Supporting Text

Selected Experimental Details and Characterization Data for the Compounds of Fig. 14

General Remarks. The solvents used were purified and dried according to common procedures. Dry solvents were stored under Argon over molsieve. All commercially available reagents were purchased in the best quality available and used without further purification. All reactions were monitored by using coated glass plates. TLC was carried out with E. Merck silica gel 60-F254 plates. The plates were usually developed with a mixture of hexane/ethyl acetate. Unless the compound was colored, UV-active spots were detected at longwave UV (254 nm) or shortwave UV (180 nm). Most plates were additionally treated with visualization reagents. Preparative column chromatography and flash chromatography (1) was performed with silica gel 60 from Merck (0.040–0.063 μm, 240–400 mesh).

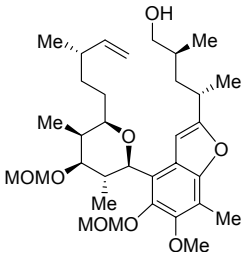
NMR spectra were recorded on either an Avance DPX 250 MHz, an Avance DRX 400 MHz, or an Avance DRX 600 MHz spectrometer (Bruker, Billerica, MA). Unless otherwise stated, all NMR spectra were measured in $CDCl_3$ solutions and referenced to the residual $CDCl_3$ signal (^1H, $\delta = 7.26$; ^{13}C, $\delta = 77.0$) or the tetramethylsilane signal (^1H, $\delta = 0.0$; ^{13}C, $\delta = 0.0$). The following abbreviations are used to describe spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, ddd = doublet of doublet of doublet, dddd = doublet of doublet of doublet of doublet etc.; other combinations derive from those listed. Coupling constants *J* are given in Hz; assignments of proton resonances were confirmed, when possible, by selective homonuclear decoupling experiments or by correlation spectroscopy.

Mass spectra were measured on a MAT 900 (Finnegan-MAT, San Jose, CA). High-resolution mass spectra (HRMS) were taken with a Finnigan MAT 8230 with a resolution of 10,000 (Finnigan-MAT, San Jose, CA).

IR spectra were recorded with a PerkinElmer 1600 Series FTIR spectrometer and are reported in wavenumbers (cm^{-1}). All compounds were measured as a thin film on a silicon single crystal plate (Si pellet). Elemental analyses were recorded on a PerkinElmer-240 Elementaranalyser. Optical rotations were measured on a P 341 PerkinElmer polarimeter. The length of the measuring chamber is 1 dm and the solution is kept at 20.0°C. The optical rotation is measured with monochromatic sodium light (589 nm) and, unless otherwise stated, $CHCl_3$ is used as solvent.

Synthesis of the Horner–Wadsworth–Emmons (HWE) Seco Compound 69

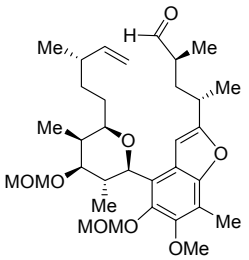
***tert*-Butyldiphenylsilyl Deprotection, → 57a**



57a

Silyl ether **57** (2.00 g, 2.46 mmol)was dissolved in dry tetrahydrofuran (THF) (50 ml) and tetrabutylammonium fluoride (3.0 ml, 1.0 M in THF) was added. The reaction mixture was stirred at ambient temperature for 20 h, then water was added, and the mixture was extracted with diethyl ether. After drying over $MgSO_4$, filtration and evaporation to dryness, a colorless oil was obtained that was purified by chromatography (hexane/ethyl acetate = 3:1 to 1:1) to give 1.39 g (98%). R_f.: 0.18 (hexane/ethyl acetate = 3:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 6.49 (s, 1H), 5.58 (ddd, *J* = 17.31, 10.11, 7.33 Hz, 1H), 5.03 (d, *J* = 5.56 Hz, 1H), 4.97 (d, *J* = 5.56 Hz, 1H), 4.88–4.78 (m, 2H), 4.74 (d, *J* = 6.82 Hz, 1H), 4.65 (d, *J* = 10.36 Hz, 1H), 4.58 (d, *J* = 6.82 Hz, 1H), 3.71 (s, 3H), 3.51 (s, 3H), 3.35–3.38 (m, 4H), 3.36 (s, 3H), 2.95 (tq, *J* = 7.07, 7.07 Hz, 1H), 2.31 (s, 3H), 2.13–2.96 (m, 3H), 1.68 (dtq, *J* = 6.57, 6.57, 6.57 Hz, 1H), 1.64–1.49 (m, 3H), 1.44–1.10 (m, 3H), 1.22 (d, *J* = 7.07 Hz, 3H), 1.05 (d, *J* = 6.82 Hz, 3H), 0.89 (d, *J* = 6.82 Hz, 3H), 0.89 (d, *J* = 6.57 Hz, 3H), 0.65 (d, *J* = 6.57, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 163.01 (s), 151.01 (s), 147.81 (s), 147.81 (d), 144.84 (d), 144.59 (s), 123.06 (s), 122.13 (s), 115.19 (s), 113.02 (t), 101.39 (d), 100.35 (t), 95.25 (t), 82.79 (d), 80.05 (d), 78.84 (d), 68.66 (t), 61.14 (q), 58.17 (q), 56.17 (q), 39.28 (t), 38.04 (d), 36.16 (d), 35.6 (d), 33.74 (d), 32.96 (t), 29.99 (t), 20.32 (q), 19.43 (q), 17.06 (q), 13.73 (q), 9.51 (q), 7.10 (q); HRMS (EI 70, eV) calc.: *m/z* = 576.3662 (M^+): found: *m/z* = 576.3650 (M^+); MS (EI 70, eV) *m/z* = 576.7 (100.0%, M^+), 470.5 (8.5%), 362.3 (59.4%), 330.2 (40.0%), 290.2 (93.4%), 193.2 (72.5%); $[\alpha]_D^{20}$ = +38.3 (*c* = 0.56, $CHCl_3$).

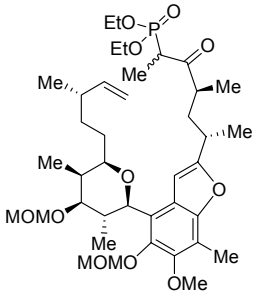
Dess–Martin Oxidation, → 57b



57b

Alcohol **57a** (240 mg, 0.42 mmol) was dissolved in 20 ml of dry CH_2Cl_2 and a suspension of $NaHCO_3$ (1.05 g, 12.5 mmol) and Dess–Martin periodinate (706.3 mg, 1.67 mmol) in 20 ml of CH_2CL_2 was added. The reaction mixture was stirred for 7 h at room temperature. Then a mixture of 20 ml of M $Na_2S_2O_3$ and 20 ml of sat. $NaHCO_3$ was added and stirred until the solution was clear. The mixture was extracted with CH_2Cl_2 (3 × 20 ml), dried over $MgSO_4$, filtered, and evaporated to dryness. A colorless oil in quantitative yield was obtained and directly used for the following reaction step. To substantiate the structure a ^1H NMR was measured. R_f.: 0.35 (hexane/ethyl acetate = 3:1); ^1H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 9.68 (d, J = 1.56 Hz, 1H), 6.61 (s, 1H), 5.68 (ddd, J = 17.25, 10.16, 7.20 Hz, 1H), 5.13 (d, J = 5.48 Hz, 1H), 5.07 (d, J = 5.48 Hz, 1H), 5.00–4.87 (m, 2H), 4.84 (d, J = 6.85, 1H), 4.75 (d, J = 10.39 Hz, 1H), 4.68 (d, J = 6.85 Hz, 1H), 3.82 (s, 3H), 3.85–3.72 (m, 1H), 3.61 (s, 3H), 3.63–3.49 (m, 1H), 3.46 (s, 3H), 3.07 (tq, J = 7.16, 7.16 Hz, 1H), 2.49 (tq, J = 7.20, 7.20 Hz, 1H), 2.41 (s, 3H), 2.26–1.96 (m, 3H), 1.94–1.56 (m, 4H), 1.57–1.18 (m, 2H), 1.36 (d, J = 6.85 Hz, 3H), 1.14 (d, J = 7.08 Hz, 6H), 0.99 (d, J = 6.62 Hz, 3H), 0.76 (d, J = 6.62 Hz, 3H).

Synthesis of the β-Ketophosphonate, → 57c

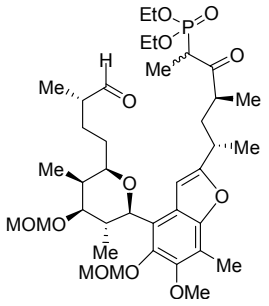


57c

A 100-ml flask was charged with diethyl ethylphosphonate (1.01 g, 6.24 mmol) in 15 ml of dry THF and cooled to –78°C. *n*-BuLi (1.67 ml, 2.5 M in hexane, 4.16 mmol) was added and the reaction mixture was stirred for 15 min at 0°C. A solution of aldehyde **57b** (239 mg, 0.42 mmol) in 5 ml of dry THF was added to the reaction by cannula. The reaction was stirred for 1 h and then quenched with 15 ml of sat. NH_4Cl. The solution was extracted with diethyl ether (3 × 20 ml). The combined organic layers were dried over $MgSO_4$, filtered, and then concentrated under reduced pressure to give a colorless oil. The oil was dissolved in 56 ml of dry CH_2Cl_2 $NaHCO_3$ (3.83 mg, 45.6 mmol), and Dess–Martin periodinate (2.58 mg, 6.08 mmol) was added and the reaction was stirred for 1 h. The reaction was diluted with diethyl ether, quenched 20 ml of 1 M $Na_2S_2O_3$ and 20 ml of sat. $NaHCO_3$, and the mixture was stirred until the solution went clear. The mixture was extracted with CH_2Cl_2 (3 × 20 ml), dried over $MgSO_4$, filtered, and evaporated to dryness. A colorless oil (278 mg, 86%) as a 1:1 mixture of diastereomers

was obtained. R_f: 0.20 and 0.24 (hexane/ethyl acetate = 1:1); ^{1}H NMR ($CDCl_3$, 400 MHz, 1 : 1 mixture of diastereomers): δ [ppm] = 6.57 (s, 0.5H) and 6.56 (s, 0.5H), 5.65 (ddd, *J* = 17.31, 10.11, 7.33 Hz, 1H), 5.10 (d, *J* = 5.56 Hz, 1H), 5.05 (d, *J* = 5.31, 0.5 H) and 5.04 (d, *J* = 5.56 Hz, 0.5H), 4.96–4.85 (m, 2H), 4.81 (d, *J* = 6.82 Hz, 0.5H) and 4.81 (d, *J* = 6.82 Hz, 0.5H), 4.72 (d, *J* = 10.36 Hz, 0.5H) and 4.71 (d, *J* = 10.36 Hz, 0.5H), 4.64 (d, *J* = 6.82 Hz, 0.5H) and 4.64 (d, *J* = 6.82 Hz, 0.5H), 4.19–4.38 (m, 6H), 3.78 (s, 1.5H) and 3.77 (s, 1.5H), 3.57 (s, 3H), 3.56–3.46 (m, 2H), 3.42 (s, 3H), 3.41–3.29 (m, 2H), 3.07 (tq, *J* = 6.91, 6.91 Hz, 0.5H) and 2.94 (tq, *J* = 6.91, 6.91 Hz, 0.5H), 2.88 (q, *J* = 6.99 Hz, 0.5H) and 2.84 (q, *J* = 7.07 Hz, 0.5H), 2.38 (s, 1.5H), 2.37 (s, 1.5H), 2.21–1.50 (m, 6H), 1.51–1.00 (m, 18H), 0.96 (d, *J* = 6.82 Hz, 3H), 0.72 (d, *J* = 6.57 Hz, 1.5H) and 0.71 (d, *J* = 6.32 Hz, 1.5 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ [ppm] = 210.67 (s) and 209.70 (s), 163.67 (s) and 162.77 (s), 151.10 (s) and 151.05 (s), 148.01 (s) and 147.85 (s), 144.81 (d), 144.70 (s) and 144.59 (s), 123.28 (s) and 123.13 (s), 122.09 (s) and 121.92 (s), 115.26 (s) and 115.11 (s), 113.04 (t), 102.05 (d) and 101.32 (d), 100.33 (t) and 100.32 (t), 95.24 (t), 82.75 (d) and 82.71 (d), 80.05 (d) and 80.03 (d), 78.84 (d) and 78.79 (d), 62.97 (t) and 62.94 (t), 62.92 (t) and 62.67 (t), 61.13 (q), 58.17 (q), 56.16 (q), 45.46 (d) and 44.96 (d), 44.75 (d), 38.02 (d) and 38.00 (d), 37.40 (t),36.20 (d), 35.64 (d), 32.97 (t), 32.02 (d) and 31.89 (d), 30.68 (t), 20.32 (q), 19.88 (q), 19.73 (q), 17.50 (q), 16.81 (q) and 16.70 (q), 13.73 (q) and 13.69 (q), 12.01 (q) and 11.90 (q), 9.53 (q) and 9.48 (q), 7.09 (q) and 7.07 (q); HRMS (EI, 70 eV) calc.: *m/z* = 738.4108 (M^+), found: *m/z* = 738.4077 (M^+); MS (EI 70 eV) *m/z* = 739.2 (30.0%, M^+), 707.2 (23.5%), 662.2 (8.4%), 516.1 (27.2%), 452.5 (20.8%).

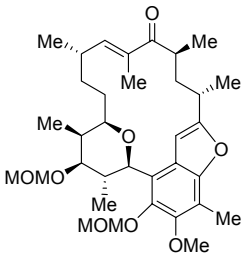
Synthesis of the HWE Seco Compound, → 69



β-Ketophosphonate **57c** (274 mg, 0.37 mmol) was dissolved in 0.63 ml of THF and 3.18 ml of *t*-BuOH. *N*-Methylmorpholine-*N*-oxide (2.04 ml, 0.2 M in H_2O, 0.41 mmol) and OsO_4 (932 µl, 0.04 M solution in *t*-BuOH, 0.04 mmol) were added and stirred at ambient temperature over night. As soon as the diol was formed, a solution of $NaIO_4$ (476 mg, 2.23 mmol) in 2.1 ml of water was added, and the resulting mixture was stirred for a further 2 h. The reaction mixture was quenched with 34 ml of a 1:1 mixture of sat. Na_2SO_3 and sat. $NaHCO_3$ and stirred for an additional hour. It was then extracted with diethyl ether, dried over $MgSO_4$, filtered, and concentrated *in vacuo* to obtain 259 mg (94%) of pure aldehyde **69** as a mixture of stereoisomers. Due to the instability of the aldehyde, it was immediately used for the following reaction step. To substantiate the

structure, a ^{1}H NMR was measured. R_f: 0.38 (ethyl acetate); ^{1}H NMR ($CDCl_3$, 250 MHz, mixture of diastereomers): δ [ppm] = 9.58 (d, *J* = 1.60 Hz, 1H), 6.58 (s, 0.5H), 6.57 (s, 0.5H), 5.15–5.04 (m, 2H), 4.82 (d, *J* = 6.85 Hz, 1H), 4.74 (d, *J* = 10.51, 1H), 4.67 (d, *J* = 6.85 Hz, 1H), 4.33–4.97 (m, 6H), 3.81 (s, 1.5H), 3.81 (s, 1.5H), 3.60 (s, 3H), 3.64–3.50 (m, 1H), 3.45 (s, 3H), 3.47–3.32 (m, 2H), 3.22–2.77 (m, 3H), 2.42 (s, 1.5H), 2.40 (s, 1.5H), 2.46–2.26 (m, 1H), 2.26–1.01 (m, 25H), 1.09 (d, *J* = 7.08 Hz, 3H), 0.75 (d, *J* = 6.40 Hz, 3H).

HWE Macrocyclization, Synthesis of Compound 70



n-BuLi (4.31 ml, 2.5 M in hexane, 10.8 mmol) was added to 230 ml of dry THF at 0°C and hydrolyzed with water (213 µl, 11.9 mmol) to form a fine suspension of LiOH. Aldehyde **69** (146.7 mg, 0.198 mmol) was added to this slurry and heated to reflux for 24 h. The reaction mixture was quenched with sat. NH_4Cl solution and extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give 55 mg (47%) of a colorless oil. R_f: 0.41 (hexane/ethyl acetate = 3:1); ^{1}H NMR ($CDCl_3$, 400 mHz): δ [ppm] = 6.59 (dd, *J* = 7.24, 1.41 Hz, 1H), 6.39 (s, 1H), 5.13 (d, *J* = 5.84 Hz, 1H), 5.04 (d, *J* = 5.84 Hz, 1H), 4.76 (d, *J* = 6.77 Hz, 1H), 4.62 (d, *J* = 6.77 Hz, 1H), 4.63 (d, *J* = 6.77 Hz, 1H), 3.78 (s, 3H), 3.55–3.49 (m, 1H), 3.51 (s, 3H), 3.44–3.41 (m, 1H), 3.40 (s, 3H), 3.00 (tq, *J* = 6.34, 6.34 Hz, 1H), 2.58–2.47 (m, 1H), 2.42 (s, 3H), 2.40–2.27 (m, 1H), 2.19–2.08 (m, 1H), 2.06–2.96 (m, 2H), 1.84–1.71 (m, 2H), 1.70–1.38 (m, 5H), 1.32 (d, *J* = 6.88, 1H), 1.27 (s, 3H), 1.04 (d, *J* = 7.09 Hz, 3H), 1.01 (d, *J* = 6.88 Hz, 3H), 0.93 (d, *J* = 6.98 Hz, 3H), 0.81 (d, *J* = 6.57 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 mHz): δ [ppm] = 206.02 (s), 160.75 (s), 145.57 (d), 143.33 (s), 134.32 (s), 126.67 (s), 123.95 (s), 121.71 (s), 114.14 (s), 105.45 (d), 104.36 (s), 99.47 (t), 94.93 (t), 82.09 (d), 78.67 (d), 78.61 (d), 60.63 (q), 57.93 (q), 55.67 (q), 39.82 (t), 38.65 (d), 37.14 (d), 37.14 (d), 31.94 (t), 31.59 (d), 31.21 (d), 28.73 (t), 19.62 (q), 19.32 (q), 18.95 (q), 13.16 (q), 13.02 (q), 9.19 (q), 7.29 (q); HRMS (EI, 70 eV) calc.: *m/z* = 586.3506 (M^+-*t*Bu), found: *m/z* = 586.3520 (M^+); MS (EI, 70 eV) *m/z* = 586.3 (100.0%, M^+), 525.4 (7.2%), 509.3 (12.5%), 309.1 (27.1%), 270.0 (16.1%); IR (neat): ν_{max} = 1687.9; $[\alpha]_D^{20}$ = +112.0 (*c* = 1.40, $CHCl_3$).

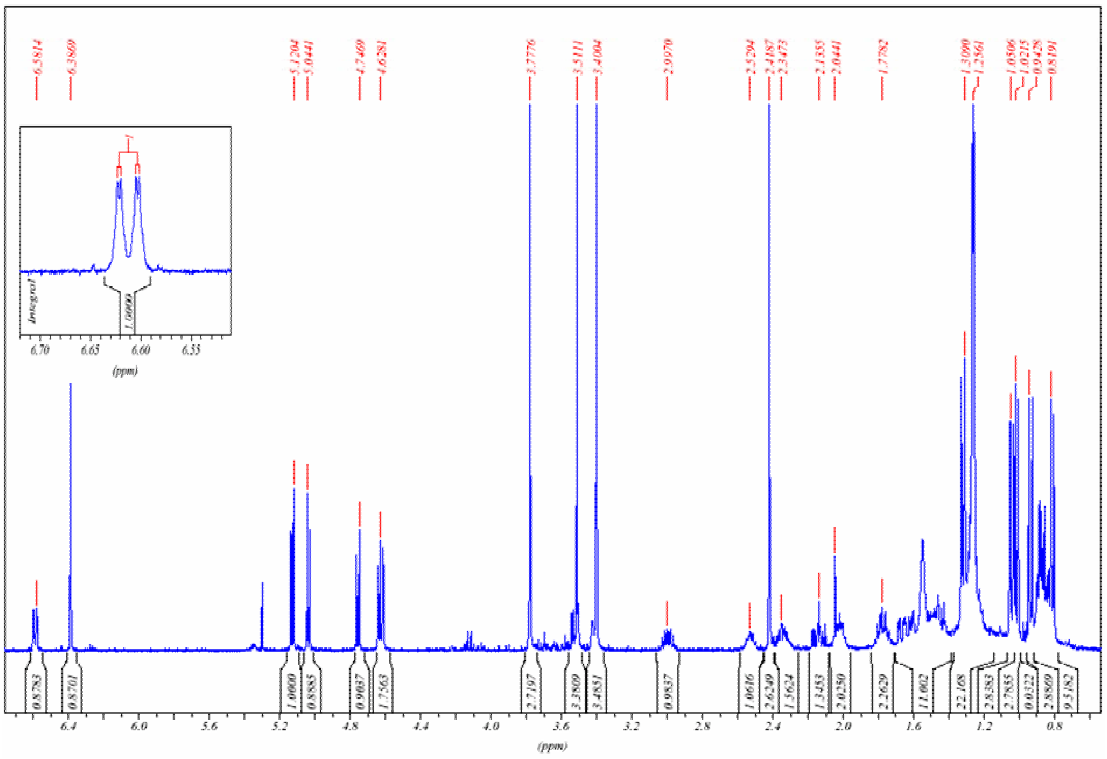
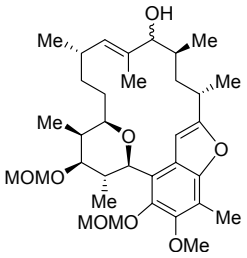


Fig. 15. ^{1}H NMR of compound **70.**

Reduction of the Carbonyl Group, Synthesis of Compound 71

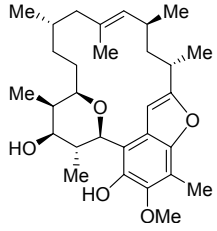
Luche reduction, → 70a



Enone **70** (30 mg, 0.051 mmol) was dissolved in 2.1 ml of MeOH and $CeCl_3 \cdot 7H_2O$ (190 mg, 0.51 mmol) and $NaBH_4$ (19 mg, 0.51 mmol) was added at –10°C. The reaction was stopped after 6 h by adding 5 ml of water and 3 ml of diethyl ether. The mixture was extracted with diethyl ether (3 × 10 ml) and the organic layers were dried over $MgSO_4$, filtered, and concentrated. Purification was carried out by chromatography (hexane/ethyl acetate = 10:1) to obtain 27.8 mg (93%) of pure allyl alcohol **70a** as a mixture of stereoisomers. R_f.: 0.27 (hexane/ethyl acetate = 3:1); ^{1}H NMR ($CDCl_3$, 400 mHz): δ [ppm] = 6.72 (bs, 1H), 5.37 (d, J = 7.83 Hz, 1H), 5.13 (d, J = 5.56 Hz, 1H), 5.02 (d, J =

5.56 Hz, 1H), 4.81 (d, J = 6.82 Hz, 1H), 4.67 (d, J = 6.57 Hz, 1H), 4.69–4.61 (m, 1H), 3.79 (s, 3H), 3.62–3.53 (m, 2H), 3.56 (s, 3H), 3.30–3.16 (m, 1H), 2.52–2.31 (m, 1H), 2.40 (s, 3H), 2.16–1.92 (m, 3H), 1.75–1.58 (m, 5H), 1.57–1.39 (m, 5H), 1.35 (d, J = 7.07 Hz, 3H), 1.31–1.24 (m, 4H), 1.27 (s, 3H), 1,14 (d, J = 7.07 Hz, 3H), 0.92 (d, J = 6.57 Hz, 3H), 0.90 (d, J = 7.07 Hz, 3H); ^{13}C NMR ($CDCl_3$, 150 mHz, quaternary carbons were missing due to slow relaxation time and diastereomeric mixture): δ [ppm] = 150.08 (s), 146.54 (s), 143.03 (s), 113.88 (s), 110.77 (s), 104.19 (d), 102.20 (t), 99.04 (t), 94.45 (t), 81.77 (d), 79.17 (d), 78.16 (d), 60.20 (q), 57.31 (q), 55.19 (q), 36.33 (d), 36.14 (t), 35.99 (d), 33.68 (d), 32.97 (d), 31.41 (d), 30.45 (d), 30.25 (d), 24.24 (t), 22.17 (t), 18.53 (q), 18.16 (q), 14.92 (q), 13.59 (q), 12.79 (q), 8.57 (q), 6.87 (q); HRMS (EI, 70 eV) calc.: *m/z* = 588.3662 (M^+), found: *m/z* = 588.3678 (M^+); MS (EI, 70 eV) *m/z* = 570.2 (13.1%, M^+), 526.2 (23.3%), 481.1 (13.4%), 229.9 (45.1%).

Barton–McCombie Deoxygenation and Methoxymethyl Chloride Deprotection, → 71



71

A solution of allylic alcohol **70a** (29 mg, 0.049 mmol) in THF (2 ml) was added to a suspension of NaH (10 mg, 0.25 mmol) in THF (2 ml). Imidazole (2 mg, 0.029 mmol) and carbon disulfide (0.3 ml, 5.0 mmol) were added, and the reaction was warmed until the reaction reached reflux temperature. After 30 h at this temperature, the reaction was allowed to cool to room temperature and methyl iodide (0.3 ml, 5.0 mmol) was added. After 12 h, water (3 ml) was added and the product extracted to ether (4 × 5 ml). The organic fractions were combined, washed with brine (10 ml), dried over $MgSO_4$, and concentrated. The crude material was purified by flash column chromatography (hexane/ethyl acetate = 6:1) to afford the xanthate, as a yellow oil (29 mg, 87%).

To a solution of xanthate (29 mg, 0.043 mmol) in degassed benzene (3 ml) was added tributyltinhydride (300 mg, 1.03 mmol) and AIBN (2 mg, 0.01 mmol). The reaction was warmed to 70°C. After 4 h, water (3 ml) was added, and the product was extracted to ether (3 × 5 ml). The organic fractions were combined, washed with brine, and dried over $MgSO_4$. The solvent was removed and the product was redissolved in ether (5 ml). A saturated aqueous solution of potassium fluoride was added, and this biphasic mixture was stirred vigorously. After 1 h, the layers were separated and the aqueous layer was

extracted with ether (3 × 5 ml). The organic fractions were combined, filtered through Celite, then washed with brine and dried over $MgSO_4$. The solvent was removed and the crude material purified by flash column chromatography with hexane and EtOAc (6:1) as eluant to afford an alkene as a colorless oil (21 mg, 86%).

To a solution of the alkene (20 mg, 0.034 mmol) in THF (3 ml) was added aqueous HCl (2 N, 0.3 ml). The reaction was warmed to 50°C. After 18 h, water (3 ml) was added and the product was extracted to ether (3 × 5 ml). The organic fractions were combined, washed with brine, and dried over $MgSO_4$. The solvent was removed and the crude material purified by flash column chromatography (hexane/ethyl acetate = 4:1) to afford alkene **71** as a white powder (16 mg, 97%).

R_f: 0.41 (hexane/ethyl acetate = 3:1); ^{1}H NMR ($CDCl_3$, 400 mHz): δ [ppm] = 6.42 (s, 1H), 5.39 (s, 1H), 4.96 (d, J = 7.32 Hz, 1H), 4.52 (d, J = 10.11 Hz, 1H), 3.76 (bd, J = 6.32 Hz, 1H), 3.69 (s, 3H), 3.54 (ddd, J = 10.48, 5.18, 5.18 Hz, 1H), 2.92 (dddd, J = 18.66, 6.85, 6.85, 4.89 Hz, 1H), 2.33 (s, 3H), 2.06–1.98 (m, 1H), 1.87 (ddd, J = 6.94, 4.67, 2.40 Hz, 1H), 1.83–1.40 (m, 7H), 1.43 (s, 3H),1.42–1.28 (m, 4H), 1.20 (d, J = 7.07 Hz, 3H), 1.09 (bs, 3H), 1.04 (d, J = 6.82 Hz, 3H), 0.79 (d, J = 6.57 Hz, 3H), 0.77 (d, J = 6.32 Hz, 3H), 0.76 (d, J = 6.32 Hz, 3H). ^{13}C NMR ($CDCl_3$, 150 mHz, quaternary carbons showed to be missing due to slow relaxation time and/or dynamic effects): δ [ppm] = 161.29 (s), 148.92 (s), 141.93 (s), 135.40 (s), 130.47 (d), 115.66 (s), 112.96 (s), 105.03 (d), 77.58 (d), 76.71 (d), 61.77 (q), 48.67 (t), 43.23 (t), 41.80 (d), 38.44 (d), 33.31 (t), 32.94 (d), 32.52 (d), 30.27 (d), 28.45 (t), 22.47 (q), 21.25 (q), 20.92 (q), 14.99 (q), 13.22 (q), 9.90 (q), 8.99 (q); HRMS (EI, 70 eV) calc.: m/z = 484.3189 (M^+), found: m/z = 484.3172 (M^+); MS (EI, 70 eV) m/z = 484.5 (100.0%, M^+), 466.3 (24.1%, M^+-H_2O).

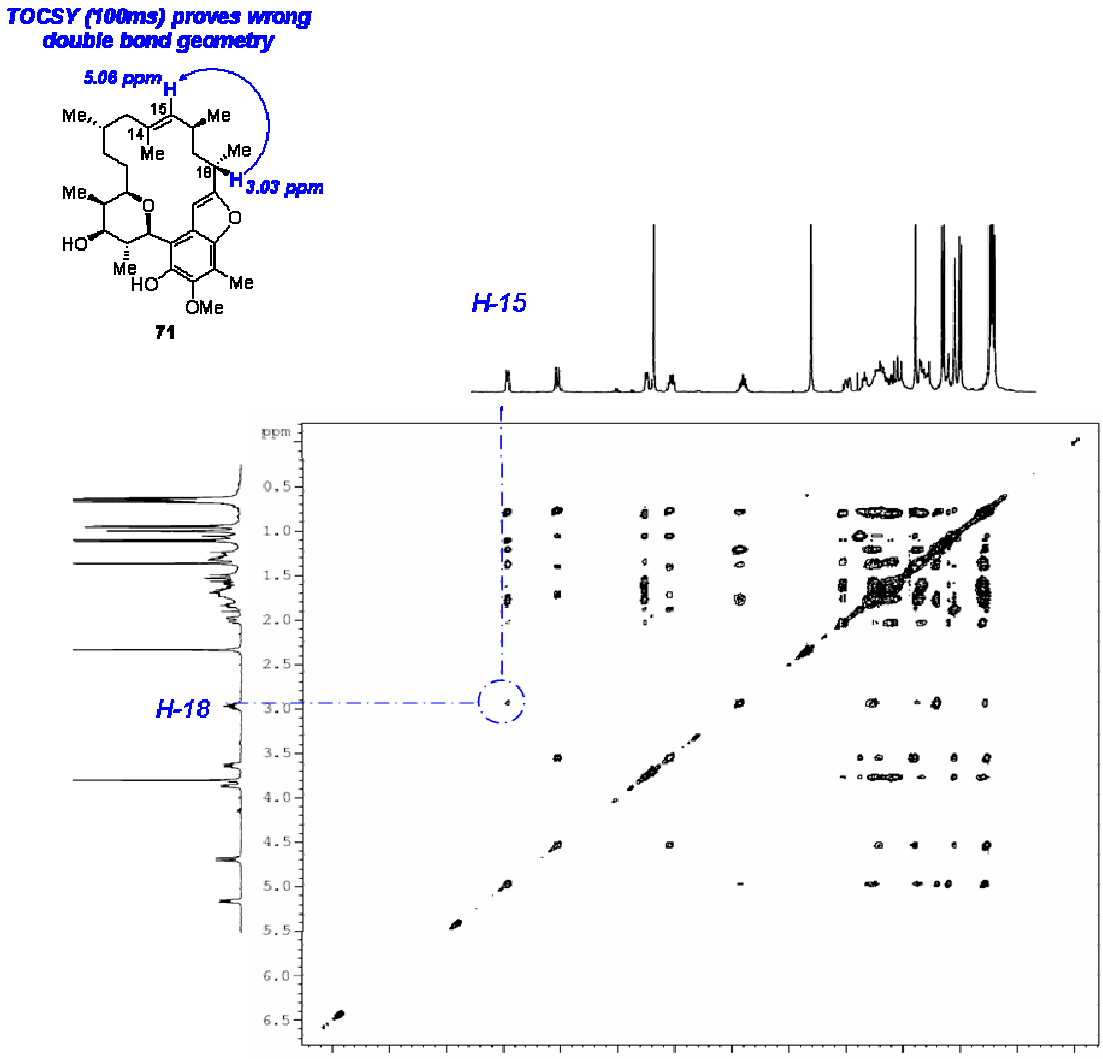


Fig. 16. 2D NMR spectrum of compound **71** (HH TOCSY).

1. Still, W. C., Kahn, M. & Mitra, A. (1978) *J. Org. Chem.* **43,** 2923.