHz, CDCl₃) δ 194.6, 167.1, 144.6, 140.1, 136.0, 133.8, 133.2, 129.7, 127.7, 121.8, 94.1, 80.5, 60.8, 59.6, 54.7, 34.2, 31.7, 28.8, 28.3, 27.7, 27.0, 24.5, 22.7, 21.2, 19.6, 14.4, 14.2, 13.0; IR (neat) ν_{max} 2958, 2930, 1690, 1170, 1144, 1113, 1000 cm⁻¹; CIHRMS M⁺ calculated for C₄₂H₅₆O₇Si: 700.3795, found: 700.3734. $[\alpha]_{\text{D}}^{23} = +63.5^\circ$ (c = 1.0, CHCl₃).

The α -heptenyl enone (22 mg, 0.031 mmol) was dissolved in 1 mL THF, and 310 μ L (0.31 mmol, 10 equiv) of 1M TBAF/AcOH (1:1 mol/mol) in THF (freshly prepared by adding 114.5 μ L of AcOH to 2 mL of commercially available 1 M TBAF solution in THF). The reaction mixture was stirred at rt for 20 h. After reducing the volume, the mixture was subjected to silica gel chromatography (30% EtOAc in hexane), to afford 11 mg (0.024 mmol, 76 %) of alcohol as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 6.52 (t, 1H, *J* = 8.0 Hz), 6.24 (m, 1H), 6.15 (d, 1H, *J* = 16.0 Hz), 4.47 (d, 1H, *J* = 11.6 Hz), 4.36 (m, 2H), 4.24 (d, 1H, *J* = 11.6 Hz), 4.23 (s, ovrlp, 1H), 4.13 (m, 1H), 3.98 (m, 1H), 2.89 (dd, 1H, *J* = 8.0, 16.0 Hz), 2.72 (dd, 1H, *J* = 8.0, 16.0 Hz), 2.23 (m, 1H), 2.12 (m, 2H), 1.83 (s, 3H), 1.58 (d, 1H, *J* = 13.6 Hz), 1.44 (s, 9H), 1.39 (t, ovrlp, 1H), 1.26 (m, 6H), 0.84 (t, 3H, *J* = 6.8 Hz); ¹³C NMR (75.0 MHz, CDCl₃) δ 194.2, 167.1, 143.6, 141.4, 134.2, 132.8, 120.5, 95.0, 80.6, 61.5, 61.2, 59.4, 58.7, 54.4, 33.9, 31.6, 28.8, 28.3, 27.7, 24.8, 22.6, 14.2, 13.0; IR (neat) ν_{max} 3446, 2927, 1684, 1653, 1140, 1081, 1000 cm⁻¹; CIHRMS M⁺ calculated for C₂₆H₃₈O₇: 462.2618, found: 462.2664. $[\alpha]_{\text{D}}^{23} = +37.0^\circ$ (c = 1.0, CHCl₃).

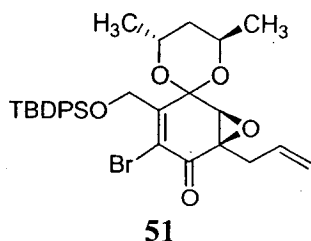
The alcohol (46 mg, 0.010 mmol) was dissolved in 10 mL of CH₃CN, followed by addition of 1 mL of 48% aqueous HF. The mixture was stirred at rt for 15 min, then quenched with sat. NaHCO₃ until no further bubbling was observed. The reaction mixture was extracted with Et₂O. The organic extracts combined, washed with brine, dried over MgSO₄, filtered and concentrated *in vacuo*. Purification on silica gel (20 % EtOAc in Hexane) provided 37.5 mg (0.093 mmol, 93 %) of quinone monoepoxide **9** as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 6.50-6.44 (m, ovrlp, 2H), 6.29 (d, 1H, *J* = 15.6 Hz), 4.54 (dd, 1H, *J* = 7.6, 12.4 Hz), 4.40 (dd, 1H, *J* = 7.6, 12.4 Hz), 3.68 (s, 1H), 2.97 (dd, 1H, *J* = 8.0, 16.0 Hz), 2.81 (dd, 1H, *J* = 8.0, 16.0 Hz), 2.33 (t, 1H, *J* = 7.6 Hz), 2.23 (m, 2H), 1.83 (s, 3H), 1.46 (s, 9H), 1.31-1.25 (m, 6H), 0.88 (t, 3H, *J* = 7.2 Hz); ¹³C NMR (75.0 MHz, CDCl₃) δ 194.6, 193.5, 166.8, 147.6, 142.4, 137.1, 133.9, 131.4, 120.9, 80.9, 61.3, 60.6, 58.1, 57.6, 34.6, 31.6, 28.3, 26.9, 22.7, 14.2, 13.1; IR (neat) ν_{max} 3502, 2930, 1684, 1367, 1278, 1166, 1127 cm⁻¹; CIHRMS M⁺ calculated for C₂₃H₃₂O₆: 404.2199, found: 404.2185. $[\alpha]_{\text{D}}^{23} = +59.2^\circ$ (c = 0.5, CHCl₃).



Non-racemic acetal 66. A mixture of **28** (1.0 g, 1.85 mmol), (2*R*, 4*R*)-(-)-pentanediol (250 mg, 2.4 mmol, 1.3 equiv.) and pyridinium *p*-toluenesulfonate (70 mg, 0.28 mmol, 15 %) was placed in a round-bottomed flask fitted with a water condenser and 20 mL benzene was added. After stirring at 70 °C for 30 min, the reaction was cooled to rt and quenched by addition of pH 7 buffer. The reaction mixture was extracted with EtOAc, and the combined

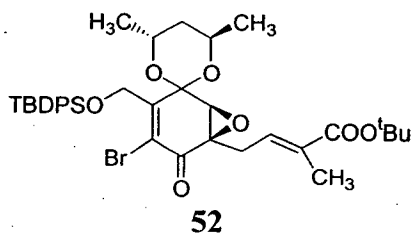
organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated *in vacuo*. Purification on silica gel (4 % EtOAc in hexane) provided 880 mg (1.51 mmol,

82%) of the non-racemic ketal **66** as a yellow solid. mp 98-99 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.75 (m, 4H), 7.40 (m, 6H), 6.77 (s, 1H), 5.80 (m, 1H), 5.12 (m, 2H), 4.54 (d, 1H, $J = 10.8$ Hz), 4.52 (d, 1H, $J = 10.8$ Hz), 4.23 (q, 1H, $J = 6.4$ Hz), 3.97 (m, 1H), 3.07 (d, 1H, $J = 6.8$ Hz), 1.68 (m, 1H), 1.47 (m, 1H), 1.14 (d, 6H, $J = 6.0$ Hz), 1.07 (s, 9H); ^{13}C NMR (75.0 MHz, CDCl_3) δ 178.6, 153.6, 139.5, 136.1, 134.5, 134.2, 133.4, 129.8, 128.9, 127.7, 118.1, 93.9, 66.0, 61.5, 61.6, 37.7, 33.6, 31.7, 27.1, 22.8, 22.5, 22.1, 19.6, 14.2; IR (neat) ν_{max} 3072, 2932, 2858, 1672, 1428, 1240, 1111, 1039 cm^{-1} ; CIHRMS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{31}\text{H}_{38}\text{BrO}_4\text{Si}$: 581.1724, found: 581.1767. $[\alpha]_{\text{D}}^{23} = +14.6^\circ$ ($c = 1.0$, CHCl_3).



Epoxide 51. 1.9 g (6.9 mmol, 4 equiv.) of Ph_3COOH was dissolved in 5 mL of THF at -78°C , then 6.9 mL (3.44 mmol, 2 equiv.) of 0.5 M KHMDS in toluene was added. After 10 min, chiral ketal (1 g, 1.7 mmol) in 5 mL of THF was added. The yellow solution formed was stirred at -35°C for 25 h. The reaction was quenched with water and extracted with EtOAc. The combined organic layers were washed with brine, dried over MgSO_4 , filtered, and concentrated *in vacuo*. Purification on silica gel (3 % Et_2O

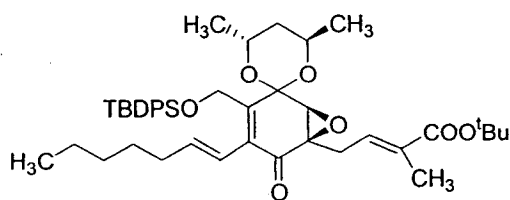
in hexane) provided 750 mg (1.26 mmol, 73%) of **51** as a light yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.71 (m, 4H), 7.39 (m, 6H), 5.72 (m, 1H), 5.18 (d, 1H, $J = 16.8$ Hz), 5.14 (d, 1H, $J = 10$ Hz), 4.63 (d, 1H, $J = 10.8$ Hz), 4.48 (d, 1H, $J = 10.8$ Hz), 4.27 (m, 1H), 4.08 (m, 1H), 3.73 (s, 1H), 2.81 (dd, 1H, $J = 7.6, 14.8$ Hz), 2.69 (dd, 1H, $J = 6.0, 14.8$ Hz), 1.61 (m, 1H), 1.32 (m, 1H), 1.15 (d, 3H, $J = 6.4$ Hz), 1.07 (s, 9H), 1.05 (d, 3H, $J = 6.0$ Hz); ^{13}C NMR (75.0 MHz, CDCl_3) δ 188.4, 151.5, 136.2, 136.1, 133.5, 133.2, 131.1, 130.0, 128.1, 127.8, 126.7, 119.5, 96.7, 65.0, 58.9, 39.5, 32.4, 27.2, 22.0, 19.6; IR (neat) ν_{max} 2932, 2858, 1702, 1428, 1382, 1170, 1113, 1017 cm^{-1} ; CIHRMS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{31}\text{H}_{38}\text{BrO}_5\text{Si}$: 597.1674, found: 597.1650. $[\alpha]_{\text{D}}^{23} = +61.5^\circ$ ($c = 1.0$, CHCl_3).



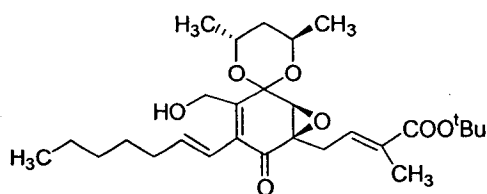
Enolate 52. Epoxide **51** (60 mg, 0.10 mmol) was dissolved in 3.6 mL of THF/water (5:1 v/v), followed by addition of 15 mg (0.13 mmol, 1.3 equiv.) of *N*-methyl-morpholine oxide (NMO) and 10 μL (0.002 mmol, 2 %) of 0.2 M solution of OsO_4 in toluene. The mixture was stirred at rt for 30 h, quenched with *sat.* $\text{Na}_2\text{S}_2\text{O}_3$, and extracted with 2:1(v/v) CHCl_3 /isopropanol. The organic extracts

were combined, washed with water, dried over MgSO_4 , and concentrated *in vacuo*. The crude diol was dissolved in 4 mL of THF, to which was added 45 mg (0.10 mmol, 1.0 equiv.) of $\text{Pb}(\text{OAc})_4$. After stirring at rt for 5 min, the reaction was quenched with *sat.* NaHCO_3 and extracted with EtOAc. The organic extracts were combined, washed with water, dried over MgSO_4 , filtered, and concentrated *in vacuo*, affording an aldehyde intermediate as a yellow solid. The aldehyde was dissolved in 3 mL of CH_2Cl_2 and the reaction was cooled to -78°C . *Tert*-butyl 2-(triphenyl phosphoranylidene) propionate (55

mg, 0.14 mmol, 1.4 equiv.) dissolved in 1 mL of CH_2Cl_2 was added dropwise over 0.5 h. The reaction mixture was slowly warmed up to -5°C over 2 h, then 5 mL of sat. NH_4Cl was added and the reaction stirred at rt for 5 min. The organic layer was separated and $2 \times 5\text{ mL}$ of CH_2Cl_2 was used to further extract the water layer. The organic extracts were combined, washed with brine, dried over MgSO_4 , filtered and concentrated *in vacuo*. Purification on silica gel (10 % EtOAc in hexane) provided 43 mg (0.06 mmol, 60 % for three steps) of enoate **52** as a pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.70 (m, 4H), 7.39 (m, 6H), 6.50 (t, 1H, $J = 6.8\text{ Hz}$), 4.62 (d, 1H, $J = 10.8\text{ Hz}$), 4.48 (d, 1H, $J = 10.8\text{ Hz}$), 4.25 (m, 1H), 4.09 (m, 1H), 3.71 (s, 1H), 2.90 (dd, 1H, $J = 8, 16\text{ Hz}$), 2.78 (dd, 1H, $J = 6, 16\text{ Hz}$), 1.84 (s, 3H), 1.59 (m, 1H), 1.46 (s, 9H), 1.33 (m, 1H), 1.15 (d, 3H, $J = 6.4\text{ Hz}$), 1.07 (s, 9H), 1.04 (d, 3H, $J = 6.4\text{ Hz}$); ^{13}C NMR (75.0 MHz, CDCl_3) δ 188.3, 167.0, 151.7, 136.2, 136.1, 133.4, 133.3, 132.4, 130.0, 127.9, 127.8, 126.4, 96.6, 80.5, 65.0, 64.8, 62.1, 58.9, 58.3, 39.5, 28.3, 27.7, 27.2, 22.0, 19.6, 13.0; IR (neat) ν_{max} 2973, 2932, 1704, 1428, 1367, 1256, 1171, 1113, 1018 cm^{-1} ; CIHRMS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{37}\text{H}_{48}\text{BrO}_7\text{Si}$: 711.2354, found: 711.2309. $[\alpha]_{\text{D}}^{23} = +60^\circ$ ($c = 1.0$, CHCl_3)

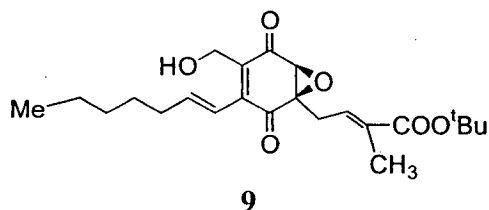
**67**

α -Heptenyl enone 67. 26 mg (0.023 mmol, 10 %) of $\text{Pd}(\text{PPh}_3)_4$ was placed in a Schlenk flask, then 160 mg (0.225 mmol) of enoate **52** dissolved in 5 mL degassed toluene was added, followed by addition of 170 μL (0.439 mmol, 2.0 equiv.) of *E*-tributyl-1-heptenyl-stannane. The mixture was stirred at 110°C for 3 h, cooled to rt, concentrated and subjected to silica gel chromatography (10 % EtOAc in hexane) providing 150 mg (0.213 mmol, 94 %) of α -heptenyl enone **67** as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.68 (m, 4H), 7.38 (m, 6H), 6.56 (dt, 1H, $J = 1.2, 7.2\text{ Hz}$), 6.12 (m, 2H), 4.55 (d, 1H, $J = 11.2\text{ Hz}$), 4.39 (d, 1H, $J = 11.2\text{ Hz}$), 4.22 (m, 1H), 4.11 (m, 1H), 3.68 (s, 1H), 2.87 (dd, 1H, $J = 7.6, 15.6\text{ Hz}$), 2.79 (dd, 1H, $J = 6.4, 15.6\text{ Hz}$), 2.00 (m, 2H), 1.83 (s, 3H), 1.57 (m, 1H), 1.46 (s, 9H), 1.41-1.22 (m, 7H), 1.15 (d, 3H, $J = 6.0\text{ Hz}$), 1.05 (s, 9H), 1.04 (d, 3H, $J = 6.4\text{ Hz}$), 0.86 (t, 3H, $J = 6.8\text{ Hz}$); ^{13}C NMR (75.0 MHz, CDCl_3) δ 196.2, 167.2, 144.7, 140.0, 136.1, 136.0, 134.6, 133.5, 132.6, 129.9, 127.8, 122.2, 96.5, 80.3, 64.5, 64.3, 59.6, 58.5, 57.4, 40.1, 34.0, 31.7, 28.8, 28.3, 27.3, 27.1, 22.7, 22.1, 21.8, 19.5, 14.1, 12.9; IR (neat) ν_{max} 2961, 2931, 2858, 2254, 1696, 1459, 1428, 1367, 1256, 1168, 1114, 1089, 910 cm^{-1} ; CIHRMS M^+ calculated for $\text{C}_{44}\text{H}_{60}\text{O}_7\text{Si}$: 728.4108, found: 728.4063. $[\alpha]_{\text{D}}^{23} = +87.5^\circ$ ($c = 1.0$, CHCl_3)

**68**

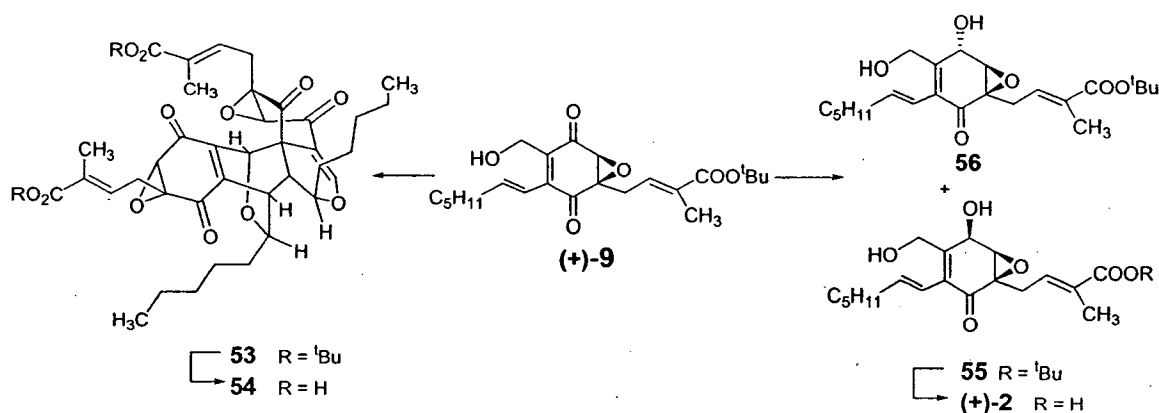
Alcohol 68. α -Heptenyl enone **67** (150 mg, 0.206 mmol) was dissolved in 5 mL of THF, and 2 mL (2 mmol, 10 equiv.) of 1M TBAF/AcOH (1:1 mol/mol) in THF (freshly prepared by adding 114.5 μL of AcOH to 2 mL of commercially available 1 M TBAF solution in THF). The reaction mixture was stirred at rt for 20 h. After reducing the volume, the

mixture was subjected to silica gel chromatography (25% EtOAc in hexane), to afford 81 mg (0.165 mmol, 80 %) of alcohol **68** as a pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 6.52 (t, 1H, $J = 7.2\text{ Hz}$), 6.22 (m, 1H), 6.17 (d, 1H, $J = 16.4\text{ Hz}$), 4.44 (m, 1H), 4.39 (d, 1H, $J = 11.6\text{ Hz}$), 4.29 (d, 1H, $J = 11.6\text{ Hz}$), 4.24 (m, 1H), 3.72 (s, 1H), 2.87 (dd, 1H, $J = 8, 16\text{ Hz}$), 2.72 (dd, 1H, $J = 7.2, 16\text{ Hz}$), 2.38 (br d, 1H, $J = 9.2\text{ Hz}$), 2.13 (app q, 2H, $J = 7.2\text{ Hz}$), 1.80 (s, 3H), 1.79 (m, 1H), 1.44 (s, 9H), 1.40 (m, 2H), 1.34 (d, 3H, $J = 6.0\text{ Hz}$), 1.26 (m, 4H), 1.21 (d, 3H, $J = 6.0\text{ Hz}$), 0.85 (t, 3H, $J = 6.8\text{ Hz}$); ^{13}C NMR (75.0 MHz, CDCl_3) δ 194.9, 167.1, 144.2, 141.0, 133.8, 133.1, 133.0, 120.8, 96.8, 80.5, 66.2, 64.8, 59.2, 58.7, 38.9, 33.9, 31.6, 28.8, 28.3, 27.5, 22.7, 22.5, 22.4, 14.2, 13.0; IR (neat) ν_{max} 3578, 2972, 2930, 1702, 1457, 1368, 1274, 1164, 1135, 1011 cm^{-1} ; CIHRMS $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{28}\text{H}_{43}\text{O}_7$: 491.3011, found: 491.3063. $[\alpha]_{\text{D}}^{23} = +200^\circ$ ($c = 1.0$, CHCl_3)



Quinone monoepoxide 9. Alcohol (80 mg, 0.163 mmol) was dissolved in 3 mL of CH₃CN, followed by addition of 2 mL of 48% HF. The mixture was stirred at 0 °C for 10 min, then quenched with sat. NaHCO₃ until no further bubbling was observed. The reaction mixture was extracted with Et₂O,

the organic extracts combined, washed with brine, dried over MgSO_4 , filtered and concentrated *in vacuo*. Purification on silica gel (20 % EtOAc in Hexane) provided 63 mg (0.156 mmol, 96 %) of quinone monoepoxide **9** as a yellow oil. This compound has identical ^1H and ^{13}C NMR, IR and mass spectra with compound **9** prepared using tartrate-mediated nucleophilic epoxidation. $[\alpha]_{\text{D}}^{23} = +59.3^\circ$ ($c = 1.0$, CHCl_3)



Di-*tert*-butyl protected torreyanic acid 53 and (+)-torreyanic acid 54. Quinone monoepoxide **9** (6.0 mg, 0.0149 mol) was dissolved in 0.5 mL of CH₂Cl₂ and 10.3 mg (0.0243 mmol, 1.6 equiv) of Dess-Martin periodinane was added. After stirring at rt for 1.5 h, the reaction mixture was neutralized with *sat.* NaHCO₃/Na₂S₂O₃ and extracted with Et₂O. The organic extracts were combined, washed with brine, dried over MgSO₄, filtered and concentrated *in vacuo*. The mixture was redissolved in 3 mL of CH₂Cl₂, approximately 8 mg of silica gel was added, and the reaction mixture was stirred for 3 h. The silica gel was filtered and the concentrated mixture purified by flash chromatography

(12:1:1 hexane/EtOAc/CH₂Cl₂, v/v/v) to afford 4.8 mg (0.0060 mmol, 80 %) of protected dimer **53** as a yellow oil.

53. ¹H NMR (400 MHz, CDCl₃) δ □ 7.87 (s, 1H), 6.45 (td, 1H, *J* = 1.6, 7.6 Hz), 6.39 (td, 1H, *J* = 1.6, 7.6 Hz), 5.70 (s, 1H), 4.33 (dd, 1H, *J* = 4.8, 9.6 Hz), 4.14 (t, 1H, *J* = 5.6 Hz), 3.66 (s, 1H), 3.62 (s, 1H), 3.29 (t, par ovrlp, 1H, *J* = 1.6 Hz), 2.95 (d, 2H, *J* = 7.2 Hz), 2.77 (dd, 1H, *J* = 7.6, 16.0 Hz), 2.67 (dd, 1H, *J* = 7.6, 16.0 Hz), 2.66 (d, 1H, *J* = 2.4 Hz), 1.85 (d, 3H, *J* = 1.2 Hz), 1.81 (d, 3H, *J* = 1.2 Hz), 1.47 (s, 9H), 1.46 (s, 9H), 1.45 (m, ovrlp, 4H), 1.24-1.05 (m, 12H), 0.84 (app q, 6H, *J* = 6.8 Hz). [α]_D²³ = + 66.7° (c = 0.24, CHCl₃).

Dimer **53** (4.8 mg, 0.0060 mmol) was dissolved in 2 mL of CH₂Cl₂ and 1.0 mL of TFA was added at 0 °C. After stirring at 0 °C for 2 h, removal of volatiles using argon gas flow and evaporation using high vacuum afforded 4.1 mg (0.006 mmol, 100 %) of (+)-torreyanic acid **54**.

54. ¹H NMR (400 MHz, CD₃OD) δ □ 7.84 (s, 1H), 6.69 (td, 1H, *J* = 1.6, 8.0 Hz), 6.56 (td, 1H, *J* = 1.6, 8.0 Hz), 5.59 (s, 1H), 4.52 (dd, 1H, *J* = 4.8, 9.6 Hz), 4.16 (t, 1H, *J* = 6.0 Hz), 3.76 (s, 1H), 3.72 (s, 1H), 2.95 (t, 2H, *J* = 8.0 Hz), 2.87 (dd, 1H, *J* = 7.2, 16.0 Hz), 2.73 (d, 1H, *J* = 2.8 Hz), 2.59 (dd, 1H, *J* = 7.2, 16.0 Hz), 1.89 (d, 3H, *J* = 1.2 Hz), 1.85 (d, 3H, *J* = 1.2 Hz), 1.46 (m, 4H), 1.28-1.04 (m, ovrlp, 12H), 0.86 (app q, 6H, *J* = 7.2 Hz). ¹³C NMR (75.0 MHz, CD₃OD) δ 201.5, 189.9, 188.8, 171.1, 159.9, 146.8, 143.9, 135.3, 134.7, 133.0, 132.7, 114.4, 83.2, 73.0, 71.0, 66.2, 64.9, 63.5, 59.9, 51.3, 40.1, 38.0, 35.8, 34.1, 32.6, 32.3, 29.1, 28.1, 26.5, 25.7, 23.5, 23.4, 14.2, 12.9. IR (neat) ν_{max} 2928, 2857, 1686, 1653, 1585, 1279, 1211, 1140 cm⁻¹; CIHRMS [M/2]⁺ calculated for C₁₉H₂₂O₆ (monomer): 346.1416, found: 346.1443. [α]_D²³ = + 88.2° (c = 0.4, MeOH) (Natural torreyanic acid : [α]_D²³ = + 92.3° (c = 0.11, MeOH)).

Synthetic and natural (+)-torreyanic acid gave the same R_f value in the following three solvent systems: 5 % CH₃OH – 95 % CH₂Cl₂ (R_f 0.13), 67 % EtOAc – 33 % Hexane (R_f 0.53), and 67 % Et₂O – 33 % Hexane (R_f 0.23).

Epoxy alcohol 55 and 56. Quinone monoepoxide **9** (90 mg, 0.22 mmol) in 8 mL of 4:1(v/v) THF/MeOH solvent was cooled to -78 °C. 220 μL (0.22 mol, 1.0 equiv) of 1M MeOBt₂ in THF was added and the reaction was stirred for 20 min. 6.8 mg (0.18 mmol, 0.8 equiv) of NaBH₄ in 0.6 mL of MeOH was added slowly and the mixture was stirred at -78 °C for 0.5 h before quenched with addition of 7 mL of HOAc. The mixture was extracted with EtOAc and the organic layer was washed with sat. NaHCO₃. The organic extracts were washed with brine, dried over MgSO₄, filtered, and concentrated *in vacuo*. The mixture was purified by flash column chromatography (1:1 ether/petroleum ether, v/v/v) to afford 43 mg (0.106 mmol, 48 %) of *syn*-epoxy alcohol **55** (*tert*-butyl-protected ambuic acid) as a yellow oil and 35 mg (0.086 mmol, 39 %) of *anti*-epoxy alcohol **56** as a yellow oil.

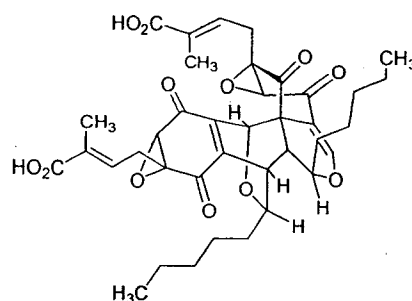
55: ¹H NMR (400 MHz, CDCl₃) δ □ 6.48 (t, 1H, *J* = 7.2 Hz), 6.04 (d, 1H, *J* = 16.4 Hz), 5.81 (dt, 1H, *J* = 6.8, 16.4 Hz), 4.85 (d, 1H, *J* = 5.6 Hz), 4.57 (d, 1H, *J* = 14.0 Hz), 4.50 (d, 1H, *J* = 14.0 Hz), 3.72 (d, 1H, *J* = 2.4 Hz), 2.89 (m, 1H), 2.65 (m, 1H), 2.11 (app q, 2H, *J* = 7.2 Hz), 1.81 (s, 3H), 1.45 (s, 9H), 1.39 (m, 2H), 1.27-1.17 (m, 4H), 0.85 (t, 3H, *J* = 6.4 Hz); ¹³C NMR (75.0 MHz, CDCl₃) δ 194.0, 167.3, 147.6, 140.3, 133.0, 130.7, 121.0, 80.8, 66.6, 61.8, 60.5, 59.1, 33.8, 31.6, 28.9, 28.4, 27.7, 22.7, 18.6, 14.2, 13.0. IR (neat) ν_{max} 3419, 2958, 2928, 2857, 1683, 1651, 1368, 1256, 1171, 1130 cm⁻¹; CIHRMS

M^+ calculated for $C_{23}H_{34}O_6$: 406.2355, found: 406.2366. $[\alpha]_D^{23} = +90.4^\circ$ ($c = 1.0$, $CHCl_3$).

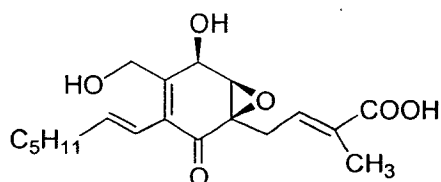
56: 1H NMR (400 MHz, $CDCl_3$) δ 6.51 (t, 1H, $J = 7.2$ Hz), 6.00 (d, 1H, $J = 16.0$ Hz), 5.84 (dt, 1H, $J = 6.4, 16.0$ Hz), 4.88 (d, 1H, $J = 4.4$ Hz), 4.64 (dd, 1H, $J = 3.2, 14.4$ Hz), 4.40 (dd, 1H, $J = 4.4, 14.4$ Hz), 3.64 (d, 1H, $J = 1.6$ Hz), 2.90 (m, 1H), 2.65 (m, 1H), 2.11 (app q, 2H, $J = 7.2$ Hz), 1.81 (s, 3H), 1.44 (s, 9H), 1.38 t, 2H, $J = 7.2$ Hz), 1.27-1.16 (m, 4H), 0.85 (t, 3H, $J = 6.0$ Hz); ^{13}C NMR (75.0 MHz, $CDCl_3$) δ 194.6, 167.7, 16.8, 140.6, 133.5, 132.8, 131.4, 120.8, 80.8, 65.1, 62.9, 60.3, 59.7, 33.9, 31.6, 28.9, 28.3, 27.9, 22.7, 14.2, 13.0. IR (neat) ν_{max} 3411, 2958, 2929, 2858, 1681, 1650, 1368, 1256, 1172, 1130, 1079 cm^{-1} ; CIHRMS M^+ calculated for $C_{23}H_{34}O_6$: 406.2355, found: 406.2356. $[\alpha]_D^{23} = +123^\circ$ ($c = 1.0$, $CHCl_3$).

Ambuic Acid (+)-2. 5 \square mg (0.0123 mmol) of *tert*-butyl protected ambuic acid **55** was dissolved in 2 mL of CH_3CN and 1 mL of 48 % HF was added. The reaction was stirred at rt for 1 h. 5 mL of EtOAc was added to dilute the mixture and 3 x 2 mL of H_2O was used to wash the organic layer. The organic extracts was dried over Na_2SO_4 , filtered, and concentrated *in vacuo*. The crude product was purified using a Waters Sep-Pak® Vac C18 cartridge (1:1 MeOH/ H_2O to 4:1 MeOH/ H_2O) to afford 3 mg (0.0086 mmol, 70 %) of (+)-ambuic acid **2** as a yellow oil. 1H NMR (400 MHz, CD_3OD) δ 6.68 (t, 1H, $J = 7.2$ Hz), 6.13 (d, 1H, $J = 16.0$ Hz), 5.83 (dt, 1H, $J = 7.2, 16.0$ Hz), 4.82 (s, 1H), 4.51 (d, 1H, $J = 13.2$ Hz), 4.39 (d, 1H, $J = 13.2$ Hz), 3.74 (d, 1H, $J = 3.2$ Hz), 2.78 (dq, 2H, $J = 7.2, 15.6$ Hz), 2.15 (q, 2H, $J = 7.2$ Hz), 1.87 (s, 3H), 1.44 (m, 2H), 1.32 (m, 4H), 0.91 (t, 3H, $J = 6.8$ Hz); ^{13}C NMR (75.0 MHz, CD_3OD) δ 196.5, 171.0, 151.0, 140.6, 137.0, 132.3, 122.9, 66.0, 61.4, 61.2, 60.5, 34.6, 32.6, 30.0, 28.9, 23.6, 14.5, 13.1. IR (neat) ν_{max} 3361, 2955, 2927, 2858, 1684, 1648, 1457, 1377, 1261, 1045 cm^{-1} ; CIHRMS M^+ calculated for $C_{23}H_{34}O_6$: 406.2355, found: 406.2339. $[\alpha]_D^{23} = +93^\circ$ ($c = 1.0$, MeOH) (Natural: $[\alpha]_D^{23} = +92.1^\circ$ ($c = 1.0$, MeOH)).

Synthetic and natural (+)-ambuic acid gave the same R_f value in the following three solvent systems: 10 % CH_3OH – 90 % CH_2Cl_2 (R_f 0.46), 67 % EtOAc – 33 % Hexane (R_f 0.2), and 100 % Et_2O (R_f 0.16).

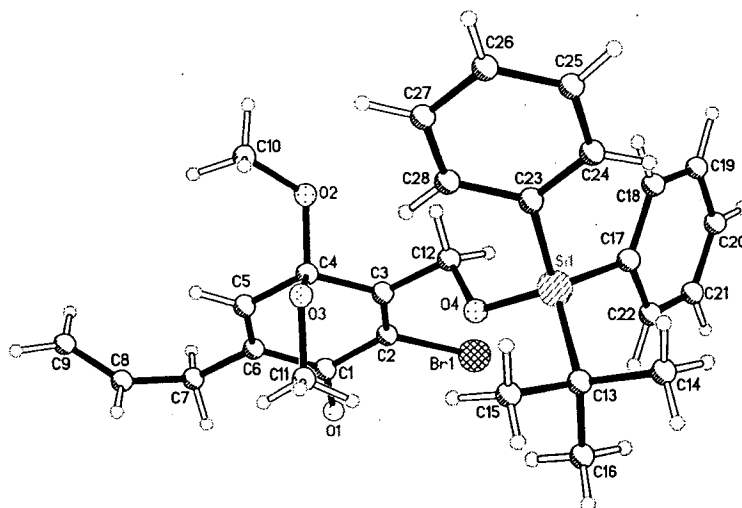
**torreyanic acid****NMR data (in CD₃OD) comparison of natural and synthetic torreyanic acid**

¹ H NMR (Hz)		¹³ C NMR (Hz)	
Natural (500 MHz)	Synthetic (400 MHz)	Natural (100 MHz)	Synthetic (75.0 MHz)
7.82 (s)	7.84 (s)	201.5	201.5
6.66 (td, 7.5, 1.5)	6.69 (td, 8.0, 1.6)	189.9	189.9
6.55 (td, 7.5, 1.5)	6.56 (td, 8.0, 1.6)	189.8	189.8
5.60 (s)	5.59 (s)	188.8	188.8
4.51 (dd, 10.0, 5.0)	4.52 (dd, 9.6, 4.8)	171.30	
4.16 (td, 6.0, 1.5)	4.16 (t, 6.0)	171.28	171.1
3.76 (s)	3.76 (s)	159.8	159.9
3.72 (s)	3.72 (s)	146.7	146.7
2.94 (t, 8.0)	2.95 (t, 8.0)	143.9	143.9
2.85 (dd, 15.0, 7.5)	2.87 (dd, 16.0, 7.2)	135.0	135.3
2.73 (d, 2.5)	2.73 (d, 2.8)	134.3	134.7
2.60 (dd, 15.0, 7.5)	2.59 (dd, 16.0, 7.2)	133.4	133.0
1.88 (d, 1.0)	1.89 (d, 1.2)	132.9	132.7
1.85 (d, 1.0)	1.85 (d, 1.2)	114.2	114.4
1.45 (m)	1.46 (m)	83.1	83.2
1.25-1.05 (m)	1.28-1.04 (m)	72.9	73.0
0.85 (t, 7.0)		71.0	71.0
0.86 (t, 7.0)	0.86 (app q, 7.2)	66.2	66.2
		64.9	64.9
		63.5	63.5
		59.8	59.9
		51.3	51.3
		40.1	40.1
		37.9	38.0
		35.8	35.8
		34.0	34.1
		32.6	32.6
		32.3	32.3
		29.0	29.1
		28.1	28.1
		26.5	26.5
		25.7	25.7
		23.5	23.5
		23.4	23.4
		14.2	14.2
		12.9	12.9

*ambuic acid***NMR data (in CD₃OD) comparison of natural and synthetic ambuic acid**

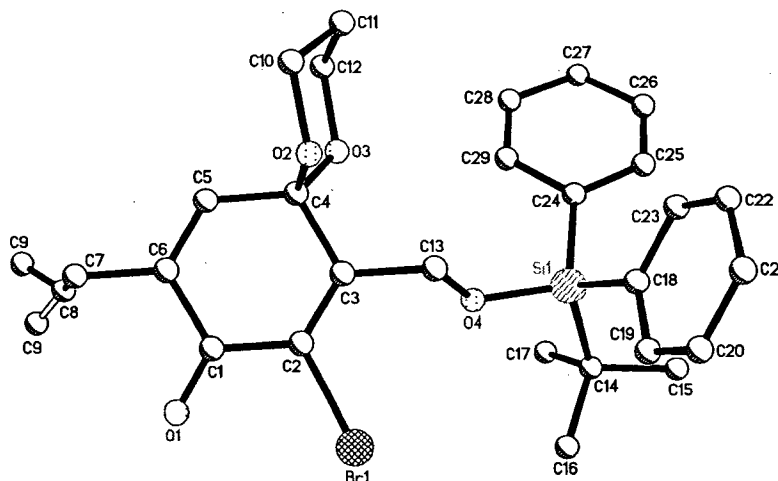
¹ H NMR (Hz)		¹³ C NMR (Hz)	
Natural (500 MHz)	Synthetic (400 MHz)	Natural (100 MHz)	Synthetic (75.0MHz)
6.67 (t, 7.5)	6.68 (t, 7.2)	196.0	196.5
6.13 (d, 15.9)	6.13 (d, 16)	171.2	171.0
5.83 (m)	5.83 (dt, 7.2 16.0)	150.7	151.0
4.82 (s)	4.82 (s)	140.3	140.6
4.51 (d, 12.9)	4.51 (d, 13.2)	136.6	137.0
4.39 (d, 12.9)	4.39 (d, 13.2)	132.0	
3.74 (d, 2.8)	3.74 (d, 3.2)	131.9	132.3
2.78 (dq, 7.8, 15.8)	2.80 (dd, 7.2, 15.6), 2.76 (dd, 7.2, 15.6)	122.8	122.9
2.15 (q, 7.0)	2.15 (q, 7.2)	66.0	66.0
1.86 (s)	1.87 (s)	61.3	61.4
1.43 (m)	1.44 (m)	61.1	61.2
1.32 (m)	1.32 (m)	60.3	60.5
0.90(t, 6.9)	0.91(t, 6.8)	34.6	34.6
		32.6	32.6
		30.0	30.0
		28.8	28.9
		23.6	23.6
		14.5	14.5
		13.0	13.1

X-ray Crystal Structure of Dimethoxyacetal **28**



Crystals of **28** suitable for x-ray analysis were obtained by slow evaporation from 2,2,4-trimethylpentane/methylene chloride. The structure was solved and refined (R-factor = 2.73%). Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC-198655). Copies of the data can be obtained free of charge by contacting the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

X-ray Crystal Structure of Cyclic Ketal **29**



Crystals of **29** suitable for x-ray analysis were obtained by slow evaporation from 2,2,4-trimethylpentane/methylene chloride. The structure was solved and refined (R-factor = 3.87%). Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC-198654). Copies of the data can be obtained free of charge by contacting the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystal data and structure refinement for dimethoxyacetal **28**.

Identification code	dimethoxyacetal 28	
Empirical formula	C ₂₈ H ₃₃ Br O ₄ Si	
Formula weight	541.54	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.0418(6) Å	α = 82.927(2)°
	b = 11.1920(9) Å	β = 89.152(2)°
	c = 15.8196(12) Å	γ = 73.488(2)°
Volume	1354.41(18) Å ³	
Z	2	
Density (calculated)	1.328 Mg/m ³	
Absorption coefficient	1.592 mm ⁻¹	
F(000)	564	
Crystal size	0.50 x 0.40 x 0.30 mm ³	
Theta range for data collection	1.91 to 28.28°	
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -21 ≤ l ≤ 20	
Reflections collected	16036	
Independent reflections	6601 [R(int) = 0.0204]	
Completeness to theta = 28.28°	98.0 %	
Absorption correction	SADABS	
Max. and min. transmission	1 and 0.724859	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6601 / 0 / 439	
Goodness-of-fit on F ²	1.005	
Final R indices [I > 2σ(I)]	R1 = 0.0273, wR2 = 0.0748	
R indices (all data)	R1 = 0.0346, wR2 = 0.0782	
Largest diff. peak and hole	0.405 and -0.204 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **28**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	8152(1)	572(1)	1473(1)	34(1)
Si(1)	10071(1)	-3760(1)	2913(1)	23(1)
O(1)	8125(1)	1122(1)	-428(1)	33(1)
O(2)	5642(1)	-2573(1)	480(1)	28(1)
O(3)	8487(1)	-3508(1)	246(1)	24(1)
O(4)	9502(1)	-2943(1)	1966(1)	25(1)
C(1)	7738(2)	147(1)	-244(1)	24(1)
C(2)	7764(2)	-434(1)	661(1)	23(1)
C(3)	7589(2)	-1578(1)	886(1)	21(1)
C(4)	7206(2)	-2328(1)	211(1)	22(1)
C(5)	7015(2)	-1662(1)	-684(1)	25(1)
C(6)	7247(2)	-530(1)	-904(1)	25(1)
C(7)	7060(2)	124(2)	-1806(1)	33(1)
C(8)	7220(3)	-740(2)	-2468(1)	48(1)
C(9)	5981(4)	-715(3)	-3009(1)	71(1)
C(10)	5093(2)	-3456(2)	61(1)	37(1)
C(11)	10193(2)	-3435(1)	15(1)	30(1)
C(12)	7738(2)	-2220(1)	1788(1)	25(1)
C(13)	12509(2)	-4416(1)	2901(1)	32(1)
C(14)	13193(3)	-5075(2)	3782(1)	52(1)
C(15)	12934(3)	-5372(2)	2249(1)	47(1)
C(16)	13417(3)	-3405(2)	2617(2)	52(1)
C(17)	9181(2)	-2644(1)	3712(1)	29(1)
C(18)	7801(2)	-2731(2)	4234(1)	37(1)
C(19)	7038(3)	-1802(2)	4747(1)	49(1)
C(20)	7645(3)	-761(2)	4736(1)	52(1)
C(21)	8984(3)	-640(2)	4222(1)	50(1)
C(22)	9757(3)	-1566(2)	3710(1)	39(1)
C(23)	9091(2)	-5105(1)	3041(1)	26(1)
C(24)	9047(2)	-5834(1)	3822(1)	32(1)
C(25)	8446(2)	-6891(2)	3874(1)	38(1)
C(26)	7867(2)	-7235(2)	3146(1)	39(1)
C(27)	7904(2)	-6531(1)	2365(1)	35(1)
C(28)	8508(2)	-5476(1)	2311(1)	29(1)

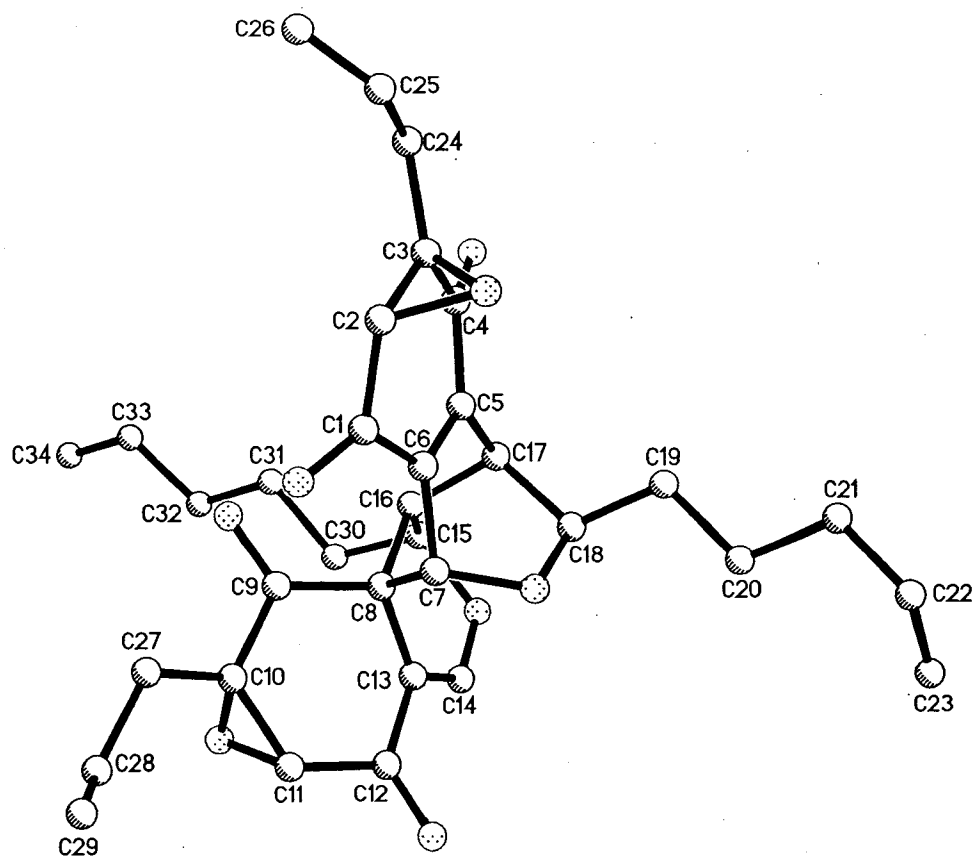
Table 1. Crystal data and structure refinement for cyclic ketal **29**.

Identification code	Compound 29	
Empirical formula	C ₂₉ H ₃₂ Br O ₄ Si	
Formula weight	552.55	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 18.137(3) Å	α = 90°.
	b = 14.917(2) Å	β = 95.999(5)°.
	c = 10.2722(17) Å	γ = 90°.
Volume	2763.9(8) Å ³	
Z	4	
Density (calculated)	1.328 Mg/m ³	
Absorption coefficient	1.562 mm ⁻¹	
F(000)	1148	
Crystal size	0.30 x 0.20 x 0.03 mm ³	
Theta range for data collection	2.42 to 24.41°.	
Index ranges	-21 ≤ h ≤ 21, -17 ≤ k ≤ 17, -11 ≤ l ≤ 11	
Reflections collected	16757	
Independent reflections	4530 [R(int) = 0.0633]	
Completeness to theta = 24.41°	99.9 %.	
Absorption correction	SADABS	
Max. and min. transmission	1 and 0.829088	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4530 / 0 / 325	
Goodness-of-fit on F ²	0.941	
Final R indices [I > 2σ(I)]	R1 = 0.0387, wR2 = 0.0857	
R indices (all data)	R1 = 0.0741, wR2 = 0.0992	
Largest diff. peak and hole	0.466 and -0.259 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 29. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Br(1)	4290(1)	961(1)	3976(1)	29(1)
Si(1)	1840(1)	119(1)	3345(1)	23(1)
O(1)	5580(1)	159(2)	2797(3)	36(1)
O(2)	4008(1)	-2305(1)	4386(2)	22(1)
O(3)	3397(1)	-2037(2)	2279(2)	22(1)
O(4)	2734(1)	-58(2)	3267(2)	23(1)
C(1)	5117(2)	-424(2)	2896(3)	26(1)
C(2)	4404(2)	-243(2)	3422(3)	20(1)
C(3)	3885(2)	-859(2)	3558(3)	19(1)
C(4)	4021(2)	-1826(2)	3185(3)	20(1)
C(5)	4737(2)	-1992(2)	2629(3)	23(1)
C(6)	5251(2)	-1364(2)	2502(3)	24(1)
C(7)	5982(2)	-1549(3)	1975(4)	32(1)
C(8)	6000(3)	-1270(5)	572(6)	80(2)
C(9)	6229(5)	-1623(9)	-329(10)	50(3)
C(9)	6289(7)	-905(11)	-128(13)	83(4)
C(10)	3909(2)	-3272(2)	4232(3)	28(1)
C(11)	3217(2)	-3465(2)	3341(3)	28(1)
C(12)	3267(2)	-2989(2)	2056(3)	28(1)
C(13)	3161(2)	-672(2)	4105(3)	22(1)
C(14)	1664(2)	1271(2)	2603(4)	29(1)
C(15)	879(2)	1590(3)	2810(5)	55(1)
C(16)	2235(2)	1950(3)	3199(4)	47(1)
C(17)	1726(3)	1209(3)	1130(4)	48(1)
C(18)	1646(2)	6(2)	5095(3)	25(1)
C(19)	1961(2)	571(3)	6076(4)	40(1)
C(20)	1864(3)	458(3)	7380(4)	46(1)
C(21)	1444(2)	-242(3)	7762(4)	40(1)
C(22)	1139(2)	-829(3)	6836(4)	40(1)
C(23)	1228(2)	-706(3)	5523(4)	35(1)
C(24)	1297(2)	-729(2)	2300(3)	26(1)
C(25)	523(2)	-793(3)	2220(4)	36(1)
C(26)	131(2)	-1356(3)	1335(4)	45(1)
C(27)	493(2)	-1872(3)	487(4)	43(1)
C(28)	1264(2)	-1831(3)	551(4)	40(1)
C(29)	1656(2)	-1269(2)	1443(4)	32(1)

X-ray Crystal Structure of Compound 33



Crystals of **33** suitable for x-ray analysis were obtained by slow evaporation from 2,2,4-trimethylpentane/methylene chloride. The structure was solved and refined (R-factor = 5.51%). Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC-159554, Ref. Code QEZFEG). Copies of the data can be obtained free of charge by contacting the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

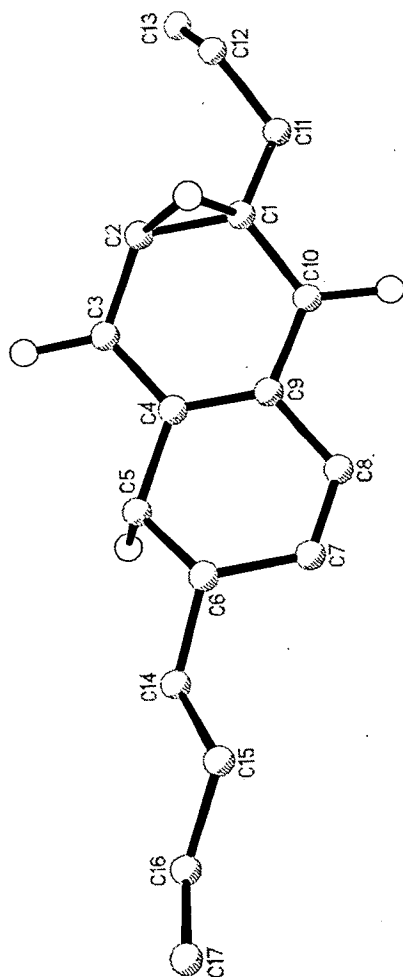
Table 1. Crystal data and structure refinement for compound 33

Identification code	porco3	
Empirical formula	C ₃₄ H ₄₀ O ₈ ; 1/2(C ₈ H ₁₈)	
Formula weight	633.77	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.1252(12) Å	α = 82.429(5)°.
	b = 13.613(2) Å	β = 78.351(5)°.
	c = 16.659(3) Å	γ = 73.558(5)°.
Volume	1725.4(4) Å ³	
Z	2	
Density (calculated)	1.220 Mg/m ³	
Absorption coefficient	0.084 mm ⁻¹	
F(000)	682	
Crystal size	0.60 x 0.10 x 0.05 mm ³	
Theta range for data collection	2.50 to 21.49°.	
Index ranges	-8 ≤ h ≤ 8, -12 ≤ k ≤ 14, -17 ≤ l ≤ 17	
Reflections collected	8486	
Independent reflections	3960 [R(int) = 0.0429]	
Completeness to theta = 21.49°	99.6 %	
Max. and min. transmission	0.9958 and 0.810194	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3960 / 0 / 565	
Goodness-of-fit on F ²	0.984	
Final R indices [I > 2σ(I)]	R1 = 0.0551, wR2 = 0.1353	
R indices (all data)	R1 = 0.0951, wR2 = 0.1586	
Largest diff. peak and hole	0.463 and -0.503 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound 33. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	809(4)	9594(2)	1644(2)	34(1)
O(2)	-2153(3)	10210(2)	284(2)	29(1)
O(3)	-4024(3)	8202(2)	862(2)	31(1)
O(4)	2396(3)	7259(2)	24(2)	20(1)
O(5)	515(4)	7350(2)	2763(2)	35(1)
O(6)	4516(3)	6001(2)	2789(2)	31(1)
O(7)	6609(3)	5518(2)	876(2)	30(1)
O(8)	2020(3)	4629(2)	968(2)	25(1)
C(1)	-133(5)	9379(3)	1253(2)	23(1)
C(2)	-1830(5)	10120(3)	1111(3)	26(1)
C(3)	-3245(5)	9735(3)	923(2)	24(1)
C(4)	-2855(5)	8601(3)	848(2)	22(1)
C(5)	-1016(5)	7998(3)	769(2)	19(1)
C(6)	245(5)	8371(3)	929(2)	21(1)
C(7)	2006(5)	7599(3)	834(2)	21(1)
C(8)	1921(5)	6634(3)	1479(2)	20(1)
C(9)	1858(5)	7020(3)	2303(2)	22(1)
C(10)	3579(5)	7028(3)	2519(2)	24(1)
C(11)	5217(5)	6478(3)	2014(2)	25(1)
C(12)	5227(5)	5908(3)	1307(2)	21(1)
C(13)	3533(5)	5784(3)	1235(2)	20(1)
C(14)	3473(5)	4911(3)	966(2)	22(1)
C(15)	492(5)	5185(3)	1523(2)	23(1)
C(16)	250(5)	6334(3)	1406(3)	21(1)
C(17)	-397(5)	6885(3)	605(2)	21(1)
C(18)	1108(5)	6774(3)	-136(2)	20(1)
C(19)	588(6)	7257(4)	-950(3)	26(1)
C(20)	2129(6)	7104(4)	-1656(3)	31(1)
C(21)	1662(7)	7645(5)	-2481(3)	42(1)
C(22)	3212(8)	7697(6)	-3140(4)	82(2)
C(23)	4479(9)	6752(6)	-3319(4)	89(2)
C(24)	-5152(6)	10305(3)	1120(3)	31(1)
C(25)	-5463(6)	11431(4)	1149(3)	35(1)
C(26)	-6406(7)	11938(5)	1763(4)	54(2)
C(27)	3536(6)	7875(4)	3022(3)	32(1)
C(28)	5221(7)	7787(5)	3283(4)	54(2)
C(29)	6085(9)	8491(7)	3112(4)	81(2)
C(30)	642(6)	4712(4)	2389(3)	26(1)
C(31)	-960(6)	5090(4)	3045(3)	31(1)
C(32)	-834(6)	4471(4)	3863(3)	36(1)
C(33)	-2285(7)	4911(5)	4553(3)	53(2)
C(34)	-2302(11)	4232(7)	5344(4)	74(2)
C(1S)	-6630(20)	10138(14)	5104(14)	152(8)
C(2S)	-8710(20)	10580(13)	4835(7)	229(8)
C(3S)	-9700(40)	10526(12)	5357(17)	530(30)
C(4S)	-8940(20)	11674(14)	5143(13)	139(8)
C(5S)	-8219(15)	10775(10)	3946(6)	164(4)

X-ray Crystal Structure of Compound 42



Crystals of **42** suitable for x-ray analysis were obtained by slow evaporation from hexane/ether. The structure was solved and refined (R-factor = 5.13%). Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC-198656). Copies of the data can be obtained free of charge by contacting the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystal data and structure refinement for compound **42**

Empirical formula	C ₁₇ H ₂₀ O ₄	
Formula weight	288.33	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 28.105(3) Å	α = 90°.
	b = 6.3582(6) Å	β = 117.599(2)°.
	c = 19.2691(18) Å	γ = 90°.
Volume	3051.5(5) Å ³	
Z	8	
Density (calculated)	1.255 Mg/m ³	
Absorption coefficient	0.089 mm ⁻¹	
F(000)	1232	
Crystal size	0.60 x 0.05 x 0.05 mm ³	
Theta range for data collection	2.39 to 24.71°	
Index ranges	-32 ≤ h ≤ 32, -7 ≤ k ≤ 7, -20 ≤ l ≤ 22	
Reflections collected	8470	
Independent reflections	2587 [R(int) = 0.0487]	
Completeness to theta = 24.71°	99.6 %	
Absorption correction	SADABS	
Max. and min. transmission	0.9956 and 0.8488	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2587 / 0 / 264	
Goodness-of-fit on F ²	1.059	
Final R indices [I > 2σ(I)]	R ₁ = 0.0513, wR ₂ = 0.1080	
R indices (all data)	R ₁ = 0.0831, wR ₂ = 0.1192	
Largest diff. peak and hole	0.219 and -0.176 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **42**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
O(1)	5938(1)	333(2)	5371(1)	37(1)
O(2)	6693(1)	2993(2)	7094(1)	33(1)
O(3)	7926(1)	2113(3)	7547(1)	30(1)
O(4)	6756(1)	-3816(2)	5571(1)	40(1)
C(1)	6176(1)	-1569(3)	5806(1)	32(1)
C(2)	6172(1)	378(4)	6214(1)	32(1)
C(3)	6667(1)	1681(3)	6613(1)	26(1)
C(4)	7107(1)	1317(3)	6415(1)	25(1)
C(5)	7587(1)	2758(3)	6756(1)	26(1)
C(6)	7882(1)	2809(4)	6259(1)	31(1)
C(7)	7924(1)	655(4)	5974(1)	36(1)
C(8)	7570(1)	-842(4)	5874(1)	34(1)
C(9)	7116(1)	-439(3)	6025(1)	27(1)
C(10)	6692(1)	-2092(3)	5786(1)	30(1)
C(11)	5808(1)	-3394(4)	5719(2)	44(1)
C(12)	5290(1)	-2793(5)	5699(2)	54(1)
C(13)	5151(2)	-3351(6)	6226(3)	83(1)
C(14)	8422(1)	3943(4)	6690(2)	38(1)
C(15)	8684(1)	4616(6)	6192(2)	56(1)
C(16)	9215(1)	5749(8)	6660(2)	88(1)
C(17)	9451(2)	7089(11)	6333(3)	56(2)
C(17)	9189(2)	7704(11)	6772(4)	71(2)

Theoretical calculations

All calculations were performed with Spartan 02, Wavefunction Inc., Irvine, CA, 2002. Unless otherwise stated, structures were optimized and subjected to frequency analysis with the semiempirical AM1 method, followed by single point B3LYP/6-31G* calculation.

trans-open monomer lower energy conformation 43

Heat of Formation: -69.011 kcal/mol
B3LYP/6-31G*//AM1 -960.6237663

Atom	Cartesian Coordinates (Angstroms)		
	X	Y	Z
1 C C12	2.2048909	0.6796611	1.1423560
2 H H15	2.7271208	0.0427098	1.8927982
3 C C15	-0.2534021	-0.0213067	-0.4732627
4 H H12	-0.9868274	0.2493285	-1.2571247
5 O O5	1.7089736	1.7644301	1.4355065
6 C C16	-0.6472533	-0.2378959	0.7899968
7 C C14	2.2225533	0.1181462	-0.2317375
8 C C17	1.1107653	-0.1586243	-0.9513553
9 C C18	3.5866098	-0.1328737	-0.7469863
10 C C19	1.2099178	-0.6223482	-2.3696395
11 C C20	3.7006369	-1.0455646	-1.9273604
12 C C21	2.4904094	-1.2963410	-2.7727963
13 O O7	4.5942770	0.3688492	-0.2427180
14 O O8	0.3005427	-0.4384783	-3.1805503
15 C C22	-2.0599544	-0.1373047	1.2250262
16 H H5	-2.4933015	-1.1751932	1.2689896
17 H H19	-2.6662361	0.4415617	0.4775423
18 C C33	-2.1771238	0.5158207	2.5886632
19 H H39	-1.7250486	1.5419800	2.5538116
20 H H40	-1.5966941	-0.0775800	3.3433830
21 C C34	-3.6245936	0.6102968	3.0208463
22 H H2	-4.0775031	-0.4158301	3.0508475
23 H H41	-4.2046740	1.2060788	2.2674789
24 C C35	-3.7484888	1.2592824	4.3833043
25 H H43	-3.2923602	2.2842074	4.3514412
26 H H44	-3.1672945	0.6629934	5.1356775
27 C C36	-5.1876922	1.3584389	4.8183980
28 H H42	-5.2563802	1.8394922	5.8237954
29 H H45	-5.6523967	0.3447107	4.8798754
30 H H46	-5.7777486	1.9701554	4.0936931
31 H H78	0.0724670	-0.5214610	1.5778327
32 H H7	4.7233563	-1.1416786	-2.3453461
33 O O1	2.9720008	-2.2774789	-1.8328657
34 C C1	2.6201306	-1.6872422	-4.2203493
35 H H1	3.4675406	-2.4174875	-4.3256418
36 H H4	1.6737776	-2.2147724	-4.5280920
37 C C2	2.8142655	-0.5037867	-5.0950602
38 H H8	2.0275980	0.2658895	-5.0055322
39 C C3	3.8253176	-0.3742959	-5.9499938

40 H H6	3.9256385	0.5016509	-6.6045881
41 H H9	4.6161807	-1.1281400	-6.0602637

 Cis -Open Monomer Lower energy conformation 44
 Heat of Formation: -66.697 kcal/mol

B3LYP/6-31G**/AM1 -960.6195929

Cartesian Coordinates (Angstroms)			
Atom	X	Y	Z

1 C C12	0.2903523	-0.4914202	-2.2188981
2 H H15	0.0631791	-0.7587160	-3.2770164
3 C C15	-0.2366538	1.9345463	-0.4790641
4 H H12	-0.0669776	2.2311365	0.5741441
5 O O5	1.4400188	-0.4248130	-1.7907191
6 C C16	0.3263268	2.6469198	-1.4625937
7 C C14	-0.9221091	-0.2829709	-1.3894771
8 C C17	-1.1396634	0.8016580	-0.6132476
9 C C18	-1.9091055	-1.3811340	-1.5038726
10 C C19	-2.3796474	0.9262617	0.2156631
11 C C20	-2.8760094	-1.5270938	-0.3728456
12 C C21	-3.1400498	-0.3390229	0.5005527
13 O O7	-1.9644623	-2.1294763	-2.4831676
14 O O8	-2.7698283	2.0131270	0.6445616
15 H H7	-3.6339093	-2.3258609	-0.5050979
16 O O1	-2.3213803	-1.4383278	0.9461006
17 C C1	-4.4488221	-0.1870194	1.2279416
18 H H1	-4.7668480	-1.1911775	1.6186439
19 H H4	-4.2817572	0.4873812	2.1144626
20 C C2	-5.4943993	0.4117420	0.3613278
21 H H8	-5.2202841	1.3849614	-0.0817440
22 C C3	-6.6855228	-0.1419957	0.1496632
23 H H6	-7.4496790	0.3402033	-0.4743145
24 H H9	-6.9830053	-1.1055295	0.5844370
25 C C4	0.1834424	2.4054912	-2.9157395
26 H H3	1.0749925	1.8090200	-3.2627959
27 H H11	-0.7279505	1.7828878	-3.1286835
28 C C5	0.1064242	3.7023380	-3.6966348
29 H H14	1.0258575	4.3150280	-3.5016513
30 H H16	-0.7736452	4.3015894	-3.3438722
31 C C6	-0.0208192	3.4358448	-5.1811272
32 H H10	0.8601644	2.8368560	-5.5334614
33 H H18	-0.9388236	2.8211712	-5.3770861
34 C C7	-0.1009165	4.7286173	-5.9654038
35 H H20	0.8134261	5.3465513	-5.7616218
36 H H21	-0.9858201	5.3235124	-5.6155045
37 H H22	0.9693827	3.5062171	-1.1970810
38 C C8	-0.2175539	4.4698686	-7.4451622
39 H H2	0.6709354	3.9052767	-7.8181316
40 H H5	-0.2821024	5.4347933	-8.0035755
41 H H17	-1.1325156	3.8703566	-7.6701619

Pyran syn diastereomer 31

AM1 Heat of Formation: -80.964 kcal/mol
 B3LYP/6-31G**/AM1 SCF total energy: -960.6474091 hartrees

Atom	Cartesian Coordinates (Angstroms)		
	X	Y	Z

1 C C12	-1.3700343	-1.4926226	-0.3586938
2 H H15	-2.3202333	-1.9611078	-0.6824093
3 C C15	0.8549050	-0.2365102	0.6542875
4 H H12	1.7194980	0.2597362	1.1252490
5 O O5	-1.5598842	-0.7772408	0.7734880
6 C C16	-0.4592046	0.0012655	1.3083550
7 C C14	-0.1790033	-1.6447192	-1.0076869
8 C C17	0.9967239	-1.0064210	-0.4463594
9 C C18	-0.1226069	-2.4416044	-2.2310656
10 C C19	2.3347620	-1.2039804	-1.0416046
11 C C20	1.1602985	-2.4222691	-3.0000079
12 C C21	2.3979098	-1.8252954	-2.4071281
13 O O7	-1.0730583	-3.1258766	-2.6327919
14 O O8	3.3667789	-0.8811956	-0.4434814
15 H H1	1.2332722	-3.2071919	-3.7819266
16 O O1	1.6317392	-1.1318263	-3.4128799
17 C C1	3.7583765	-2.2867076	-2.8606191
18 H H4	3.7276771	-2.4830221	-3.9661167
19 H H7	4.4903489	-1.4493829	-2.6820496
20 C C2	4.2106341	-3.4851848	-2.1113827
21 H H8	4.2177689	-3.3635117	-1.0142242
22 C C3	4.6116409	-4.6132999	-2.6915379
23 H H6	4.9674122	-5.4735263	-2.1094468
24 H H9	4.6172270	-4.7566210	-3.7802767
25 C C4	-0.8507655	1.4764966	1.2257757
26 H H3	0.0432547	2.0962540	1.4981098
27 H H11	-1.1333940	1.7261763	0.1701294
28 C C5	-2.0025495	1.7926894	2.1544173
29 H H13	-1.7035512	1.5777776	3.2143163
30 H H14	-2.8689771	1.1218468	1.9111909
31 C C6	-2.4224715	3.2412039	2.0282961
32 H H10	-1.5503603	3.9084032	2.2588353
33 H H18	-2.7308398	3.4534442	0.9705766
34 C C7	-3.5683359	3.5632670	2.9640849
35 H H16	-3.2576397	3.3530744	4.0216977
36 H H20	-4.4371034	2.8906524	2.7356806
37 C C8	-3.9954117	5.0027824	2.8384436
38 H H17	-3.1491623	5.6885391	3.0852501
39 H H22	-4.8397227	5.2190386	3.5365972
40 H H23	-4.3330616	5.2247413	1.7972626
41 H H24	-0.4128499	-0.3282716	2.3896457

Pyran Monomer Syn DFT Optimization 31

Energy is -960.661455978

ATOM	Coordinates (Angstroms)		
	X	Y	Z
1 C	0.195935	1.629385	-1.130663
2 H	0.083099	2.703453	-1.241970
3 C	0.423869	-1.118976	-1.113150
4 H	0.556410	-2.186056	-1.265938
5 O	-0.752737	0.937034	-1.762543
6 C	-0.894946	-0.495867	-1.471365
7 C	1.240066	1.073294	-0.464670
8 C	1.405619	-0.381148	-0.563590
9 C	2.251007	1.938641	0.153663
10 C	2.691830	-1.025130	-0.162241
11 C	3.321023	1.222917	0.938445
12 C	3.583066	-0.232907	0.771999
13 O	2.260590	3.161514	0.077315
14 O	3.009038	-2.148282	-0.521398
15 H	4.134209	1.859718	1.284785
16 O	2.834736	0.270696	1.897788
17 C	4.955292	-0.809109	1.079048
18 H	5.375162	-0.247074	1.920135
19 H	4.815616	-1.847523	1.405992
20 C	5.885831	-0.765281	-0.106702
21 H	5.602015	-1.386550	-0.954499
22 C	6.997022	-0.030643	-0.162189
23 H	7.639816	-0.033371	-1.038263
24 H	7.312760	0.596071	0.669969
25 C	-1.948225	-0.682915	-0.367024
26 H	-2.032888	-1.761845	-0.175101
27 H	-1.561070	-0.234182	0.557613
28 C	-3.324943	-0.101184	-0.711175
29 H	-3.703431	-0.575709	-1.628950
30 H	-3.219984	0.966830	-0.938618
31 C	-4.345518	-0.286769	0.418629
32 H	-4.468908	-1.359164	0.631523
33 H	-3.948788	0.161740	1.341701
34 C	-5.714256	0.329783	0.105411
35 H	-6.115603	-0.122660	-0.812793
36 H	-5.584927	1.398968	-0.114006
37 C	-6.724694	0.157071	1.243794
38 H	-6.885572	-0.903877	1.472196
39 H	-7.696431	0.593504	0.986431
40 H	-6.373662	0.643187	2.162228
41 H	-1.277427	-0.907586	-2.411818

 Pyran anti diastereomer 31'

Heat of Formation: -81.043 kcal/mol

B3LYP/6-31G**//AM1 SCF total energy: -960.6456564 hartrees

AM1 Cartesian Coordinates (Angstroms)

Atom	X	Y	Z
<hr/>			
1 C C12	-2.6790462	-0.1485837	-1.3824203
2 H H15	-3.6817071	-0.5223295	-1.6694320
3 C C15	-0.3031591	0.8645708	-0.4446574
4 H H12	0.6227947	1.2803805	-0.0130026
5 O O5	-2.7626702	0.6093281	-0.2658032
6 C C16	-1.5505992	1.1692639	0.3031192
7 C C14	-1.5344643	-0.4121770	-2.0774883
8 C C17	-0.2842657	0.1251807	-1.5749915
9 C C18	-1.6023049	-1.2220830	-3.2917663
10 C C19	0.9976347	-0.1356725	-2.2620286
11 C C20	-0.3663209	-1.2998643	-4.1303452
12 C C21	0.9394529	-0.7796937	-3.6173181
13 O O7	-2.6193430	-1.8412397	-3.6314074
14 O O8	2.0825623	0.1528647	-1.7451548
15 C C22	-1.4808971	0.6700333	1.7468074
16 H H5	-0.9971209	-0.3403682	1.7736595
17 H H19	-2.5283456	0.5516212	2.1330793
18 C C33	-0.7163785	1.6381485	2.6225605
19 H H39	-1.2222838	2.6398037	2.6119413
20 H H40	0.3187397	1.7838634	2.2142977
21 C C34	-0.6321694	1.1285074	4.0457492
22 H H2	-0.1207114	0.1299449	4.0585878
23 H H41	-1.6664900	0.9761283	4.4528916
24 C C35	0.1239906	2.0965916	4.9308882
25 H H43	-0.3906376	3.0936970	4.9193862
26 H H44	1.1556742	2.2528542	4.5180979
27 C C36	0.2168398	1.5910495	6.3473197
28 H H42	0.7520084	0.6114276	6.3823204
29 H H45	-0.8014922	1.4491064	6.7832781
30 H H46	0.7743351	2.3202341	6.9833162
31 H H78	-1.7410704	2.2844503	0.2865413
32 H H1	-0.3900364	-2.0982230	-4.9016074
33 O O1	0.1657987	-0.0497246	-4.5908937
34 C C1	2.2384052	-1.3381007	-4.1375085
35 H H4	2.1321885	-1.5476736	-5.2359451
36 H H7	3.0332217	-0.5491511	-4.0150640
37 C C2	2.6520393	-2.5535208	-3.3931384
38 H H8	2.7180749	-2.4207174	-2.2993165
39 C C3	2.9570758	-3.7102890	-3.9753259
40 H H6	3.2874371	-4.5839890	-3.3981478
41 H H9	2.9032418	-3.8656492	-5.0610787

Pyran Monomer Anti DFT Optimization 31'

Energy is -960.660082170

ATOM	Coordinates (Angstroms)		
	X	Y	Z
1 C	-0.969796	2.680733	0.819060
2 H	-1.278224	3.575036	1.351894
3 C	-0.018110	0.355534	-0.315990
4 H	0.376811	-0.616517	-0.595293
5 O	0.347884	2.482237	0.854264
6 C	0.942141	1.478013	-0.040073
7 C	-1.861583	1.832407	0.246238
8 C	-1.346696	0.544516	-0.230740
9 C	-3.297087	2.125888	0.319826
10 C	-2.281286	-0.586910	-0.507828
11 C	-4.195881	1.138954	-0.382061
12 C	-3.728994	-0.222307	-0.764013
13 O	-3.780645	3.094893	0.893180
14 O	-1.911782	-1.749169	-0.570507
15 C	2.250623	1.033355	0.619512
16 H	2.012705	0.391016	1.477244
17 H	2.741320	1.929235	1.018993
18 C	3.200494	0.311507	-0.344739
19 H	3.463188	0.989954	-1.169625
20 H	2.695428	-0.548716	-0.806522
21 C	4.482710	-0.174860	0.343508
22 H	4.216147	-0.873323	1.150421
23 H	4.981963	0.676133	0.830059
24 C	5.463848	-0.858716	-0.615600
25 H	5.744576	-0.153072	-1.410616
26 H	4.956698	-1.695448	-1.116734
27 C	6.728733	-1.369629	0.081396
28 H	6.485577	-2.111631	0.851740
29 H	7.270975	-0.550585	0.569666
30 H	7.412946	-1.843154	-0.631676
31 H	1.174906	2.018629	-0.973301
32 H	-5.260546	1.292003	-0.208976
33 O	-3.829879	0.837296	-1.737513
34 C	-4.718929	-1.366361	-0.905193
35 H	-5.652637	-0.955566	-1.303583
36 H	-4.315437	-2.066084	-1.648376
37 C	-4.966948	-2.087202	0.396026
38 H	-4.113076	-2.617661	0.814512
39 C	-6.137989	-2.105775	1.032928
40 H	-6.270510	-2.642313	1.968617
41 H	-7.013638	-1.592344	0.639875

 Anti- Cis TS 31' to 44

Heat of Formation: -47.090 kcal/mol

B3LYP/6-31G**/AM1 SCF total energy: -960.5988150 hartrees

Imaginary Mode -693.9 cm-1

Atom	Cartesian Coordinates (Angstroms)		
	X	Y	Z

1 C C12	-1.4156681	3.2722685	-0.1001030
2 H H15	-0.9719274	4.2929527	-0.0471689
3 C C15	-2.3237144	0.7368647	0.7365205
4 H H12	-2.6323326	0.1424300	1.6149593
5 O O5	-2.6705931	3.1664468	-0.1969330
6 C C16	-3.3171716	1.3049171	-0.0698105
7 C C14	-0.5061824	2.1640506	-0.0090193
8 C C17	-0.9614769	0.9672748	0.5514965
9 C C18	0.8970008	2.4184415	-0.3094344
10 C C19	0.0025268	-0.0046718	1.1376279
11 C C20	1.8332718	1.2556019	-0.1630710
12 H H23	2.6415864	1.2193330	-0.9214307
13 C C21	1.3851385	0.0209589	0.5476619
14 O O6	2.2673799	0.9727977	1.1767470
15 O O7	1.3191610	3.5094802	-0.7148947
16 O O8	-0.3096193	-0.7975578	2.0273160
17 C C23	1.9976718	-1.3233849	0.2641446
18 H H16	3.1032480	-1.1947526	0.1104661
19 H H20	1.8554212	-1.9712687	1.1751906
20 C C37	1.3670452	-1.9852818	-0.9044718
21 H H47	0.2665518	-2.0505842	-0.8650561
22 C C38	2.0542942	-2.4975163	-1.9222079
23 H H4	1.5619664	-3.0068977	-2.7610284
24 H H6	3.1495641	-2.4487334	-1.9878634
25 H H7	-4.3016519	1.5230636	0.3882997
26 C C1	-3.3217340	1.1346563	-1.5509536
27 H H2	-2.3252444	1.4343062	-1.9743687
28 H H1	-3.4508716	0.0337442	-1.7530335
29 C C2	-4.4222334	1.9133849	-2.2422370
30 H H5	-4.1730476	1.9939866	-3.3340196
31 H H8	-4.4550191	2.9573632	-1.8295863
32 C C3	-5.7777747	1.2563326	-2.0895091
33 H H3	-5.7450147	0.2164754	-2.5106242
34 H H11	-6.0358885	1.1640785	-1.0013451
35 C C4	-6.8540013	2.0530252	-2.7961673
36 H H9	-6.5997477	2.1388124	-3.8858109
37 H H13	-6.8806259	3.0953546	-2.3805195
38 C C5	-8.2080026	1.4101659	-2.6408986
39 H H10	-8.2071235	0.3781065	-3.0684505
40 H H17	-8.9847825	2.0110359	-3.1721733
41 H H18	-8.4914804	1.3419205	-1.5627538

Anti-Trans-TS 31' to 43

Heat of Formation: -52.658 kcal/mol

B3LYP/6-31G**//AM1 SCF total energy: -960.6156356 hartrees

Imaginary Mode - 704.9 cm-1

Atom	Cartesian Coordinates (Angstroms)		
	X	Y	Z

1 C C12	-1.6159907	2.9172518	-0.1866894
2 H H15	-1.3514309	3.6702517	-0.9635593
3 C C15	-2.3360350	0.4428330	0.9951252
4 H H12	-2.7541959	-0.5702499	0.8703089
5 O O5	-2.7828033	2.9479014	0.3051440
6 C C14	-0.6198040	1.9489884	0.1549334
7 C C17	-1.0277722	0.6808892	0.5890816
8 C C18	0.7682782	2.2536711	-0.1623759
9 C C19	-0.1028466	-0.4792468	0.4546128
10 C C20	1.7910744	1.2443596	0.2677431
11 H H23	2.8253038	1.4617733	-0.0691788
12 C C21	1.3605120	-0.1608279	0.5655785
13 O O6	1.6920928	0.7685552	1.6166880
14 O O7	1.1277486	3.2775589	-0.7595761
15 O O8	-0.5064944	-1.6268604	0.2547845
16 C C1	-3.1472817	1.4704615	1.5009848
17 H H3	-2.7277545	2.1543265	2.2702185
18 C C2	2.3147073	-1.3148196	0.4175845
19 H H2	3.3207269	-1.0080552	0.8124508
20 H H5	1.9417968	-2.1644920	1.0555766
21 C C3	2.4060669	-1.7790320	-0.9891737
22 H H7	1.4364277	-2.0338144	-1.4514930
23 C C4	3.5532683	-1.9178878	-1.6485838
24 H H6	3.5909580	-2.2903691	-2.6808080
25 H H8	4.5293261	-1.6748037	-1.2080140
26 C C5	-4.6288835	1.3692107	1.4568438
27 H H1	-4.9511479	0.4377764	0.9191943
28 H H9	-5.0161667	2.2465185	0.8643337
29 C C6	-5.2327485	1.3951170	2.8482603
30 H H4	-4.8634235	0.5138108	3.4361297
31 H H13	-4.9005051	2.3207697	3.3886794
32 C C7	-6.7445566	1.3630783	2.7797142
33 H H10	-7.0779692	0.4529637	2.2143598
34 H H14	-7.1146758	2.2587068	2.2139575
35 C C8	-7.3546814	1.3504925	4.1655221
36 H H11	-6.9977043	0.4439210	4.7224337
37 H H18	-7.0024544	2.2494267	4.7376713
38 C C9	-8.8602622	1.3474292	4.1044626
39 H H16	-9.2310179	0.4527611	3.5478647
40 H H19	-9.2361319	2.2627020	3.5860178
41 H H20	-9.2895794	1.3246917	5.1352271

Syn-Cis TS 31 to 44

AM1 Heat of Formation: -48.392 kcal/mol

B3LYP/6-31G**/AM1 SCF total energy: -960.6099069 hartrees

Imaginary Mode -694.9 cm⁻¹

Cartesian Coordinates (Angstroms)

Atom	X	Y	Z

1 C C12	-1.5750539	3.0006569	-0.4848040
2 H H15	-1.3287993	3.6056275	-1.3873343
3 C C15	-2.3156605	0.7836945	1.1022074
4 H H12	-2.7984662	-0.2093626	1.0863165
5 O O5	-2.7008699	3.1679346	0.0635930
6 C C14	-0.5927145	2.0478277	-0.0536570
7 C C17	-1.0192116	0.8904225	0.6051810
8 C C18	0.7804182	2.2274944	-0.5030356
9 C C19	-0.1546929	-0.3229998	0.6034887
10 C C20	1.7895818	1.2494267	0.0223432
11 H H23	2.8060402	1.3569340	-0.4085954
12 C C21	1.3247009	-0.0657876	0.5729164
13 O O6	1.7642275	1.0031835	1.4348203
14 O O7	1.1384287	3.1226638	-1.2805472
15 O O8	-0.6174856	-1.4655473	0.6148341
16 C C1	-3.0651933	1.8885608	1.5257470
17 C C2	2.2183549	-1.2761575	0.5598651
18 H H2	3.2576008	-0.9649740	0.8518992
19 H H5	1.8455384	-1.9977465	1.3402698
20 C C3	2.2094102	-1.9555278	-0.7598602
21 H H7	1.2024804	-2.1916026	-1.1474153
22 C C4	3.3119260	-2.2957139	-1.4232593
23 H H6	3.2737738	-2.8235210	-2.3854064
24 H H8	4.3233517	-2.0769180	-1.0549020
25 H H21	-4.1660321	1.8481151	1.4122352
26 C C5	-2.5608195	2.8283250	2.5659592
27 H H1	-1.5354376	3.1998743	2.2969025
28 H H4	-2.4565982	2.2358906	3.5191488
29 C C6	-3.4955041	3.9980990	2.7947081
30 H H11	-3.6136588	4.5704804	1.8362959
31 H H16	-4.5111703	3.6206284	3.0857437
32 C C7	-2.9632088	4.9118879	3.8775385
33 H H9	-1.9538350	5.3011229	3.5791992
34 H H10	-2.8264914	4.3319715	4.8284349
35 C C8	-3.9021351	6.0742879	4.1234351
36 H H13	-4.9110318	5.6835780	4.4225687
37 H H17	-4.0405599	6.6502126	3.1700651
38 C C9	-3.3753063	6.9910375	5.1971360
39 H H14	-2.3833170	7.4128524	4.9037850
40 H H18	-3.2499978	6.4398202	6.1605430
41 H H19	-4.0832696	7.8384954	5.3650033

Syn-Trans TS 31 to 43

Heat of Formation: -51.973 kcal/mol

B3LYP/6-31G**//AM1 SCF total energy: -960.6072890 hartrees

Imaginary Mode -699.7 cm⁻¹

Atom	Cartesian Coordinates (Angstroms)		
	X	Y	Z

1 C C12	-1.6366510	2.8387231	-0.1435484
2 H H15	-1.4640206	3.9381173	-0.0912811
3 C C15	-1.9263993	0.1499962	0.6903823
4 H H12	-2.1043047	-0.5602070	1.5164550
5 O O5	-2.8250357	2.4259414	-0.2860457
6 C C16	-2.9881791	0.5022445	-0.1552675
7 C C14	-0.4921533	1.9886083	0.0005259
8 C C17	-0.6618362	0.7185583	0.5647519
9 C C18	0.8171837	2.5784210	-0.2509230
10 C C19	0.4864907	0.0101738	1.1949248
11 C C20	2.0075476	1.6934780	-0.0260771
12 H H23	2.8438035	1.8616584	-0.7349816
13 C C21	1.8479931	0.3883766	0.6825796
14 O O6	2.4158597	1.5392394	1.3426988
15 O O7	0.9721109	3.7316188	-0.6753853
16 O O8	0.3383179	-0.8525067	2.0619581
17 C C22	-4.3985457	0.3151524	0.2746762
18 H H5	-4.4519894	0.0574899	1.3667493
19 H H19	-4.9362371	1.2964465	0.1365922
20 C C23	2.8027420	-0.7548679	0.4654231
21 H H16	3.8523643	-0.3511587	0.4450277
22 H H20	2.7249573	-1.4487625	1.3505281
23 C C33	-5.0894014	-0.7615347	-0.5422912
24 H H39	-5.0751671	-0.4808405	-1.6284623
25 H H40	-4.5313293	-1.7299504	-0.4388607
26 C C34	-6.5200466	-0.9494024	-0.0833351
27 H H2	-6.5348070	-1.2001516	1.0104237
28 H H41	-7.0856582	0.0118964	-0.2109181
29 C C35	-7.2068675	-2.0513252	-0.8639773
30 H H43	-7.1944586	-1.7983878	-1.9574184
31 H H44	-6.6354381	-3.0102073	-0.7396804
32 C C36	-8.6296143	-2.2470463	-0.4050105
33 H H42	-8.6605334	-2.5239260	0.6765138
34 H H45	-9.2215615	-1.3097514	-0.5434666
35 H H46	-9.1177777	-3.0626474	-0.9912067
36 C C37	2.4956101	-1.5120029	-0.7746953
37 H H47	1.4645258	-1.9011308	-0.8414691
38 C C38	3.3864623	-1.7404389	-1.7376190
39 H H78	-2.8151409	0.5397480	-1.2523242
40 H H4	3.1412635	-2.3268250	-2.6340039
41 H H6	4.4176908	-1.3653148	-1.6964697