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Supporting Information

Total Synthesis of Disciformycin A and B: Unusually Exigent Targets of Biological Significance

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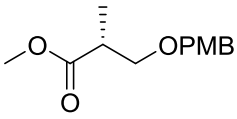
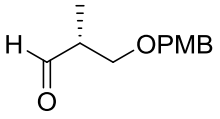
General: Unless otherwise noted, all reactions were carried out under Ar in flamed-dried glassware using anhydrous solvents. Anhydrous solvents were prepared by distillation over the indicated drying agents prior to use and were transferred under Ar: THF, Et_2O (Mg/anthracene), toluene (Na/K), CH_2Cl_2, MeOH (Mg); DMF and Et_3N were dried by an adsorption solvent purification system based on molecular sieves. Thin layer chromatography (TLC): Macherey-Nagel precoated plates (POLYGRAM®SIL/UV254). Flash chromatography: Merck silica gel 60 (40−63 µm) with technical grade solvents. NMR: Spectra were recorded on Bruker AV VIII 400 or 600 spectrometers in the solvents indicated. The solvent signals were used as references, and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_C = 77.0 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm; CD_3OD: δ_C = 49.0 ppm; residual CHD_2OD in CD_3OD: δ_H = 3.31 ppm; CD_2Cl_2: δ_C = 54.0 ppm; residual $CHDCl_2$ in CD_2Cl_2: δ_H = 5.32 ppm). ^{119}Sn NMR spectra were recorded using Me_4Sn as an external standard. IR: Bruker ALPHA Platinum-ATR, wavenumbers ($\tilde{\nu}$) in cm^{-1}. MS: Finnigan MAT 8200 (EI, 70 eV), Bruker ESQ 3000 (ESI), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or Finnigan Mat 95. Optical rotation ($[\alpha]_D^{20}$ and $[\alpha]_D^{25}$): Krüss P8000-T, 10 cm/1 mL cell. Chiral GC: Agilent 7890B GC. Unless otherwise noted, all commercially available compounds (ABCR, Acros, Aldrich, Alfa Aesar, TCI) were used as received. $[Cp^*RuCl]_4$ was prepared following a literature procedure and was stored under Ar.[1]

Preparation of the Building Blocks

Methyl (*R*)-3-((4-methoxybenzyl)oxy)-2-methylpropanoate (S1). (*R*)-Methyl 3-hydroxy-2-methylpropionate (**5**, 5.1 g, 43.1 mmol) and pyridinium *p*-toluenesulfonate (1.1 g, 4.3 mmol) were added to a solution of freshly prepared 4-methoxybenzyl-2,2,2-trichloroacetimidate (14.6 g, 51.7 mmol) in CH_2Cl_2 (110 mL). The mixture was stirred for 17 h during which time a white solid was formed. The reaction was quenched with sat. aq. $NaHCO_3$ (100 mL). After phase separation, the aqueous layer was rinsed with CH_2Cl_2. The organic extracts were combined, washed with brine (200 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was mixed with 1:1 hexane/CH_2Cl_2 and the insoluble precipitates were filtered off. The filtrate was concentrated and the residue purified by gradient flash chromatography (hexane:EtOAc, 20:1 to 10:1) to give the title compound as a colorless oil (8.7 g, 85%). $[\alpha]_D^{20}$ = −11.1 (c = 1.0, $CHCl_3$); HRMS (ESI): *m/z* calcd for $C_{13}H_{18}O_4Na$ $[M+Na]^+$: 261.1097, found: 261.1098. Spectral characteristics were identical to those previously reported in the literature.[2]



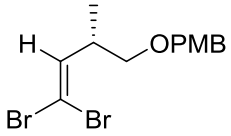
(*R*)-3-((4-Methoxybenzyl)oxy)-2-methylpropanal (6). A solution of $LiAlH_4$ (1.0 M in diethyl ether, 54.6 mL, 54.6 mmol) was added at 0 °C to a solution of ester **S1** (8.7 g, 36.4 mmol) in Et_2O (90 mL) via a dropping funnel and the resulting mixture was stirred overnight at rt. After cooling to 0 °C, sodium sulfate decahydrate



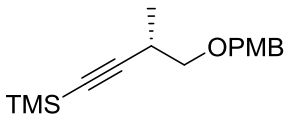
(23.4 g, 72.8 mmol) was added in small portions over 10 min. The resulting mixture was stirred for 30 min at ambient temperature, and then filtered through a pad of Celite®, eluding with Et_2O. The filtrate was concentrated in vacuo, and the residue (a pale yellow oil) was subjected to Swern oxidation without further purification.

DMSO (7.8 mL, 109.2 mmol) was added dropwise at –78 °C to a solution of oxalyl chloride (4.7 mL, 54.6 mmol) in CH_2Cl_2 (85 mL). After 30 min, a solution of the crude product described above in CH_2Cl_2 (20 mL) was added dropwise. The resulting mixture was stirred for 90 min at −78 °C. After addition of *i*-Pr_2NEt (28.5 mL, 163.7 mmol), the mixture was slowly warmed to 0 °C over 1.5 h. The reaction was then quenched with sat. aq. NH_4Cl solution at this temperature. The organic phase was separated, diluted with CH_2Cl_2, and washed with sat. aq. NH_4Cl solution (3 x). The combined aqueous layers were back-extracted with CH_2Cl_2. The organic extracts were combined, dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting crude aldehyde was used in the next step without further purification since we observed (partial) epimerization during attempted silica gel chromatography. The optical rotation was measured on the crude product: $[\alpha]_D^{20}$ = −18.3 (c = 1.0, $CHCl_3$). Spectral characteristics were identical to those previously reported.[2]

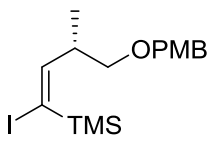
(*S*)-1-(((4,4-Dibromo-2-methylbut-3-en-1-yl)oxy)methyl)-4-methoxybenzene (S2). PPh_3 (28.6 g, 109.2 mmol) was added in portions to a stirred solution of CBr_4 (18.1 g, 54.6 mmol) in CH_2Cl_2 (260 mL) at 0 °C, and the resulting mixture was stirred for 1 h. The brown suspension was cooled to −78 °C before a solution of crude aldehyde **6** (7.6 g, 36.4 mmol) in CH_2Cl_2 (80 mL) was added dropwise over 30 min. After 1 h of additional stirring at −78 °C, the reaction was quenched by pouring the cold solution into vigorously stirred hexanes (200 mL). The resulting precipitates were filtered off and the filtrate was concentrated under reduced pressure. The residue was mixed with cold hexane (200 mL) once again, and the resulting precipitates were filtered off. The residue was concentrated in vacuo and the residue was purified by flash chromatography (CH_2Cl_2:hexane, 1:2 to 1:1) to give product **S2** as a colorless oil (10.0 g, 75% over 3 steps). $[\alpha]_D^{20}$ = −10.9 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 − 7.23 (m, 2H), 6.91 − 6.87 (m, 2H), 6.30 (d, *J* = 9.1 Hz, 1H), 4.45 and 4.44 (ABq, J_{AB} = 11.7 Hz, 2H), 3.81 (s, 3H), 3.36 and 3.33 (ABX, J_{AB} = 9.3 Hz, J_{AX} = 6.2 Hz, J_{BX} = 6.0 Hz, 2H), 2.77 (dqdd, *J* = 9.2, 6.9, 6.3, 6.0 Hz, 1H), 1.05 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 141.2, 130.3, 129.2, 113.8, 88.8, 72.7, 72.6, 55.3, 38.7, 15.9; IR (film): 2961, 2931, 2854, 2836, 1612, 1511, 1455, 1244, 1090, 1034, 818, 781 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{16}O_2Br_2Na$ $[M+Na]^+$: 384.9409, found: 384.9412.



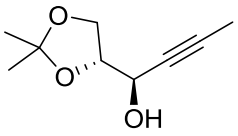
(*S*)-(4-((4-Methoxybenzyl)oxy)-3-methylbut-1-yn-1-yl)trimethylsilane (7). nBuLi (1.6 M hexane, 15.5 mL, 24.8 mmol) was added dropwise at −78 °C to a solution of dibromide **S2** (4.5 g, 12.4 mmol) in THF (62 mL) and the resulting mixture was stirred for 90 min at this temperature. TMSCl (7.9 mL, 62.2 mmol, 5 equiv) was then introduced and the cooling bath was removed. After 3 h, the reaction was quenched with sat. aq. NH_4Cl solution (60 mL). The layers were separated and the aqueous layer was rinsed with *tert*-butyl methyl ether (2 x 60 mL). The organic extracts were combined, washed with brine (60 mL), dried over $MgSO_4$, and concentrated in *vacuo*. Purification of the residue by gradient flash chromatography (hexane:EtOAc, 39:1 to 19:1) gave desired product **7** as a colorless oil (3.32 g, 96 %). $[\alpha]_D^{20}$ = −4.5 (c = 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 − 7.26 (m, 2H), 6.90 − 6.86 (m, 2H), 4.49 and 4.49 (ABq, J_{AB} = 12.3 Hz, 2H), 3.81 (s, 3H), 3.51 (dd, *J* = 9.1, 5.9 Hz, 1H), 3.33 (dd, *J* = 9.1, 7.8 Hz, 1H), 2.75 (dqd, *J* = 7.7, 6.9, 5.9 Hz, 1H), 1.20 (d, *J* = 6.9 Hz, 3H), 0.15 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 130.4, 129.2, 113.7, 109.0, 85.0, 73.7, 72.6, 55.3, 27.7, 17.8, 0.2; IR (film): 2958, 2899, 2856, 2167, 1613, 1513, 1247, 1090, 840 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{16}H_{24}O_2SiNa$ [M+Na]$^+$: 299.1438, found: 299.1435.



(*S*,*E*)-(1-Iodo-4-((4-methoxybenzyl)oxy)-3-methylbut-1-en-1-yl)trimethylsilane (8). A solution of alkyne **7** (3.3 g, 11.9 mmol) in THF (50 mL) was added to a solution of freshly prepared Schwartz's reagent (4.6 g, 17.9 mmol)[3] in THF (70 mL) via syringe. After stirring for 20 h, the mixture was cooled to −78 °C before a solution of I_2 (6.1 g, 23.9 mmol) in THF (70 mL) was added dropwise via cannula. The mixture was allowed to warm to 0 °C and stirring continued for 1 h. The reaction was quenched with sat. aq. $NaHCO_3$ solution (100 mL) followed by sat. aq. sodium thiosulfate solution (100 mL) at 0 °C. After phase separation, the aqueous layer was extracted with *tert*-butyl methyl ether (2 x), and the combined organic extracts were washed with water and brine, dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by gradient flash chromatography (30:1 to 20:1, hexane:EtOAc) gave the title compound as a bright orange oil (2.99 g, 62%). $[\alpha]_D^{20}$ = −15.5 (c = 1.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 2H), 6.96 (d, *J* = 10.5 Hz, 1H), 6.90 – 6.86 (m, 2H), 4.43 (s, 2H), 3.81 (s, 3H), 3.27 (dd, *J* = 9.1, 6.6 Hz, 1H), 3.24 (dd, *J* = 9.1, 6.6 Hz, 1H), 2.69 (app. dsext, *J* = 10.5, 6.6 Hz, 1H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.26 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 158.6, 130.4, 129.1, 113.7, 107.6, 73.6, 72.6, 55.3, 40.2, 17.2, 1.2; IR (film): 2955, 2854, 1613, 1512, 1301, 1247, 1173, 1094, 1037, 841, 759 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{16}H_{25}IO_2SiNa$ [M+Na]$^+$: 427.0561, found: 427.0565.

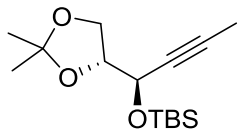


(*R*)-1-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)but-2-yn-1-ol (S3). (–)-*N*-Methyl ephedrine (5.8 g, 32 mmol) and *i*-Pr_2NEt (5.6 mL, 32 mmol) were added to a solution of $Zn(OTf)_2$ (11.7 g, 32 mmol)[4] in toluene (120 mL). The resulting white slurry was stirred for 3 h. Condensed propyne (about 7



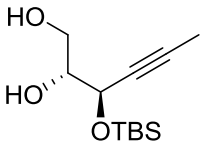
mL) was then transferred to the reaction vessel via a cannula at rt (Note: the Schlenk flask containing the condensed propyne was kept at −78 °C during the transfer). After 45 min, (*R*)-1,2-isopropylidene glyceraldehyde (**9**, 6.0 g, 23 mmol, 50 % *w/w* in CH_2Cl_2) was added in one portion, and the resulting mixture was stirred for 18 h at ambient temperature. The reaction was quenched with sat. aq. NH_4Cl (250 mL). After phase separation, the organic layer was rinsed with water (100 mL). The aqueous solutions were combined and washed with *tert*-butyl methyl ether (2 × 100 mL). The combined organic extracts were washed with brine (200 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure (Note: as the desired product is volatile, solvents were carefully evaporated at 70 mbar at 40 °C bath temperature). Purification of the residue by gradient flash chromatography (hexane:EtOAc, 8:2 to 7:3) provided the title compound as a pale yellow oil (3.9 g, quant., dr = 97:3 by GC analysis, dr = 94:6 by ^{1}H NMR by integration of the signals at 4.26 and 4.45 ppm, respectively). $[\alpha]_D^{25}$ = +17.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.26 (dq, *J* = 6.9, 2.2 Hz, 1H), 4.17 – 4.06 (m, 2H), 3.87 (dd, *J* = 8.4, 5.2 Hz, 1H), 1.85 (d, *J* = 2.2 Hz, 3H), 1.65 (brs, 1H), 1.45 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 110.4, 82.8, 79.1, 76.4, 66.2, 64.5, 26.8, 25.3, 3.6; IR (film): 3434, 2987, 2921, 2235, 1372, 1254, 1213, 1070, 853 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_9H_{14}O_3$ Na $[M+Na]^+$: 193.0835, found: 193.0836.

***tert*-Butyl(((*R*)-1-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)but-2-yn-1-yl)oxy)dimethylsilane (10)**.



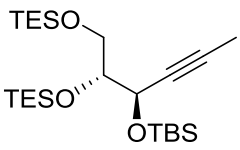
Imidazole (5.4 g, 79 mmol) was added to a solution of alcohol **S3** (6.7 g, 39 mmol) in CH_2Cl_2 (190 mL). Once the imidazole had fully dissolved (ca. 5 min), TBSCl (7.1 g, 47 mmol) was added and the resulting mixture was stirred for 2 h. The reaction was quenched with sat. aq. $NaHCO_3$ solution (250 mL). The organic layer was isolated and washed with water and brine, dried over $MgSO_4$ and filtered through a pad of silica (rinsed with CH_2Cl_2). The filtrate was evaporated under reduced pressure (130 mbar) at 40 °C to give the title compound as a colorless oil (11.0 g, 98%). $[\alpha]_D^{20}$ = −11.8 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.40 (dq, *J* = 5.9, 2.1 Hz, 1H), 4.12 – 4.02 (m, 2H), 3.96 (dd, *J* = 8.1, 5.8 Hz, 1H), 1.83 (d, *J* = 2.2 Hz, 3H), 1.43 (s, 3H), 1.35 (s, 3H), 0.90 (s, 9H), 0.13(s, 3H), 0.11 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 109.9, 81.8, 78.8, 77.4, 66.3, 65.2, 26.6, 25.8, 25.5, 18.3, 3.6, –4.7, –5.0; IR (film): 2955, 2930, 2858, 2238, 1252, 1071, 837 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{15}H_{28}O_3SiNa$ $[M+Na]^+$: 307.1700, found: 307.1698.

(2*R*,3*R*)-3-((*tert*-Butyldimethylsilyl)oxy)hex-4-yne-1,2-diol (S4). According to the procedures described by Konosu and Oida,[5] $BF_3{\cdot}OEt_2$ (0.31 mL, 2.5 mmol) was added at 0 °C to a stirred solution of compound **10** (9.5 g, 33 mmol) and 1,3-propanedithiol (8.7 mL, 87 mmol) in CH_2Cl_2 (140 mL). After 30 min, the

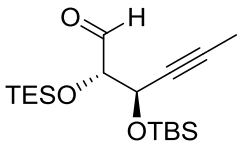


reaction was quenched with sat. aq. $NaHCO_3$ (100 mL). After phase separation, the aqueous phase was rinsed with CH_2Cl_2 (2 x 150 mL). The organic extracts were combined and washed with brine, dried over $MgSO_4$, and concentrated in vacuo (50 mbar at 40 °C). Purification of the crude product by gradient flash chromatography (hexane:EtOAc = 3:1 to 1:1) gave the title compound as a colorless oil (6.8 g, 83%). $[\alpha]_D^{20}$ = −47.1 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35 (dq, *J* = 6.9, 2.1 Hz, 1H), 3.81 (dd, *J* = 11.5, 3.8 Hz, 1H), 3.70 (dd, *J* = 11.5, 4.8 Hz, 1H), 3.64 (ddd, *J* = 6.9, 4.8, 3.8 Hz, 1H), 2.30 (brs, 2H), 1.84 (d, *J* = 2.2 Hz, 3H), 0.91 (s, 9H), 0.17 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 83.2, 77.3, 74.9, 64.4, 62.8, 25.8, 18.1, 3.5, –4.4, –5.1; IR (film): 3396, 2954, 2929, 2857, 2237, 1252, 1105, 837 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{12}H_{24}O_3SiNa$ $[M+Na]^+$: 267.1387, found: 267.1386.

(5*R*,6*R*)-9,9-Diethyl-2,2,3,3-tetramethyl-5-(prop-1-yn-1-yl)-6-((triethylsilyl)oxy)-4,8-dioxa-3,9-disilaundecane (11). Chlorotriethylsilane (3.3 mL, 19.6 mmol) was added to a solution of alcohol **S4** (2.0 g, 8.2 mmol) and imidazole (2.2 g, 32.7 mmol) in CH_2Cl_2 (60 mL). After 2.5 h, the reaction was quenched with sat. aq. $NaHCO_3$. After phase separation, the aqueous layer was extracted with CH_2Cl_2 (2 x 60 mL). The organic extracts were combined and washed with brine, dried over $MgSO_4$, and concentrated in vacuo (50 mbar at 40 °C). Purification of the crude product by gradient flash chromatography (hexane:CH_2Cl_2, 19:1 to 9:1) gave the title compound as a single diastereomer; colorless oil (3.3 g, 86%). $[\alpha]_D^{20}$ = −2.0 (c = 1.0, hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35 (dq, *J* = 4.4, 2.2 Hz, 1H), 3.86 – 3.79 (m, 1H), 3.65 – 3.58 (m, 2H), 1.81 (d, *J* = 2.2 Hz, 3H), 0.97 (t, *J* = 8.0 Hz, 9H) 0.95 (t, *J* = 8.0 Hz, 9H) 0.90 (s, 9H), 0.66 – 0.56 (m, 12H), 0.12 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 81.0, 78.7, 76.9, 64.9, 64.0, 25.8, 18.3, 6.9, 6.8, 5.0, 4.4, 3.6, –4.6, –4.9; IR (film): 2954, 2877, 1085, 1004, 835, 725 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{24}H_{52}O_3Si_3Na$ $[M+Na]^+$: 495.3117, found: 495.3115.

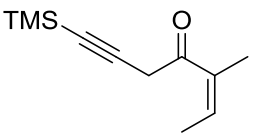


(2*S*,3*R*)-3-((*tert*-Butyldimethylsilyl)oxy)-2-((triethylsilyl)oxy)hex-4-ynal (12). A solution of DMSO (6.4 mL, 89.9 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a stirred solution of oxalyl chloride (3.9 mL, 44.9 mmol) in CH_2Cl_2 (30 mL) at −78 °C. After 30 min, a solution of compound **11** (4.3 g, 9.0 mmol) in CH_2Cl_2 (12 + 6 mL) was added dropwise to the flask. The mixture was slowly warmed to −30 °C over 30 min and held at this temperature for 3 h. The solution was then cooled back to −78 °C before *i*-Pr_2NEt (23.5 mL, 134.8 mmol) was added. The reaction mixture was slowly allowed to warm to ambient temperature over 2.5 h before it poured into a solution of sat. aq. NH_4Cl (300 mL). After stirring for 10 min, the aqueous layer was extracted with CH_2Cl_2 (2 x), and the combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude product by gradient flash chromatography

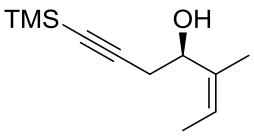


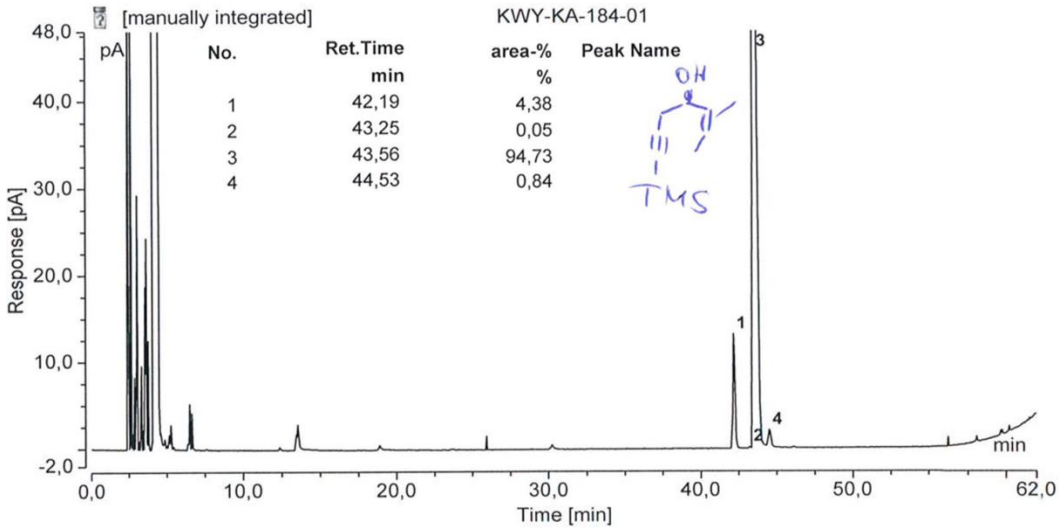
(hexane:EtOAc, 98:1) afforded the title compound as a colorless oil (2.7 g, 85%). $[\alpha]_D^{20}$ = −9.5 (c = 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (d, *J* = 1.6 Hz, 1H), 4.52 (dq, *J* = 5.0, 2.2 Hz, 1H), 3.98 (dd, *J* = 5.1, 1.6 Hz, 1H), 1.82 (d, *J* = 2.2 Hz, 3H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.89 (s, 9H), 0.63 (q, *J* = 7.9 Hz, 6H), 0.13 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 83.6, 80.3, 77.2, 65.0, 25.7, 18.2, 6.7, 4.7, 3.6, –4.6, –5.0; IR (film): 2955, 2931, 2878, 2858, 2239, 1738, 1153, 1087, 837, 744 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{36}O_3Si_2Na$ [M+Na]$^+$: 379.2095, found: 379.2092.

(*Z*)-5-Methyl-1-(trimethylsilyl)hept-5-en-1-yn-4-one (14). A freshly prepared solution of (3-(trimethylsilyl)prop-2-yn-1-yl)magnesium bromide (43 mL, 21.0 mmol, 0.5 M)[6] was added at –40 °C to a solution of (*Z*)-*N*-methoxy-*N*,2-dimethylbut-2-enamide[7] (**13**, 2.5 g, 17.5 mmol) in THF (87 mL). The resulting mixture was stirred for 1 h before the reaction was then quenched with sat. aq. NH_4Cl (100 mL). The mixture was subsequently warmed to ambient temperature, the aqueous layer was extracted with *tert*-butyl methyl ether (2 x 50 mL), the organic extracts were combined, washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue (a pale yellow oil) was carried on to the next step without further purification.

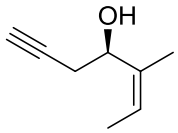


(*R*,*Z*)-5-Methyl-1-(trimethylsilyl)hept-5-en-1-yn-4-ol (S5). (*S*)-(−)-2-Methyl-CBS-oxazaborolidine (0.29 g, 1.1 mmol) and catecholborane (3.2 mL, 29.7 mmol) were added dropwise to a solution of enone **14** (crude, 17.5 mmol) in toluene (87 mL) at −78 °C. After 10 min, the mixture was warmed to −62 °C and stirring was continued until complete consumption of the starting material was observed by TLC (ca. 6 h). MeOH (50 mL) and KOH (1 g, neat) were then added and the resulting solution slowly warmed to ambient temperature over 2 h. The reaction was quenched with sat. aq. NH_4Cl (100 mL) and water (100 mL). After phase separation, the aqueous layer was extracted with *tert*-butyl methyl ether (100 mL). The combined organic extracts were washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo (50 mbar at 40 °C). Purification of the crude product by gradient flash chromatography (20:1 to 10:1, hexane:EtOAc) gave the title compound as a bright orange-colored oil (2.1 g, 61% over two steps, 91% *ee*). $[\alpha]_D^{20}$ = +15.5 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41−5.34 (m, 1H), 4.76 (ddd, *J* = 8.1, 5.6, 3.2 Hz, 1H), 2.54 (dd, *J* = 16.8, 8.1 Hz, 1H), 2.40 (dd, *J* = 16.8, 5.6 Hz, 1H), 1.96 (d, *J* = 3.2 Hz, 1H), 1.70 (app. quint, *J* = 1.5 Hz, 3H), 1.64 (dq, *J* = 6.9, 1.5 Hz, 3H), 0.15 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.6, 122.6, 103.2, 87.2, 67.7, 26.9, 17.3, 13.0, 0.0; IR (film): 3386, 2958, 2925, 2860, 2178, 1441, 1249, 1018, 843 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{11}H_{20}OSiNa$ [M+Na]$^+$: 219.1174, found: 219.1174.

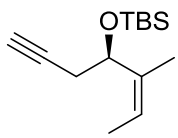




(*R*,*Z*)-5-Methylhept-5-en-1-yn-4-ol (15). K_2CO_3 (2.1 g, 16.0 mmol) was added to a solution of enone **S5** (2. 1 g, 10.7 mmol) in MeOH (54 mL). The resulting mixture was stirred for 14 h before it was diluted with H_2O (20 mL). MeOH was removed under reduced pressure (Note: when the pressure is below 150 mbar at 40 °C, the alcohol product was partially evaporated). The aqueous layer was rinsed with *tert*-butyl methyl ether (2 x 100 mL). The extracts were combined, washed with brine, dried over Na_2SO_4, and concentrated in vacuo (250 mbar at 40 °C). Purification of the crude product by flash column chromatography (1:2, *tert*-butyl methyl ether:hexane) gave the title compound as a pale yellow oil (1.3 g, quant.). $[\alpha]_D^{20}$ = +16.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 – 5.33 (m, 1H), 4.78 (ddd, *J* = 8.3, 5.6, 2.9 Hz, 1H), 2.51 (ddd, *J* = 16.6, 8.1, 2.6 Hz, 1H), 2.36 (ddd, *J* = 16.6, 5.6, 2.7 Hz, 1H), 2.04 (app. t, *J* = 2.6 Hz, 1H), 1.94 (brs, 1H), 1.71 (app. quint, *J* = 1.5 Hz, 3H), 1.64 (dq, *J* = 7.0, 1.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.6, 122.9, 81.0, 70.3, 67.8, 25.3, 17.2, 13.0; IR (film): 3364, 3298, 2971, 2942, 2922, 2863, 2121, 1442, 1377, 1024, 636 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_8H_{12}ONa$ $[M+Na]^+$: 147.0780, found: 147.0780.

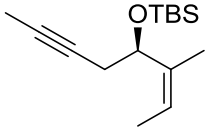


(*R*,*Z*)-*tert*-Butyldimethyl((5-methylhept-5-en-1-yn-4-yl)oxy)silane (S6). *tert*-Butyldimethylsilyl chloride (1.9 g, 12.8 mmol) was added to a solution of alcohol **15** (1.3 g, 10.7 mmol) and imidazole (1.5 g, 21.4 mmol) in CH_2Cl_2 (50 mL), and the resulting mixture was stirred for 12 h. The reaction was quenched with sat. aq. $NaHCO_3$ solution (50 mL). After phase separation, the aq. phase was extracted with CH_2Cl_2 (100 mL × 2), the extracts were combined, washed with brine, dried over $MgSO_4$, and concentrated in vacuo (250 mbar at 35 °C). The crude product was purified by flash column

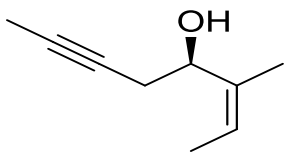


chromatography (1:1, pentane:CH_2Cl_2) to afford the title compound as a colorless oil (2.4 g, 92% over two steps). $[\alpha]_D^{20}$ = +7.2 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.33 – 5.27 (m, 1H), 4.75 (ddd, *J* = 7.0, 7.0, 0.6 Hz, 1H), 2.44 (ddd, *J* = 16.6, 7.1, 2.7 Hz, 1H), 2.32 (ddd, *J* = 16.6, 6.8, 2.7 Hz, 1H), 1.93 (app. t, *J* = 2.7 Hz, 1H), 1.67 – 1.62 (m, 6H), 0.88 (s, 9H), 0.08 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 120.8, 81.8, 69.2, 68.6, 26.1, 25.7, 18.2, 17.2, 13.2, -5.0 (2); IR (film): 3314, 2953, 2929, 2857, 2123, 1472, 1463, 1251, 1078, 833, 775, 626 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{14}H_{26}OSiNa$ [M+Na]$^+$: 261.1645, found: 261.1645.

(*R*,*Z*)-*tert*-Butyldimethyl((3-methyloct-2-en-6-yn-4-yl)oxy)silane (S7). A solution of *n*BuLi (16.3 mL, 24.1 mmol, 1.5 M in hexane) was added at −78 °C to a solution of alkyne **S6** (2.3 g, 9.6 mmol) in THF (100 mL), and the resulting mixture was stirred for 45 min at this temperature. After addition of CH_3I (3.0 mL, 48.2 mmol) at −78 °C, the solution was stirred at ambient temperature for 3 h. The reaction was quenched at 0 °C with sat. aq. NH_4Cl (150 mL). After phase separation, the aq. phase was extracted with pentane (2 x 100 mL), the extracts were combined, washed with brine, dried over $MgSO_4$, and concentrated in vacuo (250 mbar at 35 °C). The crude product was purified by flash column chromatography (25:1, pentane:diethyl ether) to afford the title compound as a colorless oil (2.4 g, 98%). $[\alpha]_D^{20}$ = +2.1 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 – 5.24 (m, 1H), 4.69 (app. td, *J* = 7.0, 0.5 Hz, 1H), 2.37 (ddq, *J* = 16.3, 7.4, 2.6 Hz, 1H), 2.22 (ddq, *J* = 16.3, 6.6, 2.6 Hz, 1H), 1.76 (app. t, *J* = 2.5 Hz, 3H), 1.65 – 1.61 (m, 6H), 0.89 (s, 9H), 0.07 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 120.3, 76.6, 76.6, 69.3, 26.4, 25.7, 18.2, 17.3, 13.1, 3.5, –5.0, –5.0; IR (film): 2954, 2929, 2857, 1472, 1462, 1250, 1078, 835, 775 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{15}H_{28}OSiNa$ [M+Na]$^+$: 275.1802, found: 275.1801.



(*R*,*Z*)-3-Methyloct-2-en-6-yn-4-ol (16). A solution of tetrabutylammonium fluoride (13.3 mL, 13.3 mmol, 1 M in THF) was added to a stirred solution of compound **S7** (2.4 g, 9.5 mmol) in THF (50 mL). After 6 h, the reaction was quenched with water (100 mL). After phase separation, the aqueous layer was extracted with *tert*-butyl methyl ether (2 x 100 mL). The combined extracts were rinsed with brine, dried over $MgSO_4$, and concentrated in vacuo (250 mbar, 40 °C). The crude product was purified by flash chromatography (5:1, pentane:diethyl ether) to afford the title compound as a colorless oil (1.2 g, 88%). $[\alpha]_D^{20}$ = +7.2 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 – 5.33 (m, 1H), 4.71 (dd, *J* = 8.5, 5.1 Hz, 1H), 2.44 (ddq, *J* = 16.3, 8.6, 2.6 Hz, 1H), 2.29 (ddq, *J* = 16.4, 5.1, 2.5 Hz, 1H), 1.93 (brs, 1H), 1.81 (app. t, *J* = 2.6 Hz, 3H), 1.70 (app. quint, *J* = 1.5 Hz, 3H), 1.63 (dq, *J* = 7.0, 1.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.0, 122.4, 78.1, 75.5, 68.2, 25.8, 17.4, 12.9, 3.6; IR (film): 3383, 2971, 2920, 2861, 1442, 1023 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_9H_{14}ONa$ [M+Na]$^+$: 161.0937, found: 161.0937.



Preparation of the Glycosyl Donor

1,2,3,5-Tetra-O-(*tert*-butyldimethylsilyl)-α-D-arabinofuranose (S8). Imidazole (2.3 g, 33.3 mmol) and TBSCl (4.8 g, 32.0 mmol) were added to a stirred solution of D-(–)-arabinose (1.0 g, 6.7 mmol) in DMF (66 mL) and the resulting mixture was stirred at 75 °C for 2 h. Upon cooling the solution to 0°C, a white precipitate was formed and subsequently collected by filtration. The crude product was purified by recrystallization from MeOH:$CHCl_3$:NH_4OH solution 25% (30:5:1.5 mL) ans subsequent recrystallization from MeOH:Et_2O (5:1), which afforded the title compound as a white solid (3.0 g. 75%). M.p. 89-90 °C; $[\alpha]_D^{20}$ = +31.4 (c = 1.0, $CHCl_3$); IR (film): 2954, 2929, 2857, 1251, 1102, 832 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{66}NO_5Si_4Na$ $[M+Na]^+$: 629.3880, found: 629.3881. Spectral characteristics were identical to those previously reported.[8]

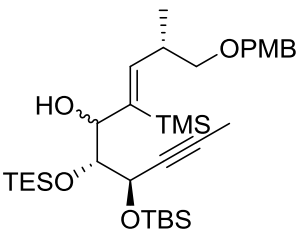
2,3,5-Tri-O-(*tert*-butyldimethylsilyl)-α-D-arabinofuranose (S9). Trifluoroacetic acid (4.5 mL) was added to a solution of compound **S8** (0.90 g, 1.5 mmol) in chloroform (18 mL) and the resulting mixture was stirred for 2 min. The mixture was immediately poured into a stirred solution of ammonium hydroxide (9.0 mL) in methanol (60 mL) at –30 °C. The mixture was then allowed to reach ambient temperature before it was partitioned between chloroform (60 mL) and water (60 mL). The organic phase was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by flash chromatography (hexane:EtOAc, 40:1 to 20:1) to afford a mixture the title compound as a colorless oil (0.42 g, 58%, ≈3:1 mixture of anomers). $[\alpha]_D^{20}$ = +5.9 (c = 1.0, $CHCl_3$); IR (film): 3445, 2954, 2929, 2858, 1252, 1103, 1079, 833, 776 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{23}H_{52}O_5Si_3Na$ $[M+Na]^+$: 515.3015, found: 515.3017. Spectral characteristics were identical to those previously reported.[8]

2,3,5-Tri-O-(*tert*-butyldimethylsilyl)-α-D-arabinofuranosyl 1-(2,2,2-trichloroethanimidate) (37). Cl_3CCN (0.41 mL, 4.1 mmol) and DBU (12 µL, 0.081 mmol) were added at 0 °C to a solution of compound **S9** (0.20 g, 0.41 mmol) in CH_2Cl_2 (2 mL). After 5 min, the mixture was allowed to warm to ambient temperature and stirring continued for 4 h. The mixture was then concentrated in vacuo and the residue purified by flash chromatography (hexane:EtOAc:Et_3N, 100:1:2) to afford the title compound as a colorless oil (0.21 g, 80 %). $[\alpha]_D^{20}$ = +34.0 (c = 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.49 (brs, 1H), 6.05 (s, 1H), 4.27 (d, *J* = 1.6 Hz, 1H), 4.17 (ddd, *J* = 6.6, 5.6, 3.3 Hz, 1H), 4.09 (ddd, *J* = 3.3, 1.6, 0.5 Hz, 1H), 3.75 (dd, *J* = 10.6, 5.5 Hz, 1H), 3.70 (dd, *J* = 10.6, 6.6 Hz, 1H), 0.91 (s, 18H), 0.89 (s, 9H), 0.13 (s, 3H) 0.13 (s, 3H) 0.11 (s, 3H) 0.10 (s, 3H) 0.08 (s, 3H) 0.07 (s, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 161.8, 107.5, 92.0, 89.6, 83.4, 79.3, 63.9, 26.3, 26.1, 26.0, 18.9, 18.4, 18.3, –4.3, –4.4, –4.4, –4.7,

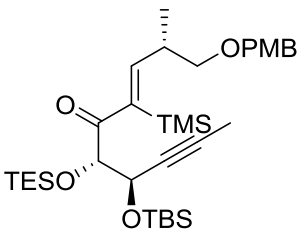
–5.1, –5.1; IR (film): 3348, 2954, 2930, 2858, 1667, 1252, 1113, 835 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{25}H_{52}NO_5Cl_3Si_3Na$ $[M+Na]^+$: 658.2111, found: 658.2116.

Fragment Coupling and Completion of the Total Synthesis

Alcohol 17. A solution of *i*-PrMgCl·LiCl (5.3 mL, 6.8 mmol, 1.3 M THF) was added at –25 °C to a solution of vinyl iodide **8** (2.1 g, 5.3 mmol) in THF (20 mL), and the resulting mixture was stirred at –15 °C for 7 h. A solution of aldehyde **12** (2.3 g, 6.3 mmol) in THF (20 mL) was then added dropwise and the reaction temperature was raised and held at 0 °C. After 14 h, the reaction was quenched with sat. aq. NH_4Cl solution (40 mL). After phase separation, the aqueous layer was extracted with *tert*-butyl methyl ether (2 x 50 mL) and the combined extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification of the crude product by gradient flash chromatography (hexane:EtOAc, 50:1 to 20:1) gave the title compound as a colorless oil (2.29 g, 69%, dr = 1.3:1); partial separation of the diastereomers allowed for individual characterization. *Major diastereomer* (less polar compound): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 6.88 – 6.85 (m, 2H), 6.11 (dd, *J* = 10.7, 0.8 Hz, 1H), 4.57 (dq, *J* = 3.3, 2.2 Hz, 1H), 4.48 – 4.39 (m, 3H), 3.80 (s, 3H), 3.58 (dd, *J* = 7.0, 3.3 Hz, 1H), 3.36 (dd, *J* = 9.0, 5.3 Hz, 1H), 3.21 (dd, *J* = 9.0, 8.3 Hz, 1H), 2.87 – 2.75 (m, 1H), 1.83 (d, *J* = 2.2 Hz, 3H), 1.25 (brs, 1H), 1.04 (d, *J* = 6.5 Hz, 3H), 0.95 (t, *J* = 7.8 Hz, 9H), 0.90 (s, 9H), 0.59 (q, *J* = 7.7 Hz, 6H), 0.19 (s, 9H), 0.16 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 146.9, 139.9, 130.7, 129.1, 113.7, 82.7, 79.1, 77.8, 75.1, 74.8, 72.7, 67.2, 55.3, 36.6, 25.7, 18.0, 17.8, 6.9, 5.3, 3.6, 1.3, –4.5, –5.1; IR (film): 3507, 2954, 1613, 1513, 1246, 1079 cm^{-1}. HRMS (ESI): *m/z* calcd for $C_{34}H_{62}O_5Si_3Na$ $[M+Na]^+$: 657.3797, found: 657.3803. *Minor diastereomer* (more polar compound): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 6.88 – 6.84 (m, 2H), 6.02 (dd, *J* = 10.7, 1.3 Hz, 1H), 4.48 – 4.38 (m, 4H), 3.80 (s, 3H), 3.61 (dd, *J* = 4.2, 3.4 Hz, 1H), 3.32 (dd, *J* = 9.1, 5.1 Hz, 1H), 3.19 (app. t, *J* = 8.8 Hz, 1H), 2.87 – 2.75 (m, 1H), 1.81 (d, *J* = 2.2 Hz, 3H), 1.25 (brs, 1H), 1.05 (d, *J* = 6.5 Hz, 3H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.91 (s, 9H), 0.71 – 0.57 (m, 6H), 0.18 (s, 9H), 0.13 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 146.0, 139.4, 130.7, 129.2, 113.7, 82.8, 79.5, 76.8, 74.8, 74.1, 72.7, 65.4, 55.3, 36.7, 26.1, 18.4, 17.9, 7.0, 5.4, 3.6, 1.3, –4.3, –4.4; IR (film): 3548, 2955, 2877, 1613, 1513, 1248, 1089, 836 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{34}H_{62}O_5Si_3Na$ $[M+Na]^+$: 657.3797, found: 657.3803.

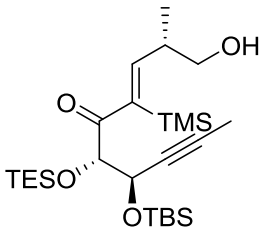


Enone S10. Dess-Martin periodinane (2.45 g, 5.77 mmol) was added to a stirred suspension of $NaHCO_3$ (2.59 g, 30.8 mmol) and alcohol **17** (2.44 g, 3.85 mmol) in CH_2Cl_2 (55 mL), and the resulting mixture was stirred for 90 min. The reaction was quenched with sat. aq. sodium thiosulfate solution. After phase separation, the aqueous layer was washed with CH_2Cl_2 (2 x 50

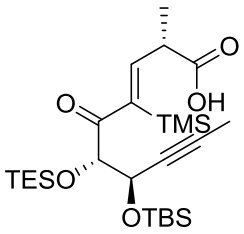


mL). The combined extracts were extracted with brine, concentrated in vacuo, and the residue was purified by flash chromatography (hexane:EtOAc, 25:1) to afford the title compound as a colorless oil (2.08 g, 85%). $[\alpha]_D^{20}$ = −33.9 (c = 1.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.22 (m, 2H), 6.96 (d, *J* = 10.5 Hz, 1H), 6.89 – 6.85 (m, 2H), 4.50 – 4.45 (m, 2H), 4.44 and 4.41 (ABq, J_{AB} = 11.7 Hz, 2H), 3.81 (s, 3H), 3.36 – 3.28 (m, 2H), 2.97 – 2.87(m, 1H), 1.75 (d, *J* = 1.8 Hz, 3H), 1.08 (d, *J* = 6.6 Hz, 3H), 0.92 (t, *J* = 8.0 Hz, 9H), 0.89 (s, 9H), 0.59 (q, *J* = 7.8 Hz, 6H), 0.19 (s, 9H), 0.11 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.6, 159.1, 157.5, 143.2, 130.4, 129.0, 113.7, 83.4, 79.9, 78.1, 74.2, 72.8, 66.2, 55.3, 36.9, 25.9, 18.5, 17.3, 6.8, 4.9, 3.7, 0.8, –4.5, –4.8; IR (film): 2955, 2929, 2876, 2856, 1668, 1513, 1248, 1086, 841 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{34}H_{60}O_5Si_3Na$ $[M+Na]^+$: 655.3641, found: 655.3638.

Primary alcohol 18. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (1.4 g, 6.2 mmol) was added at 0 °C to a solution of compound **S10** (2.1 g, 3.3 mmol) in CH_2Cl_2 (55 mL) and Sorenson's phosphate buffer (25 mL, pH 7.0). After the ice bath was removed, the mixture was stirred for another 90 min. The reaction was quenched with sat. aq. $NaHCO_3$ (100 mL) and diluted with CH_2Cl_2 (200 mL). The biphasic mixture was stirred until precipitates in the organic phase had dissolved (ca. 15 min). After phase separation, the aqueous layer was extracted with CH_2Cl_2 (100 mL × 2), the combined extracts were washed with water and brine, dried over $MgSO_4$, and concentrated in vacuo. Purification of the crude product by gradient flash chromatography (hexane:CH_2Cl_2, 1:1 to 1:3 → hexane:EtOAc, 5:1) gave the title compound as a colorless syrup (1.5 g, 91%). $[\alpha]_D^{20}$ = −45.0 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, *J* = 10.6 Hz, 1H), 4.52 (dq, *J* = 6.1, 2.1 Hz, 1H), 4.41 (d, *J* = 6.1 Hz, 1H), 3.57 – 3.47 (m, 2H), 2.88 – 2.77 (m, 1H), 1.76 (d, *J* = 2.2 Hz, 3H), 1.37 (brs, 1H), 1.05 (d, *J* = 6.6 Hz, 3H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.90 (s, 9H), 0.61 (q, *J* = 7.8 Hz, 6H), 0.21 (s, 9H), 0.12 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.8, 156.5, 144.3, 83.4, 80.6, 78.2, 67.2, 66.2, 39.2, 25.9, 18.5, 16.5, 6.8, 4.9, 3.7, 0.9, –4.5, –4.8; IR (film): 3491, 2955, 2936, 2878, 2007, 1663, 1250, 1081, 840 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{26}H_{52}O_4Si_3Na$ $[M+Na]^+$: 535.3066, found: 535.3070.

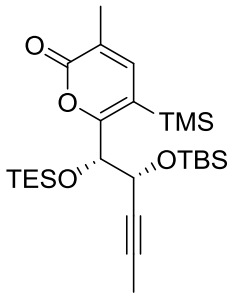


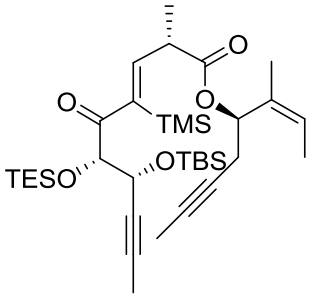
Acid 19. Dess-Martin periodinane (1.7 g, 4.1 mmol) was added to a stirred solution of alcohol **18** (1.5 g, 2.9 mmol) and $NaHCO_3$ (2.0 g, 23.5 mmol) in CH_2Cl_2 (50 mL). After 2 h, the reaction was quenched with sat. aq. sodium thiosulfate solution (40 mL). After phase separation, the aqueous layer was extracted with CH_2Cl_2 (50 mL), the combined extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The crude aldehyde was carried on to the next step without further purification.



$NaClO_2$ (1.3 g, 14.7 mmol) and NaH_2PO_4 (1.8 g, 14.7 mmol) were dissolved in H_2O (14 mL) and the resulting solution transferred into a stirred solution of the crude aldehyde and 2-methyl-2-butene (12.5 mL, 117.6 mmol) in *t*-BuOH/THF (90 mL, 1:1, *v/v*). After stirring for 1 h, a pH 4.0 aqueous buffer (30 mL) was introduced. After phase separation, the aqueous layer was extracted with *tert*-butyl methyl ether (50 mL × 3) and the combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification of the crude product by flash chromatography (hexane:EtOAc:AcOH, 100:20:1) gave the title compound as a colorless oil (1.3 g, 83%). $[\alpha]_D^{20}$ = −22.8 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.13 (d, *J* = 10.5 Hz, 1H), 4.54 (dq, *J* = 6.3, 2.2 Hz, 1H), 4.37 (d, *J* = 6.3 Hz, 1H), 3.59 (dq, *J* = 10.5, 6.9 Hz, 1H), 1.76 (d, *J* = 2.2 Hz, 3H), 1.36 (d, *J* = 6.9 Hz, 3H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.90 (s, 9H), 0.61 (q, *J* = 7.9 Hz, 6H), 0.22 (s, 9H), 0.12 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 204.6, 179.0, 151.6, 145.3, 84.0, 81.6, 78.6, 66.7, 42.5, 26.3, 18.9, 18.2, 7.2, 5.4, 4.0, 1.0, −4.3, −4.5; IR (film): 3349–2506(br), 2955, 2936, 2880, 2240, 2181, 1712, 1672, 1250, 1111, 1080, 840 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{26}H_{50}O_5Si_3Na$ [M+Na]$^+$: 549.2858, found: 549.2866.

Pyrone 20. 2,4,6-Trichlorobenzoyl chloride (16.7 mg, 4.8 µmol), 4-(dimethylamino)pyridine (0.6 mg, 4.8 µmol), and Et_3N (13.8 mg, 9.6 µmol) diluted in toluene (0.3 mL) were added at 0 °C to a stirred solution of carboxylic acid **19** (2.1 mg, 4.0 µmol) and alcohol **16** (0.8 mg, 6.0 µmol) in toluene (1 mL). After the ice bath was removed, the mixture was stirred for 12 h. The reaction was then quenched with sat. aq. NH_4Cl (3 mL). After phase separation, the aqueous layer was extracted with *tert*-butyl methyl ether (2 x 10 mL), the combined extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by flash chromatography (hexane:EtOAc, 20:1) to afford the title compound as a colorless oil (1.6 mg, 79%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 (q, *J* = 1.3 Hz, 1H), 4.57 (dq, *J* = 7.7, 2.2 Hz, 1H), 4.47 (d, *J* = 7.7 Hz, 1H), 2.10 (d, *J* = 1.3 Hz, 3H), 1.67 (d, *J* = 2.2 Hz, 3H), 0.91 (s, 9H), 0.88 (t, *J* = 8.0 Hz, 9H), 0.59 – 0.49 (m, 6H), 0.33 (s, 9H), 0.14 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.7, 163.2, 143.4, 124.1, 111.7, 83.2, 78.1, 76.1, 67.1, 25.9, 18.3, 16.8, 6.7, 5.0, 3.6, 0.4, –4.4, –4.8; IR (film): 2955, 2925, 2855, 1727, 1462, 1253, 1110, 1083, 840 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{26}H_{48}O_4Si_3Na$ [M+Na]$^+$: 531.2753, found: 531.2757.

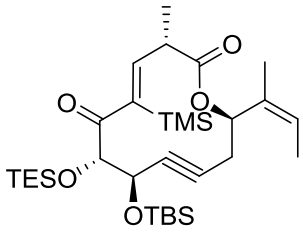




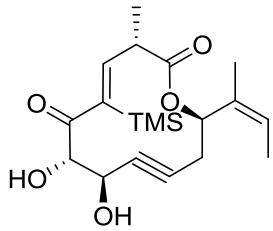
Ester 21. *N*-(3-Dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (0.56 g, 2.9 mmol) and DMAP (0.042 g, 0.42 mmol) were added at 0 °C to a stirred solution of carboxylic acid **19** (1.1 g, 2.1 mmol) and alcohol **16** (0.43 g, 3.1 mmol) in CH_2Cl_2 (40 mL). After stirring for 6.5 h, the reaction was quenched with sat. aq. NH_4Cl (50 mL). After phase separation, the aqueous layer was extracted with

CH_2Cl_2 (2 x 50 mL), the combined extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by flash chromatography (hexane:EtOAc, 100:4) to afford the title compound as a colorless oil (1.05 g, 78%). $[\alpha]_D^{20}$ = −1.5 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 10.5 Hz, 1H), 5.73 (app. t, *J* = 7.3 Hz, 1H), 5.49 – 5.42 (m, 1H), 4.50 – 4.46 (m, 2H), 3.56 (dq, *J* = 10.4, 6.9 Hz, 1H), 2.50 (ddq, *J* = 16.4, 7.4, 2.5 Hz, 1H), 2.39 (ddq, *J* = 16.4, 7.4, 2.5 Hz, 1H), 1.76 – 1.75 (m, 3H), 1.74 (app. t, *J* = 2.6 Hz, 3H), 1.71 (dq, *J* = 6.9, 1.5 Hz, 3H), 1.67 – 1.65 (m, 3H), 1.32 (d, *J* = 6.9 Hz, 3H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.91 (s, 9H), 0.60 (q, *J* = 7.9 Hz, 6H), 0.22 (s, 9H), 0.14 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.1, 172.2, 151.5, 144.8, 131.9, 125.0, 83.7, 80.0, 78.1, 77.4, 74.1, 71.2, 66.2, 42.3, 25.9, 22.8, 18.5, 18.0, 17.7, 13.2, 6.8, 4.8, 3.7, 3.4, 0.7, –4.4, –4.8; IR (film): 2955, 2927, 2878, 2857, 2009, 1737, 1676, 1461, 1250, 1167, 1081, 841 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{35}H_{62}O_5Si_3Na$ $[M+Na]^+$: 669.3797, found: 669.3802.

Cycloalkyne 22. A solution of diyne **21** (105 mg, 0.16 mmol) in freshly distilled toluene (75 mL) was stirred at 90 °C. In a separate flask under argon atmosphere, CH_2Cl_2 (0.25 mL, 4.0 mmol) was added to a solution of complex **30** (35 mg, 0.06 mmol)[9] in freshly distilled toluene (2 mL). The resulting homogeneous solution was transferred via syringe to the flask containing the diyne substrate. After being stirred for 16 h, the mixture was cooled to ambient temperature and filtered through a pad of silica. The filtrate was concentrated in vacuo and the residue purified by gradient flash chromatography (hexane:EtOAc, 25:1 to 20:1) to give the title compound as a pale yellow oil (89 mg, 93%). $[\alpha]_D^{20}$ = +7.0 (c = 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.14 (d, *J* = 11.1 Hz, 1H), 5.63 (ddd, *J* = 10.7, 3.7, 0.7 Hz, 1H), 5.46 – 5.34 (m, 1H), 4.50 (ddd, *J* = 6.2, 3.1, 1.8 Hz, 1H), 4.14 (d, *J* = 6.2 Hz, 1H), 3.58 (dq, *J* = 11.1, 6.6 Hz, 1H), 2.73 (ddd, *J* = 16.8, 10.7, 1.8 Hz, 1H), 2.40 (ddd, *J* = 16.9, 3.7, 3.1 Hz, 1H), 1.70 – 1.67 (m, 6H), 1.18 (d, *J* = 6.6 Hz, 3H), 0.96 (t, *J* = 8.1 Hz, 9H), 0.88 (s, 9H), 0.62 (q, *J* = 8.0 Hz, 6H), 0.27 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 203.3, 173.1, 152.5, 144.9, 133.5, 124.3, 84.7, 83.8, 81.4, 70.9, 66.8, 43.9, 26.1, 24.4, 18.8, 18.2, 15.4, 13.3, 7.0, 5.1, 1.5, –4.5, –5.0; IR (film): 2955, 2934, 2880, 2256, 1742, 1678, 1596, 1460, 1250, 1173, 1086, 1004, 840, 779 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{31}H_{56}O_5Si_3Na$ $[M+Na]^+$: 615.3328, found: 615.3326.

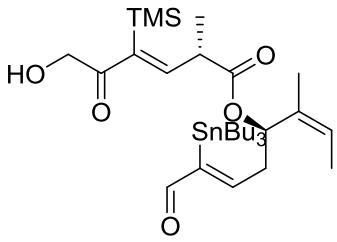


Diol 23. *p*-Toluenesulfonic acid monohydrate (23 mg, 0.12 mmol) was added to a solution of alkyne **22** (30 mg, 0.05 mmol) in CH_2Cl_2/MeOH (2:1, 3 mL). After stirring for 15 h, the reaction was quenched with sat. aq. $NaHCO_3$ (5 mL), the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL), and the combined extracts were washed with brine (10 mL), dried over $MgSO_4$, and filtered.

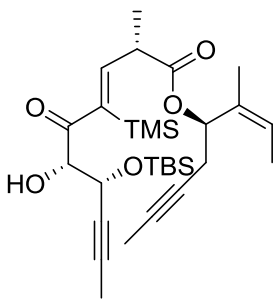


The filtrate was concentrated in vacuo and the residue purified by flash chromatography (hexane:EtOAc, 2:1) to give the title compound as a colorless syrup (28 mg, 81%). $[\alpha]_D^{20}$ = +379.2 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (d, *J* = 11.0 Hz, 1H), 5.80 (dd, *J* = 11.9, 3.3 Hz, 1H), 5.46 – 5.40 (m, 1H), 4.28 (dd, *J* = 9.4, 7.4 Hz, 1H), 3.92 (dd, *J* = 9.5, 2.7 Hz, 1H), 3.80 (d, *J* = 7.4 Hz, 1H), 3.45 (dq, *J* = 11.0, 6.6 Hz, 1H), 3.20 (s, 1H), 2.80 (ddd, *J* = 16.9, 11.9, 2.9 Hz, 1H), 2.33 (dd, *J* = 16.9, 3.3 Hz, 1H), 1.71 (dq, *J* = 7.0, 1.5 Hz, 3H), 1.68 – 1.66 (m, 3H), 1.25 (d, *J* = 6.6 Hz, 3H), 0.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.8, 172.0, 147.8, 147.6, 131.5, 125.1, 85.2, 79.3, 79.0, 70.2, 63.6, 43.6, 23.9, 17.6, 14.7, 13.0, –0.1; IR (film): 3439, 2972, 2031, 1739, 1678, 1593, 1254, 1176, 1066, 844 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{19}H_{28}O_5SiNa$ $[M+Na]^+$: 387.1598, found: 387.1595.

Aldehyde 24. A freshly prepared solution of tributyltin hydride (8.8 mg, 30 μmol) in CH_2Cl_2 (0.9 mL) was added over 15 min to a stirred solution of $[Cp^*RuCl]_4$ (0.8 mg, 2.7 μmol) and diol **23** (10 mg, 27 μmol) in CH_2Cl_2 (1 mL). The resulting mixture was stirred for 15 min before all volatile materials were evaporated. Purification of the residue by gradient flash chromatography (hexane:EtOAc, 20:3) gave the title compound as a colorless oil (5.4 mg, 30%). $[\alpha]_D^{20}$ = +24.8 (c = 1.0, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.15 (dd, *J* = 7.4, 6.8 Hz, 1H), 6.63 (d, *J* = 10.4 Hz, 1H), 5.79 (dd, *J* = 7.9, 6.7 Hz, 1H), 5.50 – 5.46 (m, 1H), 4.41 and 4.36 (ABX, J_{AB} = 18.7 Hz, J_{AX} = 4.5 Hz, J_{BX} = 4.5 Hz, 2H), 3.54 (dq, *J* = 10.4, 7.0 Hz, 1H), 3.22 (app. t, *J* = 4.7 Hz, 1H), 2.84 – 2.76 (m, 1H), 2.64 – 2.57 (m, 1H), 1.70 (dq, *J* = 7.0, 1.5 Hz, 3H), 1.68 (app. quint, *J* = 1.5 Hz, 3H), 1.50 – 1.43 (m, 6H), 1.32 (d, *J* = 7.0 Hz, 3H), 1.30 (app. sext, *J* = 7.4 Hz, 6H), 1.10 – 0.98 (m, 6H), 0.88 (t, *J* = 7.3 Hz, 9H), 0.24 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 205.5, 199.3, 172.1, 162.6, 151.0, 149.5, 143.7, 131.6, 125.3, 71.7, 66.0, 42.3, 36.9, 29.0, 27.3, 18.2, 17.8, 13.6, 13.3, 10.9, 0.4; IR (film): 3470, 2956, 2926, 2872, 2855, 1736, 1675, 1599, 1456, 1377, 1251, 1170, 1071, 845 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{31}H_{56}O_5SiSnNa$ $[M+Na]^+$: 679.2811, found: 679.2814.

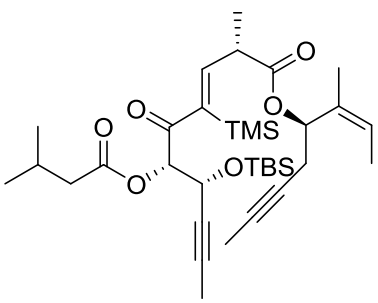


α-Hydroxy ketone S11. *p*-Toluenesulfonic acid monohydrate (0.031 g, 0.16 mmol) was added at –41 °C to a solution of compound **21** (1.04 g, 1.6 mmol) in CH_2Cl_2 and MeOH (32 mL, 3:1, *v*/*v*), and the resulting mixture was stirred for 4.5 h. This reaction was then quenched with sat. aq. $NaHCO_3$ (30 mL), and the mixture was allowed to warm to ambient temperature. After phase separation, the aqueous layer was extracted with CH_2Cl_2 (100 mL × 2). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification of the crude product by gradient flash chromatography (hexane:EtOAc, 20:1) gave the title compound as a colorless oil



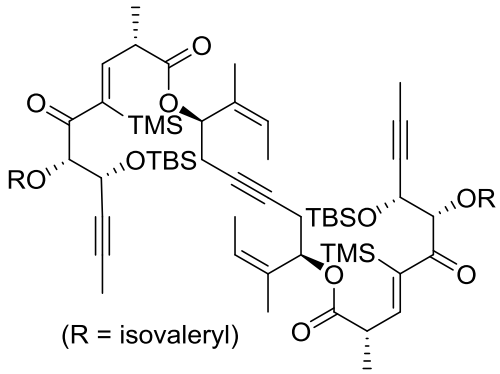
(0.75 g, 88%). $[\alpha]_D^{20}$ = +25.6 (c = 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 (d, *J* = 10.5 Hz, 1H), 5.71 (app. t, *J* = 7.1 Hz, 1H), 5.46 – 5.40 (m, 1H), 4.65 – 4.63 (m, 1H), 4.60 (dd, *J* = 7.5, 3.7 Hz, 1H), 3.58 – 3.50 (m, 2H), 2.51 (ddq, *J* = 16.5, 7.7, 2.5 Hz, 1H), 2.35 (ddq, *J* = 16.5, 6.6, 2.6 Hz, 1H), 1.81 (d, *J* = 2.2 Hz, 3H), 1.71 (app. t, *J* = 2.5 Hz, 3H), 1.57 (dq, *J* = 6.9, 1.5 Hz, 3H), 1.63 (app. quint, *J* = 1.5 Hz, 3H), 1.34 (d, *J* = 6.9 Hz, 3H), 0.87 (s, 9H), 0.25 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.3, 172.1, 150.5, 145.0, 131.9, 124.9, 83.3, 77.5, 77.4, 76.7, 74.1, 71.4, 65.6, 42.6, 25.9, 22.9, 18.3, 17.9, 17.7, 13.2, 3.6, 3.4, 0.5, –4.2, –4.7; IR (film): 3467, 2955, 2929, 2857, 1737, 1667, 1250, 1172, 1089, 842, 780 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{29}H_{48}O_5Si_2Na$ $[M+Na]^+$: 555.2933, found: 555.2937.

Diyne 25. $CeCl_3$·THF (44 mg, 0.14 mmol) was added to a solution of alcohol **S11** (0.75 g, 1.4 mmol) in THF (18 mL). After 5 min, isovaleric anhydride (2.8 mL, 14.1 mmol) was introduced and the resulting mixture stirred until complete consumption of starting material was observed by TLC (ca. 4.5 h). The mixture was diluted with EtOAc (30 mL) and the reaction quenched with sat. aq. $NaHCO_3$ (30 mL). After phase separation, the aqueous layer was extracted with EtOAc (30 mL × 2). The combined organic phases were washed with water (30 mL) and brine (30 mL), dried over $MgSO_4$, and concentrated in vacuo. Purification of the crude material by gradient flash chromatography (hexane:EtOAc, 40:1 to 20:1) gave the title compound as a colorless syrup (0.83 g, 95%). $[\alpha]_D^{20}$ = +27.7 (c = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (d, *J* = 10.6 Hz, 1H), 5.71 (app. t, *J* = 7.2 Hz, 1H), 5.47 – 5.38 (m, 2H), 4.68 (dq, *J* = 6.0, 2.2 Hz, 1H), 3.51 (dq, *J* = 10.6, 6.9 Hz, 1H), 2.52 (ddq, *J* = 16.4, 7.2, 2.5 Hz, 1H), 2.37 (ddq, *J* = 16.4, 7.3, 2.5 Hz, 1H), 2.24 and 2.23 (ABX, J_{AB} = 15.0 Hz, J_{AX} = 7.7 Hz, J_{BX} = 6.5 Hz, 2H), 2.17 – 2.06 (m, 1H), 1.78 (d, *J* = 2.2 Hz, 3H), 1.72 (app. t, *J* = 2.5 Hz, 3H), 1.70 (dq, *J* = 7.0, 1.5 Hz, 3H), 1.63 (app. quint, *J* = 1.5 Hz, 3H), 1.33 (d, *J* = 7.0 Hz, 3H), 0.96 (d, *J* = 6.6 Hz, 6H), 0.89 (s, 9H), 0.21 (s, 9H), 0.14 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.6, 172.0, 171.9, 150.6, 144.6, 132.0, 124.8, 83.9, 78.7, 77.4, 76.9, 74.2, 71.3, 63.1, 43.0, 42.5, 25.7, 25.6, 22.8, 22.4, 22.4, 18.3, 18.0, 17.6, 13.2, 3.7, 3.4, 0.4, –4.6, –4.8; IR (film): 2985, 2929, 2858, 2234, 2027, 1739, 1684, 1251, 1168, 1097, 841 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{34}H_{56}O_6Si_2Na$ $[M+Na]^+$: 639.3508, found: 639.3517.



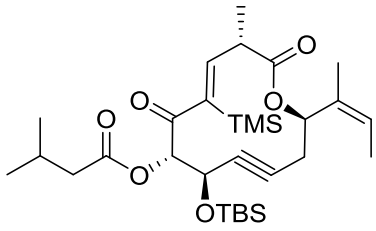
Acyclic dimer 26. A stirred solution of diyne **25** (6.0 mg, 9.7 µmol) and MS 5Å (100 mg) in freshly distilled toluene (5 mL) was heated at reflux. In a separate flask under argon atmosphere, complex **29** was generated upon addition of tris(*tert*-butyl(3,5-dimethylphenyl)amino)-(propylidyne)-molybdenum (2.6 mg, 3.9 µmol)[10] to a solution of ((2,4,6-triethylbenzene-1,3,5-triyl)tris(propane-3,1-diyl))tris(diphenylsilanol) (3.5 mg, 3.9 µmol)[11] in freshly distilled toluene (1

mL). The resulting homogeneous mixture was transferred via syringe to the flask containing the diyne substrate. After stirring for 2 h, the mixture was cooled to ambient temperature before it was filtered through a pad of silica, eluting with *tert*-butyl methyl ether. The filtrate was concentrated in vacuo and the residue was purified by gradient flash chromatography (hexane:EtOAc, 25:1 to 20:1) to give the title compound **26** as a colorless oil (2.5 mg, 44%) and cycloalkyne **27** (2.1 mg, 38%).



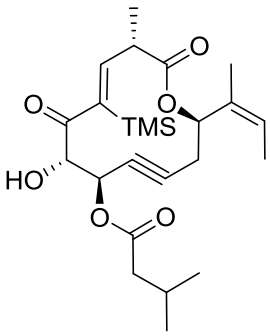
Analytical and spectral data of compound **26**: $[\alpha]_D^{20}$ = +39.5 (c = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, *J* = 10.6 Hz, 2H), 5.67 (dd, *J* = 7.9, 6.3 Hz, 2H), 5.46 – 5.36 (m, 4H), 4.68 (dq, *J* = 6.0, 2.2 Hz, 2H), 3.48 (dq, *J* = 10.5, 6.9 Hz, 2H), 2.54 – 2.36 (m, 4H), 2.24 (A of ABX, J_{AB} = 14.9 Hz, J_{AX} = 7.7 Hz, 2H), 2.23 (B of ABX, J_{AB} = 14.9 Hz, J_{BX} = 6.5 Hz, 2H), 2.17 – 2.06 (m, 2H), 1.78 (d, *J* = 2.2 Hz, 6H), 1.69 (dq, *J* = 7.0, 1.5 Hz, 6H), 1.62 – 1.61 (m, 6H), 1.32 (d, *J* = 6.9 Hz, 6H), 0.96 (d, *J* = 6.6 Hz, 12H), 0.89 (s, 18H), 0.20 (s, 18H), 0.14 (s, 6H), 0.10 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.6, 171.9, 171.9, 150.6, 144.7, 131.6, 125.3, 83.9, 78.7, 77.2, 76.9, 70.9, 63.1, 43.0, 42.6, 25.8, 25.6, 22.5, 22.4, 22.4, 18.3, 18.0, 17.5, 13.3, 3.7, 0.5, –4.6, –4.8; IR (film): 2958, 2929, 2858, 1737, 1684, 1598, 1463, 1372, 1294, 1250, 1167, 1096, 1050, 840, 779 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{64}H_{106}O_{12}Si_4Na$ $[M+Na]^+$: 1201.6654, found: 1201.6675.

Cycloalkyne 27. A solution of diyne **25** (325 mg, 0.53 mmol) in freshly distilled toluene (210 mL) was stirred at 90 °C. In a separate flask under argon atmosphere, dry CH_2Cl_2 (1 mL) was added to a solution of complex **30** (100 mg, 0.18 mmol)[9] in freshly distilled toluene (2 mL). The resulting homogeneous mixture was transferred via syringe to the flask containing the diyne substrate. After stirring for 36 h, the mixture was cooled to ambient temperature before it was filtered through a pad of silica. The filtrate was concentrated in vacuo and the residue was purified by gradient flash chromatography (hexane:EtOAc, 25:1 to 20:1) to give the title compound as a colorless oil (248 mg, 84%). $[\alpha]_D^{20}$ = +134.0 (c = 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.27 (d, *J* = 11.2 Hz, 1H), 5.70 (dd, *J* = 11.2, 3.5 Hz, 1H), 5.49 – 5.36 (m, 2H), 4.34 (ddd, *J* = 8.9, 2.7, 1.4 Hz, 1H), 3.53 (dq, *J* = 11.2, 6.6 Hz, 1H), 2.80 (ddd, *J* = 17.0, 11.2, 2.8 Hz, 1H), 2.33 (ddd, *J* = 16.9, 3.5, 1.4 Hz, 1H), 2.33 – 2.08 (m, 3H), 1.72 (dq, *J* = 7.0, 1.5 Hz, 3H), 1.69 – 1.68 (m, 3H), 1.22 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 6H), 0.87 (s, 9H), 0.37 (s, 9H), 0.12 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 172.4, 171.5, 150.6, 148.3, 131.9, 124.8, 85.4, 80.2, 80.1, 77.2, 69.9, 62.6, 43.3, 43.2, 25.6, 23.8, 22.4, 22.4, 18.2, 17.7, 14.6, 13.0, 0.6, –4.7, –5.0; IR (film):

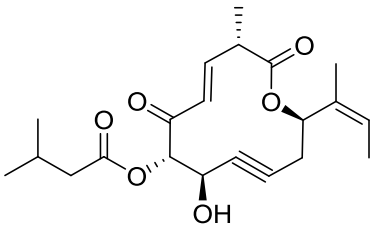


2958, 2930, 2857, 2180, 1742, 1172, 1091, 842 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{30}H_{50}O_6Si_2Na$ $[M+Na]^+$: 585.3038, found: 585.3045.

Homopropargyl alcohol 28. *p*-Toluenesulfonic acid monohydrate (3.5 mg, 18.7 µmol) was added to a solution of compound **21** (2.1 mg, 3.7 µmol) in CH_2Cl_2 and MeOH (2 mL, 3:1, *v/v*), and the resulting mixture was stirred for 5 d. This reaction was then quenched with sat. aq. $NaHCO_3$ (5 mL). After phase separation, the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Purification of the crude product by flash chromatography (hexane:EtOAc, 10:1) gave the title compound as a colorless oil (1.5 g, 90%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.14 (d, *J* = 11.1 Hz, 1H), 5.73 (ddd, *J* = 11.7, 3.3, 0.5 Hz, 1H), 5.43 (qqd, *J* = 7.0, 1.5, 0.7 Hz, 1H), 5.18 (ddd, *J* = 9.9, 3.0, 0.9 Hz, 1H), 4.43 (dd, *J* = 9.9, 8.3 Hz, 1H), 3.47 (d, *J* = 8.3 Hz, 1H), 3.46 (dq, *J* = 11.1, 6.6 Hz, 1H), 2.80 (ddd, *J* = 16.9, 11.7, 3.0 Hz, 1H), 2.31 (ddd, *J* = 16.9, 3.3, 0.8 Hz, 1H), 2.28 (dd, *J* = 14.8, 7.4 Hz, 1H), 2.25 (dd, *J* = 14.8, 6.9 Hz, 1H), 2.19 – 2.11 (m, 1H), 1.70 (dq, *J* = 7.0, 1.5 Hz, 3H), 1.67 (app. quint, *J* = 1.5 Hz, 3H), 1.25 (d, *J* = 6.6 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 6H), 0.36 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.5, 171.8, 171.8, 148.5, 147.9, 131.5, 125.2, 86.0, 77.7, 77.1, 70.1, 63.6, 43.6, 43.2, 25.7, 23.8, 22.4, 22.3, 17.6, 14.6, 13.0, 0.0; IR (film): 3455, 2961, 2934, 1743, 1680, 1596, 1253, 1177, 845 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{24}H_{36}O_6SiNa$ $[M+Na]^+$: 471.2173, found: 471.2172.



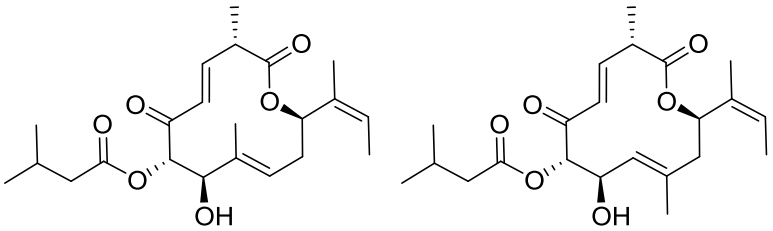
Propargyl alcohol 31. Glacial HOAc (0.18 mL, 3.1 mmol) was diluted with distilled water (1.2 mL) and the resulting solution added to a solution of compound **27** (0.25 g, 0.44 mmol) in a mixture of THF and MeOH (5 mL, 1:1, v/v). AgF (0.34 g, 2.6 mmol) was then added and the resulting mixture stirred for 24 h in the dark. The milky solution was filtered through a pad of Celite® and the filtrate was concentrated. The residue was dissolved in CH_2Cl_2 and the solution washed with brine, dried over Na_2SO_4, and concentrated in vacuo.



Without further purification, the crude material was dissolved in THF (2 mL) and H_2O (1.2 mL). Formic acid (2 mL) was added and the resulting mixture was stirred for 33 h. Upon complete consumption of the starting material, as indicated by TLC, the mixture was diluted with *tert*-butyl methyl ether and then carefully poured into an Erlenmeyer flask containing a sat. aq. solution of $NaHCO_3$ (70 mL) at 0 °C. After phase separation, the aqueous layer was extracted with *tert*-butyl methyl ether (2 x). The combined organic phases were washed with sat. aq. $NaHCO_3$ (30 mL) and brine (50 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude

product (a yellow oil) was used in the next step without further purification. For analytical purposes, an aliquot was purified by flash chromatography (acidic silica gel,[12] hexane:EtOAc, 7:3) but undesirable partial migration of the acyl group could not be avoided; colorless oil: $[\alpha]_D^{20}$ = 78.0 (c = 0.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.83 (A of ABX, J_{AB} = 15.8 Hz, J_{AX} not observed, 1H), 6.80 (B of ABX, J_{BA} = 15.8 Hz, J_{BX} = 6.8 Hz, 1H), 5.49 (dd, *J* = 10.4, 3.4 Hz, 1H), 5.45 – 5.40 (m, 1H), 5.16 (d, *J* = 9.0 Hz, 1H), 4.44 – 4.40 (m, 1H), 3.46 (app. quint, *J* = 6.8 Hz, 1H), 2.81 (ddd, *J* = 17.2, 10.5, 2.6 Hz, 1H), 2.48 (d, *J* = 4.1 Hz, 1H), 2.42 (ddd, *J* = 17.1, 3.5, 2.0 Hz, 1H), 2.36 – 2.26 (m, 2H), 2.18 – 2.08 (m, 1H), 1.70 – 1.68 (m, 6H), 1.31 (d, *J* = 6.8 Hz, 3H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 172.0, 171.6, 145.9, 132.1, 130.5, 124.5, 86.3, 80.4, 77.7, 70.9, 61.9, 42.6, 42.0, 25.8, 23.5, 22.3 (2), 17.9, 14.1, 13.0; IR (film): 3459, 2960, 2937, 2873, 2241, 1738, 1706, 1626, 1169 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{21}H_{28}O_6Na$ $[M+Na]^+$: 399.1778, found: 399.1780.

Disciformycin B Aglycone 35 and Isomer 36



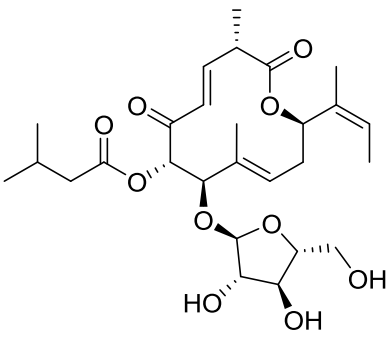
$[Cp^*RuCl]_4$ (7.2 mg, 26.5 µmol) was added to a solution of the crude propargyl alcohol **31** in CH_2Cl_2 (4 mL). After stirring for 2 min, the resulting mixture was cooled to –45 °C before a diluted solution of $HSnBu_3$ (51 mg, 0.18 mmol) in CH_2Cl_2 (2 mL) was added to the flask via syringe pump over 25 min. The resulting light brown solution was stirred for 2 h at this temperature, the solvents were removed under reduced pressure, and the residue was immediately carried on to the next step without further purification and characterization.

Chloro(1,5-cyclooctadiene)methylpalladium(II) (117 mg, 0.44 mmol)[13] was added to a solution of the crude alkenyl stannanes (**32**+**33**) in a mixture of THF/Sorenson's phosphate pH 7.0 buffer (4.4 mL, 10:1). The mixture was stirred at 55 °C for 4.5 h, the solution was cooled to ambient temperature and filtered through cotton wool, rinsing with *tert*-butyl methyl ether (2 x 5 mL). The combined filtrates were concentrated in vacuo and the crude material was rapidly purified by gradient flash chromatography using "acidic silica gel"[12] as the stationary phase (5:1 to 4:1, hexane:EtOAc) to give aglycone **35** as a colorless oil (14 mg, 20% over four steps) and isomer **36** (7%, admixed with unreacted **31**). This second fraction was further purified by preparative LC (YMC PVA-Sil 5 µm, 250 mm × 10 mm, n-heptane/*tert*-butyl methyl ether/MeOH, 90:10:1, 5.0 mL/min, 5.0 MPa, 308 K) to give **36** in analytically pure form.

Analytical and spectral data of compound **35**: $[\alpha]_D^{20}$ = +21.0 (c = 0.1, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.57 (dd, *J* = 15.3, 9.1 Hz, 1H), 6.38 (d, *J* = 15.3 Hz, 1H), 5.40 (q, *J* = 6.6 Hz, 1H), 5.38 – 5.33 (m, 2H), 5.20 (d, *J* = 10.0 Hz, 1H), 4.11 (d, *J* = 10.1 Hz, 1H), 3.33 (dq, *J* = 9.0, 6.6 Hz, 1H), 2.90 (ddd, *J* = 14.8, 11.5, 11.5 Hz, 1H), 2.47 (brs, 1H), 2.38 (dd, *J* = 14.9, 7.1 Hz, 1H), 2.32 (dd, *J* = 15.0, 7.1 Hz, 1H), 2.22 – 2.10 (m, 1H), 2.03 – 1.97 (m, 1H), 1.92 (s, 3H), 1.71 – 1.68 (m, 6H), 1.26 (d, *J* = 6.7 Hz, 3H), 1.02 (d, *J* = 6.7 Hz, 3H), 1.01 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.3, 172.1, 171.5, 145.6, 134.1, 133.1, 130.0, 128.9, 123.4, 79.1, 76.9, 72.9, 42.9 (2), 32.0, 25.8, 22.4, 18.0, 14.1, 13.0, 11.7; IR (film): 3490, 2959, 2927, 2855, 1737, 1706, 1627, 1173 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{22}H_{32}O_6Na$ $[M+Na]^+$: 415.2091, found: 415.2092.

Analytical and spectral data of compound **36**: $[\alpha]_D^{20}$ = +31.2 (c = 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.62 (d, *J* = 15.4 Hz, 1H), 6.55 (dd, *J* = 15.3, 8.4 Hz, 1H), 5.61 (dd, *J* = 12.4, 2.8 Hz, 1H), 5.47 – 5.43 (m, 1H), 5.42 – 5.36 (m, 1H), 4.99 (d, *J* = 9.6 Hz, 1H), 4.44 (app. t, *J* = 9.5 Hz, 1H), 3.34 (dq, *J* = 8.4, 6.7 Hz, 1H), 2.72 (dd, *J* = 14.1, 12.3 Hz, 1H), 2.36 (A of ABX, J_{AB} = 14.8 Hz, J_{AX} = 7.3 Hz, 1H), 2.30 (B of ABX, J_{BA} = 14.8 Hz, J_{BX} = 6.9 Hz, 1H), 2.20 – 2.09 (m, 2H), 1.71 (dq, *J* = 7.0, 1.5 Hz, 3H), 1.68 – 1.66 (m, 3H), 1.58 (brs, 1H) 1.48 (s, 3H), 1.26 (d, *J* = 6.7 Hz, 3H), 1.01 (d, *J* = 6.6 Hz, 3H), 1.00 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0, 172.2, 171.4, 144.4, 138.5, 132.9, 130.8, 125.0, 123.3, 81.3, 69.6, 67.7, 44.0, 42.8, 42.7, 25.9, 22.4 (2), 17.9, 15.6, 14.0, 12.9; IR (film): 3479, 2962, 2938, 2872, 1736, 1704, 1627, 1176 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{22}H_{32}O_6Na$ $[M+Na]^+$: 415.2091, found: 415.2091.

Disciformycin B (2). A freshly prepared solution of TMSOTf (2.5 mg, 11.2 µmol) in CH_2Cl_2 (0.2 mL) was added at –45 °C to a solution of aglycone **35** (11.0 mg, 28.0 µmol) and glycosyl donor **37** (32.0 mg, 50.4 µmol) in CH_2Cl_2 (1.2 mL). The resulting mixture was stirred at this temperature for 2 h and subsequently at –25 °C for another 2 h. The reaction was then quenched with Sorenson's phosphate buffer (pH 7.0, 3 mL) at –25 °C before the mixture was allowed to reach ambient temperature. After phase separation, the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL), the combined extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The resulting crude product was immediately used in the next step without further purification.



In a Nalgene® vial, aqueous HF (0.3 mL, 48% *w/w*) was added at 0 °C to a solution of the crude material in a mixture of CH_2Cl_2 and MeCN (3 mL, 1:2, v/v). The cooling bath was removed and stirring continued at rt for 15. The reaction was then carefully quenched with sat. aq. $NaHCO_3$ (10 mL). After phase separation, the aqueous layer was extracted with EtOAc (3 × 10 mL), and the combined organic phases were washed with brine (10 mL), dried over Na_2SO_4, and

concentrated in vacuo. Purification of the residue by preparative LC (YMC PVA-Sil 5 µm, 250 mm × 10 mm, *n*-heptane/*tert*-butyl methyl ether/MeOH, 6:4:1, 5.0 mL/min, 8.0 MPa, 308 K) furnished **disciformycin B** (**2**) as a colorless syrup (4.0 mg, 27% over two steps); a second fraction contained recovered aglycone **35** (2.0 mg, 20% over two steps). $[\alpha]_D^{20}$ = +187.5 (c = 0.04, MeOH); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.59 (dd, *J* = 15.3, 9.2 Hz, 1H), 6.36 (dd, *J* = 15.3, 1.0 Hz, 1H), 5.42 – 5.39 (m, 2H), 5.33 (dd, *J* = 11.5, 2.8 Hz, 1H), 5.31 (d, *J* = 10.3 Hz, 1H), 5.18 (brs, 1H), 4.11 (app. q, *J* = 2.0 Hz, 1H), 4.08 (d, *J* = 10.3 Hz, 1H), 4.02 – 4.01 (m, 2H), 3.87 (dd, *J* = 11.7, 2.5 Hz, 1H), 3.81 (dd, *J* = 11.7, 1.9 Hz, 1H), 3.33 (dq, *J* = 9.2, 6.7 Hz, 1H), 2.86 (ddd, *J* = 14.7, 11.5, 11.3 Hz, 1H), 2.35 (dd, *J* = 15.0, 7.3 Hz, 1H), 2.30 (dd, *J* = 15.0, 7.1 Hz, 1H), 2.15 (app. sept, *J* = 6.8 Hz, 1H), 2.05 – 2.02 (m, 1H), 1.90 (app. t, *J* = 1.4 Hz, 3H), 1.70 (dq, *J* = 6.9, 1.4 Hz, 3H), 1.68 (q, *J* = 1.4 Hz, 3H), 1.26 (d, *J* = 6.7 Hz, 3H), 1.01 (d, *J* = 6.6 Hz, 3H), 1.01 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.1, 172.4, 171.5, 145.9, 133.3, 133.0, 129.8, 129.3, 123.4, 108.1, 88.0, 81.0, 78.3, 78.2, 78.2, 72.7, 62.0, 43.0, 42.8, 32.0, 25.8, 22.4, 22.3, 18.0, 14.0, 13.0, 12.5; IR (film): 3397, 2963, 2920, 2874, 2853, 1738, 1703, 1626, 1456, 1298, 1177, 1071, 1026 cm^{-1}. HRMS (ESI): *m*/*z* calcd for $C_{27}H_{40}O_{10}Na$ $[M+Na]^+$: 547.2514, found: 547.2513.

Isomerization of Disciformycin B into Disciformycin A (1). A solution of Et_3N (10 mg) in CH_2Cl_2 (0.1 mL) was added to a solution of disciformycin B (0.2 mg) in CH_2Cl_2/CH_3CN (0.8 mL, 1:1, *v*/*v*). After stirring for 5 h, the reaction mixture was concentrated in vacuo and the residue passed through a short pad of silica, eluding with CH_2Cl_2:EtOAc (4:6). Evaporation of the combined filtrated gave disciformycin A (**1**) as a white solid (0.2 mg, quant.). $[\alpha]_D^{20}$ = –76.7 (c = 0.03, MeOH); ^{1}H NMR (600 MHz, CD_3OD) δ 5.84 (ddq, *J* = 7.8, 7.8, 1.5 Hz, 1H), 5.57 (dd, *J* = 11.9, 3.4 Hz, 1H), 5.39 – 5.35 (m, 1H), 5.30 – 5.26 (m, 1H), 5.09 (brs, 1H), 5.01 (d, *J* = 9.0 Hz, 1H), 4.22 (d, *J* = 9.5 Hz, 1H), 4.02 (dd, *J* = 3.2, 1.3 Hz, 1H), 3.97 (dd, *J* = 18.5, 7.8 Hz, 1H), 3.90 (ddd, *J* = 6.0, 5.2, 3.3 Hz, 1H), 3.84 (dd, *J* = 6.0, 3.2 Hz, 1H), 3.69 (dd, *J* = 11.9, 3.3 Hz, 1H), 3.60 (dd, *J* = 11.9, 5.2 Hz, 1H), 3.54 (dd, *J* = 18.5, 7.8 Hz, 1H), 2.78 (ddd, *J* = 14.7, 11.7, 11.7 Hz, 1H), 2.26 (app. d, *J* = 7.1 Hz, 2H), 2.11 – 2.03 (m, 2H), 1.92 (brs, 3H), 1.87 (app. t, *J* = 1.4 Hz, 3H), 1.70 (dq, *J* = 7.0, 1.5 Hz, 3H), 1.61 (app. quint, *J* = 1.5 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.96 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 203.9, 174.5, 169.1, 134.9, 134.8, 134.5, 129.9, 128.8, 123.6, 110.6, 86.3, 84.2, 83.8, 80.8, 79.1, 75.4, 63.0, 44.0, 43.4, 31.8, 27.0, 22.7, 22.7, 21.2, 18.3, 13.2, 12.3; IR (film): 3410, 2961, 2934, 2926, 1728, 1377, 1251, 1190, 1125, 1078, 1037, 1007, 995 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{27}H_{40}O_{10}Na$ $[M+Na]^+$: 547.2514, found: 547.2515.

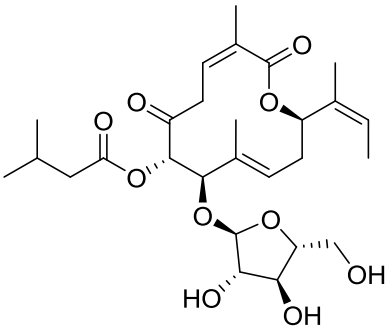
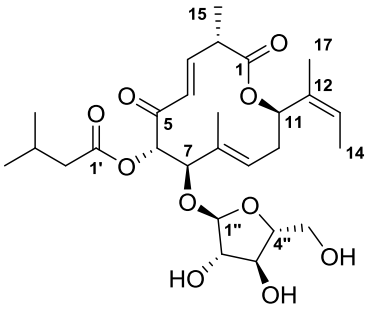


Table S1. Comparison of NMR data of disciformycin B (**2**) in $CDCl_3$ (calibration: $CHCl_3 \equiv 7.26$ ppm (^{1}H NMR); $CDCl_3 \equiv 77.0$ ppm (^{13}C NMR)); numbering scheme as shown in the Insert



disciformycin B

#	Synthetic compound		Literature[14]		Δδ ^{13}C (ppm)	Δδ ^{1}H (ppm)
	^{13}C (150 MHz)	^{1}H (600 MHz)	^{13}C (170 MHz)	^{1}H (700 MHz)		
1	171.5	-	171.5	-	0	-
2	43.0	3.33	43.0	3.34	0	0.01
3	145.9	6.59	145.9	6.59	0	0
4	129.8	6.36	129.9	6.37	0.1	0.01
5	192.1	-	192.1	-	0	-
6	78.2	5.31	78.2	5.32	0	0.01
7	81.0	4.08	81.1	4.09	0.1	0.01
8	133.3	-	133.3	-	0	-
9	129.3	5.40	129.4	5.42	0.1	0.02
10	32.0	2.86	32.1	2.87	0.1	0.01
		2.03		2.04		0.01
11	72.7	5.33	72.8	5.33	0.1	0
12	133.0	-	133.0	-	0	-
13	123.4	5.40	123.4	5.40	0	0
14	13.0	1.70	13.0	1.71	0	0.01
15	14.0	1.26	14.1	1.27	0.1	0.01
16	12.5	1.90	12.5	1.91	0	0.01
17	18.0	1.68	18.0	1.69	0	0.01
1'	172.4	-	172.5	-	0.1	-
2'	42.8	2.35	42.8	2.36	0	0.01
		2.30		2.31		0.01
3'	25.8	2.15	25.8	2.16	0	0.01
4'	22.4	1.01	22.4	1.02	0	0.01
5'	22.3	1.01	22.4	1.02	0.1	0.01
1''	108.1	5.18	108.2	5.19	0.1	0.01
2''	78.2	4.02	78.2	4.03	0	0.01
3''	78.3	4.02	78.3	4.03	0	0.01
4''	88.1	4.11	88.1	4.13	0	0.02
5''	62.0	3.87	62.1	3.89	0.1	0.02
		3.81		3.83		0.02

Table S2. Comparison of NMR data of disciformycin A (**1**) in [D_4]-MeOH (calibration: $CHD_2OH \equiv$ 3.31 ppm (^{1}H NMR); [D_4]-MeOH ≡ 49.0 ppm (^{13}C NMR))

#	Synthetic compound		Literature[14]		Δδ ^{13}C (ppm)	Δδ ^{1}H (ppm)
	^{13}C (150 MHz)	^{1}H (600 MHz)	^{13}C (150 MHz)	^{1}H (600 MHz)		
1	169.1	-	169.1	-	0	-
2	134.5	-	134.5	-	0	-
3	129.9	5.84	130.0	5.88	0.1	0.04
4	44.0	3.97	44.0	4.01	0	0.04
		3.54		3.58		0.04
5	203.9	-	203.9	-	0	-
6	80.8	5.01	80.8	5.05	0	0.04
7	84.2	4.22	84.2	4.26	0	0.04
8	134.8	-	134.9	-	0.1	-
9	128.8	5.28	128.8	5.32	0	0.04
10	31.8	2.78	31.8	2.82	0	0.04
		2.09		2.13		0.04
11	75.4	5.57	75.4	5.58	0	0.01
12	134.9	-	134.9	-	0	-
13	123.6	5.37	123.6	5.41	0	0.04
14	13.2	1.70	13.1	1.74	0.1	0.04
15	21.2	1.92	21.2	1.96	0	0.04
16	12.3	1.87	12.3	1.91	0	0.04
17	18.3	1.61	18.3	1.65	0	0.04
1'	174.5	-	174.5	-	0	-
2'	43.4	2.26	43.4	2.30	0	0.04
		2.26		2.30		0.04
3'	27.0	2.08	27.0	2.11	0	0.03
4'	22.7	0.97	22.7	1.01	0	0.04
5'	22.7	0.96	22.7	1.00	0	0.04
1''	110.6	5.09	110.6	5.13	0	0.04
2''	83.8	4.02	83.8	4.06	0	0.04
3''	79.1	3.84	79.1	3.88	0	0.04
4''	86.3	3.90	86.3	3.94	0	0.04
5''	63.0	3.69	63.0	3.73	0	0.04
		3.60		3.64		0.04

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