Enantioselective Synthesis of the Oxadecalin Core of Phomactin A via a Highly Stereoselective Diels–Alder Reaction

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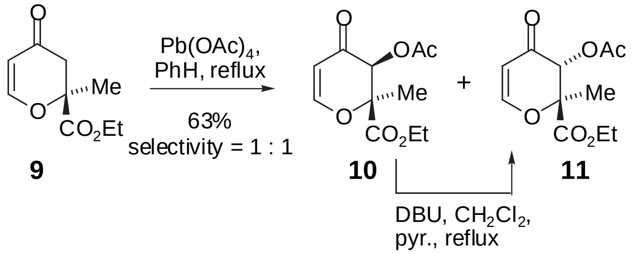
Supplementary Material

General. All glassware was dried in an oven at 140° C before use. All experiments were conducted under an atmosphere of dry argon unless indicated otherwise. Preparative reactions were stirred magnetically. Concentration *in vacuo* was performed on a Büchi rotary evaporator. Solvents were dried as follows: Methylene chloride, diethyl ether, tetrahydrofuran (THF), benzene and toluene were obtained from a dry solvent system (alumina) and used without further drying. Pyridine was freshly distilled from CaH_2. All NMR spectra were recorded on a Bruker model AMX-400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) or a Bruker model DRX-500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) NMR spectrometer. Chemical shifts are reported in parts per million (ppm) from internal tetramethylsilane (^{1}H-NMR spectra, δ 0.00 ppm) or the residual solvent signal of $CDCl_3$ (^{13}C-NMR spectra, δ 77.23 ppm). Spectra were taken in $CDCl_3$ unless noted otherwise. The following abbreviations were used in reporting spectra: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, bs = broad singlet, bd = broad doublet. Infrared spectra were taken on an Perkin Elmer 1600 Series FTIR Spectrometer using thin film deposition on polished NaCl plates. Peaks are reported in wave numbers (cm^{-1}). Low and high resolution mass spectra were obtained from a PE Sciex API 100 instrument under EI mode, and are reported in units of *m/e*. Column chromatography (low-pressure chromatography) was performed with E. Merck silica gel 60 (40-63 mesh). Thin layer chromatography (TLC) was carried out on Merck silica gel 60 F-254 glass-backed plates. TLC visualization was done with a 254 nm UV lamp and potassium permanganate or sulfo molybdic acid staining solution. All chemicals were purchased from Aldrich Chemical Co. and used as received.

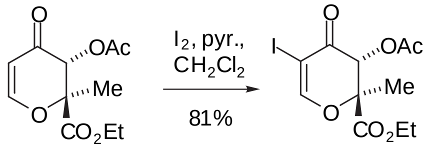


Pyrone 11. A solution of pyrone **9** (2.6 g, 14.1 mmol) in benzene (90 mL) was treated with $Pb(OAc)_4$ (19.0 g, 42.4 mmol, 3 equiv) and was refluxed for 36 h. The solution was

cooled to 23 °C and filtered through a fritted funnel with Et_2O washings. The resulting solution was concentrated *in vacuo*. ^{1}H NMR analysis of the crude mixture revealed that a 1 : 1 ratio of α-acetoxy pyrones **10** and **11** had been formed. Purification by chromatography on SiO_2 (5-40% Et_2O/hexanes eluent) gave 0.98 g (29% yield) of the undesired diastereomer **10**, eluting first, followed by 1.17 g (34% yield) of the desired pyrone **11**, contaminated with ca. 10% of pyrone **10**. This mixture was further purified by HPLC (41 mm column, 30% EtOAc/hexanes eluent). The undesired pyrone **10** could be converted to the desired pyrone **11** via epimerization. Thus, **10** (0.98 g, 4.05 mmol) in CH_2Cl_2 (20 mL) was treated with pyridine (0.16 mL, 2.02 mmol) and DBU (0.060 mL, 0.40 mmol) and the resulting solution was refluxed for 6 h. The solution was cooled to 23 °C and washed with 1 N aqueous HCl (5 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product, a 1.4 : 1 ratio of pyrones **10** and **11**, was purified as described above. After two more recycles of pyrone **10**, an additional 0.65 g of pyrone **11** (19% with respect to starting pyrone **9**) was obtained.

Data for major **11**: $[\alpha]^{27}_{D}$ = + 60.0 ° (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 6.0 Hz, 1 H), 5.56 (s, 1 H), 5.47 (d, *J* = 6.0 Hz, 1 H), 4.30-4.18 (m, 2 H), 2.17 (s, 3 H), 1.67 (s, 3 H), 1.27 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.7, 169.1, 167.9, 160.4, 105.2, 84.2, 72.9, 62.4, 20.7, 20.5, 13.9; IR (neat) 3086.4, 2988.1, 1752.0, 1697.5, 1599.2, 1446.5, 1397.4, 1370.1, 1222.8, 1140.9, 1091.8, 1031.8 cm^{-1}; LRMS (CI) calcd for $C_{11}H_{14}O_6Na$ $(M + Na)^+$ 265.1, found 265.0.

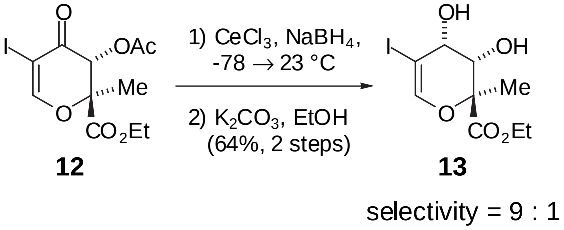
Data for minor **10**: $[\alpha]^{27}_{D}$ = + 130.8 ° (c = 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 6.0 Hz, 1 H), 5.79 (s, 1 H), 5.49 (d, *J* = 6.0 Hz, 1 H), 4.26 (q, *J* = 3.5 Hz, 2 H), 2.17 (s, 3 H), 1.60 (s, 3 H), 1.29 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 169.1, 168.4, 161.1, 105.5, 84.5, 71.3, 62.8, 20.5, 17.1, 13.9; IR (neat) 3086.4, 2988.1, 1752.0, 1686.5, 1593.8, 1446.5, 1408.3, 1370.1, 1206.4, 1130.0, 1097.3, 1037.2 cm^{-1}; ; LRMS (CI) calcd for $C_{11}H_{14}O_6Na$ $(M + Na)^+$ 265.1, found 264.9.



11 **12**

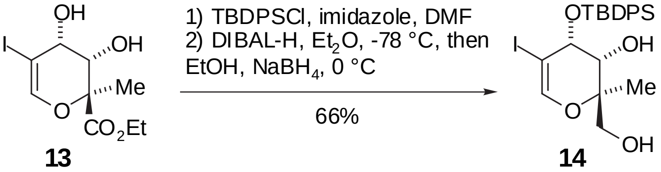
Vinyl iodide 12. A solution of pyrone **11** (0.85 g, 3.51 mmol) in CH_2Cl_2 (20 mL) was treated with pyridine (1.2 mL, 14.0 mmol, 4 equiv) and iodine (1.78 g, 7.02 mmol, 2 equiv) at 23 °C. After 5 h, the reaction was diluted with Et_2O (100 mL) and was washed with 10% aqueous sodium thiosulfate (2 x 10 mL), then with 1 M aqueous HCl (2 x 10 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. Chromatography on SiO_2 (10-30% EtOAc/hexanes eluent) then afforded 1.05 g (81%) of the vinyl iodide **12**.

Data for **12**: $[\alpha]^{27}_{D}$ = -6.9 ° (c = 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1 H), 5.70 (s, 1 H), 4.29-4.17 (m, 2 H), 2.17 (s, 3 H), 1.68 (s, 3 H), 1.25 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.1, 168.8, 167.3, 162.8, 85.0, 72.9, 72.2, 62.6, 20.6, 20.4, 13.9; IR (neat) 2983.3, 1753.3, 1705.4, 1571.2, 1441.7, 1369.8, 1249.9, 1221.2, 1134.9, 1082.2 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{17}INO_6$ $(M + NH_4)^+$ 386.0101, found 386.0085.



Diol 13. A solution of pyrone **12** (1.05 g, 2.85 mmol) in a 1 : 1 mixture of CH_2Cl_2 and anhydrous EtOH (30 mL) was treated with $CeCl_3$•$7H_2O$ (1.62 g, 4.35 mmol, 1.5 equiv). This solution was sonicated for 5 min, stirred at 23 °C for 15 min, then was cooled to –78 °C. Solid $NaBH_4$ (0.165 g, 4.35 mmol, 1.5 equiv) was then added and after being stirred at –78 °C for one hour, the mixture was warmed to 0 °C and stirred an additional hour. The reaction was quenched with sat. aqueous $NaHCO_3$ (10 mL), then was extracted with Et_2O (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. ^1H NMR analysis of the crude residue revealed a mixture of two isomers resulting from transfer of the acetate between the two diols. This mixture was dissolved in 95% aqueous EtOH (20 mL), treated with K_2CO_3 (0.2 g) and was stirred for 3 h at 23 °C. The mixture was then diluted with H_2O (20 mL) and was extracted with Et_2O (3 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. ^1H NMR analysis of the crude residue revealed a 9 : 1 ratio of diastereomers. Chromatography on SiO_2 (10-50% EtOAc/hexanes eluent) then afforded 0.61 g (64%) of the pure diol **13**.

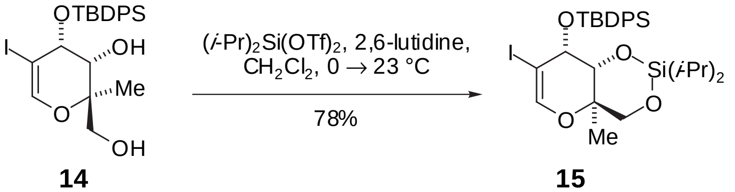
Data for **13**: $[\alpha]^{27}_D = -18.3$ ° (c = 0.36, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.68 (s, 1 H), 4.32-4.18 (m, 3 H), 4.04 (dd, *J* = 9.4, 4.4 Hz, 1 H), 3.41 (d, *J* = 9.5 Hz, 1 H), 2.81 (d, *J* = 6.6 Hz, 1 H), 1.57 (s, 3 H), 1.30 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 146.8, 78.7, 72.5, 68.4, 62.2, 21.6, 14.0; IR (neat) 3472.3, 2983.3, 1734.2, 1619.1, 1446.5, 1374.6, 1249.9, 1168.4, 1110.9, 1096.5, 1015.0 cm^{-1}; HRMS (EI) calcd for $C_9H_{17}INO_5$ $(M + NH_4)^+$ 346.0152, found 346.0149.



Diol 14. Diol **13** (0.261 g, 0.795 mmol) in DMF (1.5 mL) was treated at 23 °C with TBDPSCl (0.312 g, 1.19 mmol, 1.5 equiv) and imidazole (0.162 g, 2.39 mmol, 3 equiv). After being stirred for 48 h, the reaction was quenched with sat. aqueous $NaHCO_3$ (5 mL), diluted with H_2O (10 mL) and extracted with Et_2O (2 x 50 mL). The organic extract was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting residue was dissolved in Et_2O (4 mL), cooled to –78 °C and was treated with DIBAL-H (4 mL of a 1 M solution in hexanes, 5 equiv). After being stirred overnight at –78 °C, this solution was treated with anhydrous EtOH (9 mL) and $NaBH_4$ (0.150 g, 4 mmol, 5 equiv). The solution was warmed to 0 °C, stirred 1 h, then was quenched with sat. aqueous $NaHCO_3$ (5 mL) and poured into an Erlenmyer flask containing 20 mL of a 1 M solution of Rochelle's salt (KNa-tartrate). After being vigorously stirred for 1 h, this solution was extracted with Et_2O (3 x 50 mL) and the organic extract was dried over $MgSO_4$, filtered

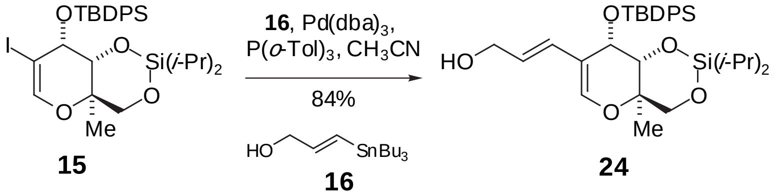
and concentrated *in vacuo*. Chromatography on SiO_2 (10-50% EtOAc/hexanes eluent) afforded 0.276 g (66%) of diol **14**.

Data for **14**: $[\alpha]^{27}_D$ = - 8.2 ° (c = 1.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.82 (m, 2 H), 7.75-7.73 (m, 2 H), 7.50-7.40 (m, 6 H), 6.67 (d, *J* = 1.0 Hz, 1 H), 4.34 (dd, *J* = 4.0, 1.0 Hz, 1 H), 3.68 (dd, *J* = 11.6, 3.3 Hz, 1 H), 3.53 (dd, *J* = 11.4, 8.6 Hz, 1 H), 3.27 (dd, *J* = 3.7, 2.6 Hz, 1 H), 2.76 (d, *J* = 2.5 Hz, 1 H), 2.29 (dd, *J* = 8.7, 3.8 Hz, 1 H), 1.17 (s, 9 H), 0.96 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 136.5, 135.9, 133.0, 132.0, 130.4, 130.2, 128.0, 127.7, 78.8, 71.5, 69.9, 68.4, 67.0, 27.2, 19.7, 18.3; IR (neat) 3429.8, 2930.8, 1618.0, 1427.5, 1178.6, 1111.4, 1072.9, 1049.4, 701.1 cm^{-1}; HRMS (FAB) calcd for $C_{23}H_{29}IO_4SiNa$ $(M + Na)^+$ 547.0778, found 547.0754.



Silylene 15. Diol **14** (0.245 g, 0.467 mmol) in CH_2Cl_2 (2 mL) at 0 °C was treated with a solution of $(i\text{-Pr})_2Si(OTf)_2$ (0.21 mL, 0.70 mmol, 1.5 equiv) and 2,6-lutidine (0.27 mL, 2.34 mmol, 5 equiv) in CH_2Cl_2 (2 mL). After 3 h, the mixture was warmed to 23 °C and stirred an additional hour. The reaction was then quenched with sat. aqueous $NaHCO_3$ (5 mL), diluted with H_2O (5 mL) and was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with 1 N HCl (2 x 5 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Chromatography on SiO_2 (5-10% Et_2O/hexanes) afforded 0.232 g (78%) of the diisopropyl silylene **15**.

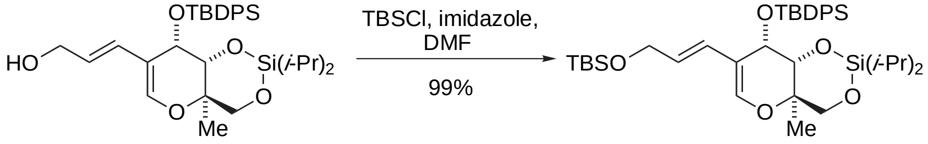
Data for **15**: $[\alpha]^{27}_D$ = + 29.0 ° (c = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.82 (m, 4 H), 7.47-7.32 (m, 6 H), 6.61 (s, 1 H), 4.42 (m, 1 H), 3.71 (A of ABq, J_{AB} = 12.1 Hz, 1 H), 3.56 (B of ABq, *J* = 12.1 Hz, 1 H), 3.51 (d, 3.7 Hz, 1 H), 1.20 (s, 9 H), 1.10-0.95 (m, 8 H), 0.83 (s, 3 H), 0.77 (s, 3 H), 0.74 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.3, 135.7, 135.3, 133.3, 132.7, 129.1, 128.9, 126.8, 126.7, 73.7, 71.4, 70.0, 67.2, 26.3, 19.2, 18.1, 16.0, 15.9, 15.8, 13.0, 11.8; IR (neat) 3046.8, 2940.0, 2862.2, 1619.9, 1464.4, 1425.6, 1386.7, 1367.3, 1143.8, 1095.3, 910.7, 852.4 cm^{-1}; HRMS (FAB) calcd for $C_{29}H_{41}IO_4Si_2Na$ $(M + Na)^+$ 659.1486, found 659.1518.



Diene 24. A solution of $P(o\text{-Tol})_3$ (0.022 g, 0.073 mmol, 0.2 equiv) in CH_3CN (1 mL) was degassed with a stream of Ar(g) (10 min), then was treated with $Pd_2(dba)_3$ (0.034 g, 0.037 mmol, 0.1 equiv) and this mixture was heated under argon(g) for 1 h at 90 °C. The solution was then cooled to 23 °C and treated with a mixture of vinyl iodide **15** (0.232 g, 0.365 mmol) and vinylstannane **16** (0.190 g, 0.547 mmol, 1.5 equiv) in CH_3CN (1 mL), then heated overnight under Ar(g) at 90 °C. The crude mixture was filtered through celite with a 1 : 1 Et_2O/hexanes wash and the solvent was removed *in vacuo*.

Chromatography of the crude residue on SiO_2 (5-20% EtOAc/hexanes) then afforded 0.174g (84%) of diene **24**.

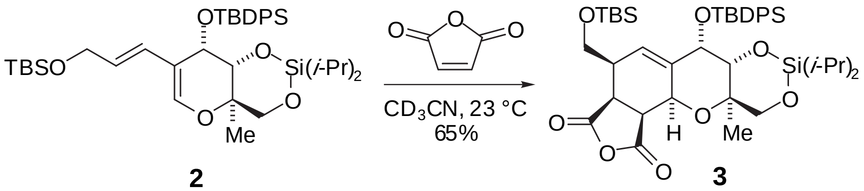
Data for **24**: $[\alpha]^{27}_{D}$ = + 54.6 ° (c = 0.8, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.0 Hz, 2 H), 7.73 (d, *J* = 7.0 Hz, 2 H), 7.44-7.36 (m, 6 H), 6.45 (s, 1 H), 6.25 (d, *J* = 15.5 Hz, 1 H), 5.82-5.76 (dt, *J* = 15.5, 6.0 Hz, 1 H), 4.57 (m, 1 H), 4.11-4.03 (m, 2 H), 3.76 (A of ABq, J_{AB} = 12.0 Hz, 1 H), 3.70 (B of ABq, J_{AB} = 13.0 Hz, 1 H), 3.64 (d, *J* = 3.8 Hz, 1 H), 1.12 (s, 9 H), 1.06-1.00 (m, 7 H), 0.92-0.82 (m, 7 H), 0.71 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.5, 136.0, 134.0, 134.0, 129.8, 129.7, 128.0, 127.6, 127.5, 125.2, 111.6, 71.8, 71.1, 67.1, 64.2, 27.0, 19.8, 18.7, 16.9, 16.8, 16.6, 13.8, 12.6; IR (neat) 3402.8, 3053.6, 2933.6, 2868.1, 1626.5, 1462.8, 1184.6, 1140.9, 1097.3, 917.2, 862.6, 704.4 cm^{-1}; HRMS (FAB) calcd for $C_{32}H_{46}O_5SiNa$ $(M + Na)^+$ 589.2782, found 589.2803.



21 **2**

Diene 2. Alcohol **21** (0.056 g, 0.099 mmol) in DMF (0.5 mL) was treated with imidazole (0.013 g, 0.198 mmol, 2 equiv) and TBSCl (0.022 g, 0.149 mmol, 1.5 equiv) at 23 °C. After being stirred for 18 h, the reaction was quenched with sat. aqueous $NaHCO_3$ (5 mL), diluted with H_2O (5 mL) and extracted with Et_2O (2 x 20 mL). The combined organic layers were washed with H_2O (5 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Chromatography of the crude residue on SiO_2 (5-10% Et_2O/hexanes) afforded 0.067 g (99%) of diene **2**.

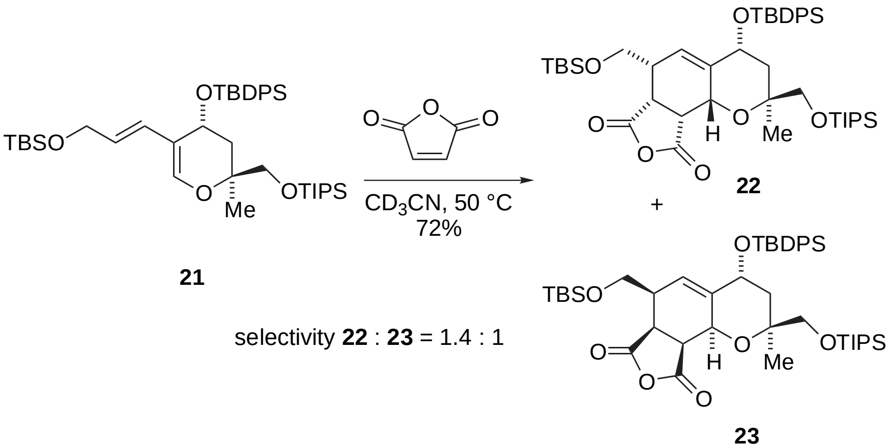
Data for **2**: $[\alpha]^{27}_{D}$ = + 44.0 ° (c = 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 6.7 Hz, 2 H), 7.72 (d, *J* = 6.8 Hz, 2 H), 7.45-7.34 (m, 6 H), 6.43 (s, 1 H), 6.30 (d, *J* = 15.6 Hz, 1 H), 5.77 (dt, *J* = 15.6, 5.7 Hz, 1 H), 4.57 (m, 1 H), 4.22-4.13 (m, 2 H), 3.72 (A of ABq, J_{AB} = 12.0 Hz, 1 H), 3.61 (B of ABq, J_{AB} = 12.0 Hz, 1 H), 3.50 (d, *J* = 3.8 Hz, 1 H), 1.11 (s, 9 H), 1.04 (d, *J* = 7.0 Hz, 3 H), 1.00 (d, *J* = 6.1 Hz, 3 H), 0.91 (m, 1 H), 0.91 (s, 9 H), 0.89-0.78 (m, 7 H), 0.67 (s, 3 H), 0.08 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 136.5, 136.4, 134.6, 134.3, 130.2, 130.0, 128.0, 127.9, 126.5, 126.2, 112.2, 77.0, 72.1, 71.5, 67.7, 65.0, 27.5, 26.5, 20.2, 19.2, 17.3, 17.2, 17.0, 14.2, 13.0, -4.7; IR (neat) 2922.7, 2857.2, 1626.5, 1462.8, 1386.4, 1250.0, 1184.6, 1146.4, 1097.3, 911.8, 862.6, 704.4 cm^{-1}; LRMS (CI) calcd for $C_{38}H_{60}O_5Si_3Na$ $(M + Na)^+$ 704.0, found 703.3.



2 **3**

Oxadecalin 3. A solution of diene **2** (0.039 g, 0.057 mmol) in CD_3CN (1 mL) in an NMR tube was treated with maleic anhydride (0.028 g, 0.286 mmol, 5 equiv) at 23 °C. ^{1}H NMR analysis after 6 h reaction time revealed that the reaction was complete and highly stereoselective (only one isomer observed). The solvent was removed *in vacuo* and chromatography on SiO_2 (10-60% EtOAc/hexanes eluent) of the crude mixture afforded 0.0388 g (65%) of the Diels-Alder adduct **3**, slightly contaminated (ca 2-5%) with maleic anhydride. The adduct was re-purified by HPLC (30% EtOAc/hexanes eluent, 21 mm column) for characterization purposes. It is worth noting that the crude ^{1}H NMR spectrum of the reaction mixture indicates very clean conversion of **2** to **3**. It is possible that the moderate yield of the reaction may be due to decomposition of the product during chromatography, perhaps through the opening of the anhydride moiety.

Data for **3**: $[\alpha]^{27}_D$ = + 28.6 ° (c = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.69 (m, 2 H), 7.57-7.55 (m, 2 H), 7.48-7.34 (m, 6 H), 6.00 (m, 1 H), 4.56 (dd, *J* = 5.9, 2.3 Hz, 1 H), 4.53 (m, 1 H), 4.24 (dd, *J* = 9.5, 9.5 Hz, 1 H), 4.02 (dd, *J* = 9.9, 6.5 Hz, 1 H), 3.92 (d, *J* = 11.9 Hz, 1 H), 3.63-3.51 (m, 4 H), 2.48 (m, 1 H), 1.13 (s, 9 H), 1.05-0.99 (m, 6 H), 0.98-0.90 (m, 17 H), 0.75 (s, 3 H), 0.12 (s, 3 H), 0.12 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 168.2, 140.3, 135.9, 135.3, 133.7, 132.6, 130.1, 130.0, 128.0, 127.8, 120.9, 78.0, 75.9, 70.0, 68.7, 67.5, 62.2, 44.9, 41.1, 38.1, 27.0, 25.9, 23.9, 19.4, 18.2, 17.3, 17.1, 16.9, 16.9, 12.3, 11.9, -5.4, -5.4; IR (neat) 2954.5, 2858.7, 1854.0, 1782.1, 1470.5, 1254.7, 1192.4, 1106.1, 928.7, 837.6 cm^{-1}; LRMS (CI) calcd for $C_{42}H_{62}O_8Si_3Na$ (M + Na) 802.1, found 801.4.



Oxadecalins 22 and 23. A solution of diene **21** (0.151 g, 0.213 mmol) in CD_3CN (1 mL) was treated with maleic anhydride (0.104 g, 1.06 mmol, 5 equiv) at 23 °C. After 0.5 h, the solvent was removed *in vacuo*. ^{1}H NMR analysis (400 MHz) of the crude mixture indicated the presence of two diastereomers in a ratio of 1.4 : 1. Chromatography on SiO_2 (10% EtOAc/hexanes eluent) afforded 0.123 g (72%) of the Diels-Alder adducts **22** and **23**. These adducts were separated by HPLC (10% EtOAc/hexanes eluent, 21 mm column) where the major isomer **22** eluted first. The relative configurations of **22** and **23** were determined by analysis of their NOESY spectra.

Data for **22**: $[\alpha]^{27}_D$ = + 66.6 ° (c = 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.61 (m, 4 H), 7.43-7.33 (m, 6 H), 5.66 (s, 1 H), 4.62 (m, 1 H), 4.58 (d, *J* = 7.8 Hz, 1 H), 4.15 (dd, *J* = 9.2, 9.2 Hz, 1 H), 3.86 (dd, *J* = 9.6, 7.5 Hz, 1 H), 3.57 (d, *J* = 10.1 Hz, 1 H), 3.51-3.37 (m, 3 H), 2.50 (m, 1 H), 2.02 (dd, *J* = 13.1, 5.0 Hz, 1 H), 1.57 (dd, *J* = 13.1, 9.3 Hz, 1 H), 1.10 (s, 3 H), 1.07 (s, 9 H), 0.95-0.91 (m, 21 H), 0.87 (s, 9 H), 0.09 (s, 3 H), 0.09 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 168.4, 139.1, 135.8, 133.9, 133.5, 129.7, 129.7, 127.6, 120.0, 76.1, 69.5, 68.3, 64.9, 63.1, 46.0, 42.5, 40.1, 36.2, 27.1, 26.5, 25.9, 19.3, 18.2, 18.0, 11.7, -5.4; IR (neat) 2932.5, 2865.9, 1789.7, 1462.5, 1107.6 cm^{-1}; HRMS (FAB) calcd for $C_{45}H_{70}O_7Si_3Na$ (M + Na)$^+$ 829.4327, found 829.4316.

Data for **23**: $[\alpha]^{27}_{D}$ = - 24.4 ° (c = 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.58 (m, 4 H), 7.45-7.33 (m, 6 H), 5.30 (s, 1 H), 4.65 (d, J = 7.7 Hz, 1 H), 4.40 (m, 1 H), 4.04 (dd, *J* = 9.2, 9.2 Hz, 1 H), 3.74 (dd, *J* = 9.7, 7.2 Hz, 1 H), 3.47-3.29 (m, 4 H), 2.41 (m, 1 H), 2.00 (dd, *J* = 13.7, 4.5 Hz, 1 H), 1.69 (dd, *J* = 13.7, 7.3 Hz, 1 H), 1.44 (s, 3 H), 1.06 (s, 9 H), 1.02-0.98 (m, 21 H), 0.99, 0.88 (s, 9 H), 0.06 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 168.4, 140.4, 135.6, 133.4, 133.3, 129.8, 127.7, 127.6, 120.5, 76.7, 70.6, 69.7, 62.8, 62.6, 45.3, 40.3, 40.1, 36.6, 27.0, 25.9, 21.9, 19.3, 18.2, 18.0, 11.8, -5.5; IR (neat) 2932.5, 2865.9, 1789.7, 1462.5, 1107.6 cm^{-1}; HRMS (FAB) calcd for $C_{45}H_{70}O_7Si_3Na$ (M + Na)$^+$ 829.4327, found 829.4364.