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Supporting Information

Total Synthesis and Biological Evaluation of the Cytotoxic Resin Glycosides Ipomoeassin A-F and Analogues

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Experimental Section

General: All reactions were carried out under Ar in flame-dried glassware. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Mg/anthracene), CH_2Cl_2, Et_3N, CH_3CN, DMSO, (CaH_2), pentane, hexane, toluene (Na/K), DMF (Desmodur 15, dibutyl tin dilaurat), MeOH, EtOH (Mg). Flash chromatography (FC): Merck silica gel 60 (230–400 mesh). NMR: Spectra were recorded on Bruker DPX 300, AMX 300, AV 400, DPX 600 and AVIII 600 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_C \equiv 77.0$ ppm; residual $CHCl_3$ in $CDCl_3$: $\delta_H \equiv 7.26$ ppm; CD_2Cl_2: $\delta_C \equiv 53.8$ ppm; residual ^1H: $\delta_H \equiv 5.32$ ppm; CD_3OD $\delta_C \equiv 49.0$ ppm; residual ^1H: $\delta_H \equiv 3.30$ ppm; $[D]_8$-acetone: $\delta_C \equiv 29.8$ ppm; residual ^1H: $\delta_H \equiv 2.05$ ppm). Where indicated, the signal assignments are unambiguous; the numbering scheme is arbitrary as shown in the inserts. The assignments are based upon 1D and 2D spectra recorded using the following pulse sequences from the Bruker standard pulse program library: DEPT; COSY (*cosygs, cosydqtp*, and *cosygpqf*); HSQC (*invietgssi*, and *hsqcedetgpsisp*^{2}*.2*) optimized for $^1J(C,H) = 145$ Hz; HMBC (*inv4gslplrnd*, and *hmbcetgpl3nd*); for correlations via $^nJ(C,H)$; HSQC-TOCSY (*invietgsml*) using an MLEV17 mixing time of 120 ms; NOESY (*noesygpph*). IR: Magna IR750 (Nicolet) or Spectrum One (Perkin-Elmer) spectrometer, wavenumbers ($\tilde{\nu}$) in cm^{-1}; MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ3000 (Bruker), accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or Mat 95 (Finnigan). Melting points: Büchi melting point apparatus B-540 (corrected). Elemental analyses: H. Kolbe, Mülheim/Ruhr. All commercially available compounds (Fluka, Lancaster, Aldrich) were used as received.

Building blocks

(*S*)-1-Hepten-4-ol (10a): A solution of EtMgCl (2 M in THF, 16.2 mL, 32.4 mmol) was added dropwise to a solution of (*S*)-epichlorohydrine **7** (2.00 g, 21.6 mmol) and CuCN (193 mg, 2.16 mmol) in THF (30 mL) at −78 °C. The mixture was warmed to −20 °C over 3 h

before it was poured into sat. aq. NH_4Cl. The organic layer was separated, the aqueous phase was extracted with Et_2O, the combined organic layers were dried over $MgSO_4$, filtered and evaporated to afford crude (*S*)-1-chloro-pentan-2-ol (**8a**), which was used without further purification.

Powdered NaOH (4.80 g, 121 mmol) was added to a solution of the crude **8a** in Et_2O (30 mL) and the resulting mixture was stirred at room temperature for 22 h before it was poured into water (10 mL). The organic layer was separated, the aqueous layer was repeatedly extracted with Et_2O (3 x 10 mL), the combined organic phases were dried over $MgSO_4$, filtered and evaporated to give (*S*)-2-propyloxirane (**9a**), which was used without further purification.

To a stirred solution of crude **9a** thus formed and CuCN (193 mg, 2.16 mmol) in THF (15 mL) was added a solution of vinylmagnesium bromide (1 M in THF, 28.1 mL, 28.1 mmol) at −78 °C over a period of 45 min. The resulting mixture was allowed to warm to 0 °C before the reaction was quenched with sat. aq. NH_4Cl. The aqueous layer was repeatedly extracted with Et_2O, the combined ethereal extracts were washed with brine, dried over $MgSO_4$, filtered and evaporated. The residue was purified by flash chromatography (hexanes/*tert*-butyl methyl ether, 4/1) to give **10a** as a pale yellow oil (1.91 g, 77 %). The NMR data are in full agreement with those previously reported in the literature.[1] $[\alpha]_D^{20}$ = –12.8 (*c* = 0.52, $CHCl_3$); lit. $[\alpha]_D^{20}$ = +12.7 (*c* = 0.54, $CHCl_3$) for (*R*)-enantiomer (99 % *ee*).

(*S*)-Non-1-en-4-ol (10b): Prepared analogously as a colorless oil (1.34 g, 74 % overall). $[\alpha]_D^{20}$ = –7.7 (*c* = 1.52, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.84 (dddd, *J* = 12.0, 9.4, 7.9, 6.5 Hz, 1 H), 5.15-5.17 (m, 1 H), 5.11-5.13 (m, 1 H), 3.66 (ddt, *J* = 9.8, 7.8, 4.9 Hz, 1 H), 2.28-2.35 (m, 1 H), 2.11-2.18 (m, 1 H), 1.28-1.59 (m, 8 H), 0.90 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.2, 118.3, 70.9, 42.2, 37.0, 32.1, 25.6, 22.8, 14.2; IR (film): $\tilde{\nu}$ = 3372, 3077, 2956, 2930, 2857, 1641, 1466, 1378, 1124, 1029, 994, 912, 725; MS (EI):

[1] S.-K. Kang, D.-C. Park, H.-S. Rho, C.-M. Yu, J.-H. Hong, *Synth. Commun.* **1995**, *25*, 203-214.

m/*z* (%): 124 (1) [M^+], 101 (24), 83 (70), 57 (12), 55 (100), 43 (30), 41 (37), 29 (18); HRMS (CI): *m*/*z*: calcd for $C_9H_{19}O$ [M^+ + H]: 143.1436, found: 143.1435.

Compound 12a: A solution of HBr in HOAc (30 % *w*/*w*, 7.1 mL) was added dropwise to a cold (0 °C) solution of 1,2,3,4-tetra-*O*-acetyl-D-fucopyranose (2.08 g, 6.26 mmol)[2] in CH_2Cl_2 (10 mL) and Ac_2O (0.96 mL) and the resulting mixture was stirred for 0.5 h at room temperature once the addition was complete. The mixture was then concentrated in vacuo and the resulting oil was azeotroped with toluene (3 x 10 mL) to give crude glycosyl bromide **11** which was used in the following step without further purification.

A solution of the crude bromide **11** prepared above in CH_2Cl_2 (120 mL) was added to a suspension of activated MS 4 Å in CH_2Cl_2 (50 mL) and the resulting mixture was stirred at room temperature for 10 min before (*S*)-1-hepten-4-ol (**10a**) (476 mg, 4.17 mmol), 2,6-di-*tert*-butylpyridine (2.40 g, 12.5 mmol) and AgOTf (1.90 g, 7.32 mmol) were successively added. Stirring was continued for 14 h before the suspension was filtered through a pad of Celite. The filtrate was evaporated and the residue purified by flash chromatography (hexanes/*tert*-butyl methyl ether, 6/1) to give compound **12a** as a colorless syrup (1.36 g, 84 %). $[\alpha]_D^{20}$ = –20.1 (*c* = 0.73, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.77 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1 H), 5.21 (dd, *J* = 3.5, 1.1 Hz, 1 H), 5.17-4.99 (m, 4 H), 4.48 (d, *J* = 7.9 Hz, 1 H), 3.76 (dq, *J* = 6.5, 1.0 Hz, 1 H), 3.64 (m, 1 H), 2.25-2.22 (m, 2 H), 2.17 (s, 3 H), 2.04 (s, 3 H), 1.98 (s, 3 H), 1.63-1.34 (m, 4 H), 1.20 (d, *J* = 6.7 Hz, 3 H), 0.89 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.8, 170.3, 169.4, 134.4, 117.1, 100.4, 79.7, 71.5, 70.4, 69.3, 68.9, 38.4, 36.6, 20.9, 20.7, 20.6, 18.3, 16.1, 14.0; IR (film): $\tilde{\nu}$ = 3076, 2961, 2937, 2873, 1752, 1641, 1368, 1250, 1223, 1074, 915; MS (EI): *m*/*z* (%): 273 (27), 157 (17), 153 (25), 115 (13), 111 (24), 83 (12), 55 (23), 43 (100); HRMS (ESI): *m*/*z*: calcd for $C_{19}H_{30}O_8Na$ [M^+ + Na]: 409.18314, found: 409.18329.

[2] K. C. Nicolaou, C. W. Hummel, M. Nakada, K. Shibayama, E. N. Pitsinos, H. Saimoto, Y. Mizuno, K.-U. Baldenius, A. L. Smith, *J. Am. Chem. Soc.* **1993**, *115*, 7625-7635.

Compound 12b: Prepared analogously as a colorless syrup (602 mg, 67 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.77 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1 H), 5.22 (dd, *J* = 3.5, 1.0 Hz, 1 H), 5.16 (dd, *J* = 10.5, 7.9 Hz, 1 H), 5.07 (ddt, *J* = 4.2, 2.2, 1.2 Hz, 1 H), 4.98-5.04 (m, 2 H), 4.48 (d, *J* = 7.9 Hz, 1 H), 4.13 (q, *J* = 7.1 Hz, 1 H), 3.77 (qd, *J* = 6.4, 0.9 Hz, 1 H), 3.63 (pent., *J* = 5.9 Hz, 1 H), 2.24 (t, *J* = 6.2 Hz, 2 H), 2.17 (s, 3 H), 2.04 (s, 3 H), 1.98 (s, 3 H), 1.23-1.61 (m, 7 H), 1.20 (d, *J* = 6.4 Hz, 3 H), 0.89 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.0, 170.5, 169.7, 134.7, 117.3, 100.8, 80.4, 71.8, 70.6, 69.5, 69.2, 38.7, 34.6, 32.0, 24.9, 22.8, 21.1, 21.0, 20.9, 16.3, 14.3; IR (film): $\tilde{\nu}$ = 3078, 2985, 2955, 2934, 2861, 1749, 1436, 1367, 1249, 1220, 1173, 1073, 1016, 913, 727; MS (EI): *m*/*z* (%): 273 (52), 213 (12), 184 (17), 171 (15), 157 (34), 153 (48), 142 (16), 115 (23), 111 (40), 83 (17), 69 (14), 55 (12), 43 (100); HRMS (ESI): *m*/*z*: calcd for $C_{21}H_{34}O_8Na$ [M^+ + Na]: 437.2146, found: 437.2145.

Compound 13a: Compound **12a** (1.92 g, 4.97 mmol) was dissolved in MeOH (20 mL) and treated with KOMe (18 mg, 0.25 mmol) for 3 h. The mixture was neutralized with HCl (1 M) and the solvent was evaporated. The residue was suspended in EtOAc, the mixture passed through a short-pad of silica to remove the inorganic salts, and the filtrate was evaporated. A solution containing the resulting crude product, 2,2'-dimethoxypropane (4.4 mL) and $TsOH \cdot H_2O$ (ca. 20 mg) in acetone (15 mL) was stirred at room temperature for 15 h. For work-up, the solvent was evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 6/1 $\rightarrow$ 4/1) to give glycoside **13a** as a colorless syrup (1.46 g, 98 %). $[\alpha]_D^{20}$ = +3.4 (*c* = 1.18, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.83 (ddt, *J* = 17.1, 10.1, 7.2 Hz, 1 H), 5.13-5.08 (m, 2 H), 4.17 (d, *J* = 8.2 Hz, 1 H), 4.04-3.98 (m, 2 H), 3.83 (dq, *J* = 6.6, 2.2 Hz, 1H), 3.72-3.66 (m, 1 H), 3.50 (dd, *J* = 8.2, 7.3 Hz, 1 H), 2.35-2.23 (m, 3 H), 1.65-1.33 (m, 13 H), 0.91 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.9, 117.6, 109.8, 101.6, 78.8, 78.7, 76.3, 73.8, 69.1, 38.7, 37.0, 28.2, 26.3, 18.4, 16.6, 14.0; IR (film): $\tilde{\nu}$ = 3483, 3076, 2983, 2959, 2935, 2872, 1641, 1380, 1073, 1036, 990, 918; MS (EI): *m*/*z* (%): 187 (84), 129 (16), 113 (12), 101 (43), 100 (37), 97 (19), 85 (20), 83 (26), 73 (22), 71 (45), 59 (100), 57 (34), 55 (79), 43 (72), 41 (36), 29 (20); HRMS (ESI): *m*/*z*: calcd for $C_{16}H_{28}O_5Na$ [M^+ + Na]: 323.18287, found: 323.18290.

Compound 13b: Prepared analogously as a colorless syrup (757 mg, 83 %). $[\alpha]_D^{20}$ = +8.8 (*c* = 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 5.84 (ddt, *J* = 17.1, 10.2, 7.1 Hz, 1 H), 5.09-5.14 (m, 2 H), 4.18 (d, *J* = 8.3 Hz, 1 H), 4.03 (dd, *J* = 7.2, 5.5 Hz, 1 H), 3.99 (dd, *J* = 5.5, 2.2 Hz, 1 H), 3.84 (qd, *J* = 6.6, 2.1 Hz, 1 H), 3.65-3.71 (m, 1 H), 3.51 (dd, *J* = 8.2, 7.3 Hz, 2 H), 2.24-2.34 (m, 2 H), 1.54 (s, 3 H), 1.50-1.68 (m, 2 H), 1.41 (d, *J* = 6.6 Hz, 3 H), 1.36 (s, 3 H), 1.22-1.39 (m, 6 H), 0.89 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 135.2, 117.8, 110.0, 101.9, 79.5, 79.0, 76.6, 74.1, 69.4, 38.9, 35.0, 32.0, 28.5, 26.6, 25.0, 22.8, 16.9, 14.3; IR (film): $\tilde{\nu}$ = 3477, 3074, 2984, 2934, 2862, 1641, 1457, 1380, 1244, 1218, 1181, 1154, 1129, 1069, 1034, 991, 916, 869, 801, 687; MS (EI): *m*/*z* (%): 313 (4), 287 (4), 187 (100), 129 (19), 113 (13), 101 (36), 100 (35), 99 (57), 85 (17), 83 (20), 55 (30), 43 (41), 29 (11); HRMS (ESI): *m*/*z*: calcd for $C_{18}H_{32}O_5Na$ [M^+ + Na]: 351.2153, found: 351.2142.

(*Z*)-(3-Iodo-3-phenylallyloxy)dimethyl(phenyl)silane (23): Alcohol **22** (1.6 mL, 12.83 mmol) was added dropwise to a solution of sodium bis(2-methoxyethoxy)aluminum hydride (RED-Al, 7.75 mL, 25.7 mmol) in Et_2O (43 mL) at 0 °C and the resulting dark mixture was stirred at ambient temperature for 4 h. For work up, the mixture was cooled to 0 °C and the reaction quenched by slow addition of EtOAc (1.25 mL, 12.83 mmol). After additional 15 min at 0 °C, the mixture was cooled to −78 °C before I_2 (4.89 g, 19.25 mmol) was added in one portion. The mixture was allowed to reach room temperature over the course of 5 h before it was quenched with aq. sat. $Na_2S_2O_3$ (20 mL). The resulting mixture was diluted with water (20 mL), the aqueous layer was extracted with *tert*-butyl methyl ether (3 x 100 mL), the combined organic layers were dried over $MgSO_4$ and evaporated, and the residue was purified by flash chromatography (hexanes/Et_2O, 20:1) to give (*Z*)-3-iodo-3-phenylprop-2-en-1-ol (2.86 g, 86 %) as a pale yellow oil, which analyzed as follows: ^{1}H NMR (300 MHz, $CDCl_3$): δ= 7.47-7.51 (m, 2 H), 7.28-7.36 (m, 3 H), 6.27 (t, *J* = 5.7 Hz, 1 H), 4.40 (d, *J* = 5.7 Hz, 2 H), 1.75 (br. s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ= 142.4, 137.2, 128.9, 128.6, 128.5, 105.3, 68.5; IR (film): $\tilde{\nu}$ = 3325, 3081, 3058, 2912, 2874, 1622, 1591, 1573, 1487, 1442, 1217, 1033, 853, 751, 692; MS (EI): *m*/*z* (%): 261 (1) [M^+ + 1], 260 (18) [M^+], 133 (100), 115 (16),

105 (26), 104 (13), 103 (79), 102 (22), 77 (30), 55 (37), 51 (13); HRMS (EI): *m*/*z*: calcd for C_9H_9IO: 259.9698, found: 259.9699.

Et_3N (1.531 mL, 10.98 mmol) was added to a solution of this alcohol (2.80 g, 10.77 mmol) in CH_2Cl_2 (54 mL) at 0 °C and the mixture was stirred for 10 min before a solution of chlorodimethylphenylsilane (1.84 mL, 10.98 mmol) in CH_2Cl_2 (10 mL) was added over 15 min. Stirring was continued at 0 °C for 2 h before the reaction was quenched with aq. sat. NH_4Cl (25 mL). The aqueous layer was extracted with CH_2Cl_2 (50 mL), the combined organic phases were dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (hexanes/Et_2O, 20:1) to give product **23** as a pale yellow oil (4.09 g, 96 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46-7.49 (m, 2 H), 7.24-7.28 (m, 5 H), 7.11-7.15 (m, 3 H), 6.03 (t, *J* = 5.2 Hz, 1 H), 4.24 (d, *J* = 5.2 Hz, 2 H), 0.32 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.4, 139.1, 138.6, 134.7, 131.0, 129.7, 129.6, 129.4, 129.2, 104.1, 70.4, –0.5; IR (film): $\tilde{\nu}$ = 3069, 3022, 2956, 2865, 1623, 1591, 1575, 1488, 1443, 1427, 1252, 1116, 1059, 877, 826, 787, 741, 694; MS (EI): *m*/*z* (%): 394 (1) [M^+], 267 (36), 247 (13), 194 (12), 193 (75), 165 (12), 136 (13), 135 (100), 115 (25), 91 (15), 75 (25); HRMS (ESI): *m*/*z*: calcd for $C_{17}H_{19}OISiNa$ [M^+ +Na]: 417.0148, found: 417.0150.

(*Z*)-3-(Dimethyl(phenyl)silyl)-3-phenylprop-2-en-1-ol (24): *t*BuLi (1.5 M in pentane, 3.72 ml, 5.58 mmol) was added over 10 min to a solution of vinyl iodide **23** (1.00 g, 2.54 mmol) in THF (13 mL) at −78 °C. After stirring for 2 h at that temperature, the reaction was quenched with aq. sat. NH_4Cl (20 mL), the aqueous layer was extracted with *tert*-butyl methyl ether (3 x 25 mL), the combined extracts were dried over $MgSO_4$ and evaporated, and the residue was purified by flash chromatography (hexanes/Et_2O, 5:1) to give vinylsilane **24** (385 mg, 57 %) as a colorless syrup. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45-7.48 (m, 2 H), 7.24-7.28 (m, 3 H), 7.05-7.19 (m, 3 H), 6.99-6.95 (m, 2 H), 6.24 (t, *J* = 6.9 Hz, 1 H), 3.98 (d, *J* = 6.8 Hz, 2 H), 1.27 (br. s, 1 H), 0.22 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.0, 145.4, 144.9, 139.4, 133.9, 129.5, 128.4, 128.2, 127.6, 126.2, 62.5, –0.2; IR (film): $\tilde{\nu}$ = 3337, 3069, 3052, 3019, 3022, 2956, 2898, 1596, 1489, 1441, 1427, 1251, 1110, 1030, 881, 811, 778, 731, 700; MS

(EI): *m*/*z* (%): 268 (0.6) [M^+], 253 (10), 250 (31), 236 (13), 235 (54), 191 (18), 190 (30), 175 (48), 173 (23), 137 (59), 135 (100), 116 (45), 115 (70), 107 (14), 105 (15), 91 (14), 75 (72), 45 (11), 43 (15); HRMS (ESI): *m*/*z*: calcd for $C_{17}H_{20}OSiNa$ [M^+ + Na]: 291.1176, found: 291.1174.

(*Z*)-3-Dimethyl(phenyl)silyl-2-propenoic acid (26): Oxalyl chloride (0.13 mL, 1.49 mmol) was added dropwise at −78 °C to a solution of DMSO (0.21 mL, 2.99 mmol) in CH_2Cl_2 (5 mL) and the mixture as stirred for 15 min at that temperature. A solution of alcohol **24** (267 mg, 1.00 mmol) in CH_2Cl_2 (2.0 mL) was introduced and the resulting suspension was stirred for 45 min, at which point Et_3N (0.56 mL, 3.98 mmol) was added. The mixture was allowed to warm to 0 °C over 1.5 h before the reaction was quenched with sat. aq. NH_4Cl. The aqueous layer was repeatedly extracted with ether, the combined organic phases were washed with brine, dried over Na_2SO_4, and the solvent was evaporated to afford the corresponding aldehyde **25** as a pale yellow oil which was used without further purification (239 mg, 90 %). Characteristic data: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 9.83 (d, J = 8.4 Hz, 1 H), 7.61-7.58 (m, 2 H), 7.42-7.30 (m, 6 H), 7.16-7.13 (m, 2 H), 6.51 (d, J = 8.4 Hz, 1 H), 0.34 (s, 6 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 192.9, 168.4, 144.6, 143.7, 138.2, 134.1, 130.0, 128.6, 127.8, 126.7, 0.3; IR (film): $\tilde{\nu}$ = 2839, 2739, 1677, 1489, 1428, 1254, 1111, 814, 783, 733, 701, 641, 472; MS (EI): *m*/*z* (%): 135 (51), 189 (78), 251 (100), 266 (9); HRMS (ESI): *m*/*z*: calcd for $C_{17}H_{18}OSiNa$ [M^+ + Na]: 289.10192, found: 289.10184.

A solution of NaH_2PO_4 (73 mg, 0.61 mmol) in water (0.48 mL), 2-methyl-2-butene (0.21 mL), and $NaClO_2$ (109 mg, 1.2 mmol) were successively added to a solution of the crude aldehyde **25** (100 mg, 0.38 mmol) in *t*BuOH (3.0 mL). The mixture was stirred for 2.5 h, all volatiles were evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc/AcOH, 100:10:0.1) to give acid **26** (99.8 mg, 93 %) as a white solid. M.p. = 77-78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.51-7.49 (m, 2 H), 7.30-7.24 (m, 6 H), 7.08-7.05 (m, 2 H), 6.44 (s, 1 H), 0.37 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 144.8, 138.2, 133.7, 132.9, 128.7, 128.0, 127.5, 126.9, 126.4, 95.7, –0.9; IR (film): $\tilde{\nu}$ = 3022, 2954, 1694,

1589, 1489, 1410, 1313, 1251, 815, 701; MS (EI): *m*/*z* (%): 75 (20), 205 (60), 267 (100), 282 (1); HRMS (EI): *m*/*z*: calcd for $C_{17}H_{17}O_2Si$: 281.10033, found: 281.10064.

***dl*-5-Hydroxy-5-(2-furyl)-1-pentene (*rac*-40):** Magnesium turnings (335 mg, 13.8 mmol) in THF (1 mL) were activated with 1,2-dibromoethane (25 μL) before additional THF (7.0 mL) was added. A solution of 1-bromo-3-pentene (1.70 g, 12.5 mmol) in THF (2.0 mL) was introduced over 30 min and the mixture was stirred at ambient temperature for 1 h. The solution of the resulting Grignard reagent was cooled to 0 °C before aldehyde **39** (1.0 g, 10.4 mmol) was added at that temperature. After 2 h, the mixture was quenched with aq. HCl (5 mL, 1 M), the aqueous layer was repeatedly extracted with Et_2O, and the combined ethereal phases were washed with brine, dried over $MgSO_4$, filtered and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 9/1) to give product *rac*-**40** as a pale yellow oil (1.30 g, 82%), which should be quickly used in the next step or stored at −78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.37 (dd, J = 1.8, 0.8 Hz, 1 H), 6.33 (dd, J = 3.2, 1.8 Hz, 1 H), 6.24 (d, J = 3.2 Hz, 1 H), 5.84 (ddt, J = 17.0, 10.3, 6.6 Hz, 1H), 5.08-4.97 (m, 2 H), 4.70 (t, J = 6.7 Hz, 1 H), 2.20-2.12 (m, 2 H), 1.98-1.92 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 156.6, 142.0, 137.8, 115.2, 110.1, 105.9, 67.2, 34.6, 29.7; IR (film): $\tilde{\nu}$ = 3366, 2943, 2863, 1641, 1505, 1149, 1066, 1009, 913, 738, 599; MS (EI): *m*/*z* (%): 152 (3), 134 (5), 123 (3), 110 (23), 97 (100), 69 (12), 41 (35), 39 (28), 29 (12), 27 (13); HRMS (EI): *m*/*z*: calcd for $C_9H_{12}O_2$: 152.08358, found: 152.08373.

Kinetic resolution: preparation of (–)-40. D-(–)-DIPT (2.50 g, 11.8 mmol) was added to a solution of Ti(O*i*Pr)$_4$ (2.90 mL, 9.86 mmol) in CH_2Cl_2 (45 mL) at −20 °C. After stirring for 10 min, the mixture was cooled to −30 °C and a solution of *rac*-**40** (1.50 g, 9.86 mmol) in CH_2Cl_2 (2 mL) was slowly introduced. After stirring for 30 min, a solution of *tert*-butylhydroperoxide (5 M in decane, 1.18 mL, 5.92 mmol) was added, and the mixture was stirred for 24 h at −20 °C. For work-up, the mixture was filtered through a pad of silica and the filtrate was evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 9/1) to give (–)-**40** as a pale yellow oil (701 mg, 47 %, > 99 % *ee*), which

should be quickly used in the next step or stored at −78 °C. The *ee* was determined by HPLC (Chiralcel OB-H, hexane/*i*PrOH = 95/5). The NMR data are identical with those of the racemic sample described above. $[\alpha]_D^{20}$ = –6.6 (*c* = 1.12, $CHCl_3$).

Compound 41: To a solution of alcohol (–)-**40** (333 mg, 2.19 mmol) and $VO(acac)_2$ (6.00 mg, 0.023 mmol) in CH_2Cl_2 (2.0 mL) was added *tert*-butylhydroperoxide (TBHP, 5 M in decane, 0.44 mL, 2.19 mmol). After stirring for 1 h at room temperature, additional $VO(acac)_2$ (6.00 mg, 0.023 mmol) and TBHP (0.44 mL, 2.19 mmol) were added and stirring was continued for 2 h. The mixture was then passed through a short pad of silica, the filtrate was evaporated, and the residue purified by flash chromatography (hexanes/EtOAc, 4/1) to give compound **41** as a mixture of diastereomers (262 mg, 71 %, major/minor = 69/31). ^{1}H NMR (400 MHz, $CDCl_3$): δ=6.94 (dd, *J* = 10.3, 1.5 Hz, 1 H of minor isomer), 6.90 (dd, *J* = 10.3, 3.5 Hz, 1 H of major isomer), 6.16 (dd, *J* = 10.3, 1.6 Hz, 1 H of minor isomer), 6.11 (d, *J* = 10.3 Hz, 1 H of major isomer), 5.87-5.76 (m, 1 H), 5.66-5.65 (m, 1 H), 5.18-4.98 (m, 2 H), 4.59 (dd, *J* = 8.3, 3.8 Hz, 1 H of major isomer), 4.11 (ddd, *J* = 8.6, 3.8, 1.2 Hz, 1 H of minor isomer), 3.34 (br, 1 H of minor isomer), 3.06 (br, 1 H of major isomer), 2.24-2.18 (m, 2 H), 2.07-2.03 (m, 1 H), 1.18-1.74 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 196.5 (major), 196.1 (minor), 147.6 (minor), 144.2 (major), 137.7 (major), 137.5 (minor), 128.8 (minor), 127.7 (major), 115.5 (minor), 115.4 (major), 90.9 (minor), 87.7 (major), 78.0 (minor), 73.3 (major), 29.7 (minor), 29.1 (minor), 29.0 (major), 28.8 (major); IR (film): $\tilde{\nu}$ = 3411, 3077, 2926, 1690, 1641, 1089, 1033, 916; MS (EI): *m*/*z* (%): 168 (4), 114 (20), 84 (100), 56 (28), 55 (39), 39 (10), 29 (12), 28 (12), 27 (14); HRMS (EI): *m*/*z*: calcd for $C_9H_{12}O_3$: 168.07864, found: 168.07852.

Compound 42: Jones' reagent (1.7 mL)[3] was added dropwise to an ice-cold solution of hemiacetal **41** (413 mg, 2.46 mmol) in acetone (13 mL). The resulting mixture was stirred for 3 h at room temperature before the mixture was diluted with *tert*-butyl methyl ether (50 mL)

[3] M. P. Georgiadis, A. Tsekouras, S. I. Kotretsou, S. A. Haroutounian, M. G. Polissiou, *Synthesis* **1991**, 929-932.

and washed with water. The organic phase was dried over Na_2SO_4, filtered, and evaporated to give the crude oxidation product.

To a solution of this material in $CHCl_3$ (26 mL) and AcOH (17 mL) was added zinc powder (1.2 g), the suspension was stirred for 3 h, excess zinc was filtered off through Celite, the filtrate was evaporated azeotropically with benzene to remove residual HOAc, and the crude product was purified by flash chromatography (hexanes/*tert*-butyl methyl ether, 2/1 → 1/1) to give compound **42** as a colorless oil (324 mg, 78 %). $[\alpha]_D^{20}$ = –246.3 (*c* = 1.08, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.77 (ddt, *J* = 16.9, 10.3, 6.7 Hz, 1 H), 5.11-5.02 (m, 2 H), 4.68 (dd, *J* = 8.2, 4.0 Hz, 1 H), 2.93-2.89 (m, 2 H), 2.79-2.64 (m, 2 H), 2.34-2.19 (m, 2 H), 2.13-2.04 (m, 1 H), 1.96-1.86 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=205.4, 170.0, 136.5, 116.4, 82.2, 33.8, 29.6, 28.6, 28.2; IR (film): $\tilde{\nu}$ = 3079, 2929, 1759, 1735, 1641, 1267, 1171, 999, 919; MS (EI): *m*/*z* (%): 168 (5), 114 (72), 98 (3), 86 (5), 56 (100), 55 (27), 42 (10), 41 (12), 39 (13), 29 (18), 28 (53), 27 (22); HRMS (EI): *m*/*z*: calcd for $C_9H_{12}O_3$: 168.07865, found: 168.07886.

Compound 43: To a solution of ketolactone **42** (100 mg, 0.59 mmol) and 2-trimethylsilylethanol (0.17 mL, 1.18 mmol) in CH_2Cl_2 (1.0 mL) was added *p*-TsOH·H_2O (2 mg). After stirring for 15 h, the mixture was neutralized with triethylamine and passed through a pad of silica which was carefully rinsed with EtOAc. The filtrate was evaporated, the residue dissolved in CH_2Cl_2 (10 mL) and treated with triethylamine (0.50 mL, 3.54 mmol), Ac_2O (0.22 mL, 2.36 mmol) and DMAP (10 mg, 0.08 mmol). After 3 h, the suspension was filtered through a pad of silica which was carefully rinsed with EtOAc. Evaporation of the solvent followed by flash chromatography of the residue (hexanes/EtOAc, 10/1) gave compound **43** as a colorless oil (156 mg, 93 %, 97 % *ee*). The *ee* was determined by HPLC (Chiralcel AD, heptane/*i*PrOH = 98/2). $[\alpha]_D^{20}$ = –4.3 (*c* = 0.62, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 5.81 (ddt, *J* = 17.0, 10.3, 6.6 Hz, 1 H), 5.09-4.98 (m, 3 H), 4.14 (m, 2 H), 2.78-2.72 (m, 2 H), 2.56-2.51 (m, 2 H), 2.21-2.11 (m, 5 H), 1.92-1.80 (m, 2 H), 0.97 (m, 2 H), 0.04 (s, 9 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 206.2, 172.7, 170.8, 137.4, 115.9, 78.0,

63.2, 33.7, 30.1, 29.6, 27.9, 20.8, 17.6, –1.5; IR (film): $\tilde{\nu}$ = 3079, 2954, 1732, 1642, 1249, 1235, 1063, 996, 919, 860, 839, 695; MS (EI): *m*/*z* (%): 43 (47), 73 (100), 117 (33), 133 (10), 173 (82); HRMS (ESI): *m*/*z*: calcd for $C_{16}H_{28}O_5SiNa$ [M^+ + Na]: 351.15983, found: 351.15998.

Acid 44: A solution of compound **43** (50 mg, 0.176 mmol) in DMF (1.0 mL) was added to a solution of TASF (73 mg, 0.264 mmol) in DMF (1.0 mL). After stirring for 3 h, the mixture was filtered through a pad of silica which was rinsed with EtOAc several times, and the combined filtrates were evaporated. Flash chromatography (hexanes/EtOAc/HOAc, 2/1/0.01) of the residue gave carboxylic acid **44** as a colorless oil (28 mg, 68 %). $[\alpha]_D^{20}$ = –2.1 (*c* = 0.60, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 5.81 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.09-4.99 (m, 3 H), 2.80-2.60 (m, 4 H), 2.20-2.12 (m, 5 H), 1.92-1.80 (m, 2 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 206.1, 177.9, 170.9, 137.4, 115.9, 78.0, 33.5, 30.0, 29.6, 27.5, 20.8; IR (film): $\tilde{\nu}$ = 3079, 2928, 1741, 1731, 1713, 1642, 1237, 999, 918; MS (EI): *m*/*z* (%): 43 (100), 85 (12), 101 (40), 114 (7), 132 (5), 174 (6); HRMS (ESI): *m*/*z*: calcd for $C_{11}H_{16}O_5Na$ [M^+ + Na]: 251.08899, found: 251.08903.

Compound 48: *p*TsOH·H_2O (4 mg) was added to a solution of compound **42** (200 mg, 1.19 mmol) and 2-trimethylsilyl ethanol (0.34 mL, 2.38 mmol) in CH_2Cl_2 (2.0 mL). After stirring at room temperature for 2 h, the reaction was quenched with triethylamine and the mixture passed through a short pad of silica which was carefully rinsed with EtOAc. The combined filtrates were evaporated and the residue purified by flash column chromatography (hexanes/EtOAc, 6/1) to give a mixture of the corresponding ester and residual 2-trimethylsilyl ethanol. PMB trichloroacetimidate (701 mg, 2.48 mmol)[4] and TfOH (5 µL, 0.0573 mmol) were added to a solution of this material in Et_2O (12 mL) at 0 °C. After stirring for 20 min, triethylamine was introduced and the mixture was filtered through a short pad of silica which was carefully rinsed with EtOAc. Evaporation of the combined filtrates and purification of the residue by flash chromatography (hexanes/EtOAc, 20/1) gave compound

[4] R. Hong, Y. Chen, L. Deng, *Angew. Chem.* **2005**, *117*, 3544-3547; *Angew. Chem. Int. Ed.* **2005**, *44*, 3478-3481.

48 (307 mg, 63 % over both steps, 97 % *ee*). The *ee* was determined by HPLC (Chiralpack AD, heptane/*i*PrOH = 98/2). $[\alpha]_D^{20}$ = –26.6 (*c* = 0.68, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.28 (d, *J* = 8.8 Hz, 2 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 5.79 (ddt, *J* = 17.1, 10.5, 6.5 Hz, 1 H), 5.04-4.96 (m, 3 H), 4.52 (d, *J* = 11.1 Hz, 1 H), 4.36 (d, *J* = 11.1 Hz, 1 H), 4.15 (m, 2 H), 3.84 (dd, *J* = 7.8, 5.0 Hz, 1 H), 3.80 (s, 3 H), 2.82 (dt, *J* = 6.6, 2.6 Hz, 2 H), 2.55-2.52 (m, 2 H), 2.15-2.10 (m, 1 H), 1.78-1.71 (m, 2 H), 0.99 (m, 2 H), 0.05 (s, 9 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 211.5, 173.0, 159.9, 138.2, 130.4, 130.0, 115.4, 114.2, 84.2, 72.5, 63.1, 55.6, 33.2, 31.9, 29.7, 28.1, 27.1, 17.6, –1.5; IR (film): $\tilde{\nu}$ = 3076, 2953, 2837, 1730, 1641, 1613, 1586, 1514, 1303, 1250, 1092, 996, 917, 838, 762; MS (EI): *m*/*z* (%): 73 (13), 111 (7), 121 (100), 173 (11), 201 (7), 204 (7); HRMS (ESI): *m*/*z*: calcd for $C_{22}H_{34}O_5SiNa$ [M^+ + Na]: 429.20677, found: 429.20718.

Acid 49: A solution of **48** (212 mg, 0.52 mmol) in DMF (2.0 mL) was added to a solution of TASF (215 mg, 0.78 mmol) in DMF (1.0 mL) and the resulting mixture stirred for 3 h. For work up, aq. sat. NH_4Cl (100 µL) was added, the mixture filtered through a pad of silica, which was rinsed with EtOAc. The combined filtrates were evaporated and the residue was purified by flash chromatography (hexanes/EtOAc, 1/1) to give acid **49** as a colorless syrup (120 mg, 76 %, 97 % *ee*). The *ee* was determined by HPLC (Chiralcel OD-H, heptane/*i*PrOH = 1/1). $[\alpha]_D^{20}$ = –15.2 (*c* = 0.46, CH_2Cl_2); ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.27 (d, *J* = 8.7 Hz, 2 H), 6.88 (d, *J* = 8.7 Hz, 2 H), 5.78 (ddt, *J* = 17.0, 10.3, 6.6 Hz, 1 H), 5.04-4.95 (m, 2 H), 4.50 (d, *J* = 11.1 Hz, 1 H), 4.36 (d, *J* = 11.1 Hz, 1 H), 3.84 (dd, *J* = 7.5, 5.3 Hz, 1 H), 3.79 (s, 3 H), 2.84 (m, 2 H), 2.61 (t, *J* = 6.2 Hz, 2 H), 2.18-2.09 (m, 2 H), 1.78-1.69 (m, 2 H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 211.4, 117.8, 159.9, 138.1, 130.2, 130.0, 115.5, 114.1, 84.1, 72.5, 55.6, 32.9, 31.8, 29.6, 27.5; IR (film): $\tilde{\nu}$ = 3076, 3001, 2936, 1712, 1641, 1612, 1586, 1514, 1250, 1091, 1034, 917, 822. MS (EI): *m*/*z* (%): 77 (3), 78 (3), 91 (2), 121 (100), 137 (4), 170 (4), 222 (4); HRMS (ESI): *m*/*z*: calcd for $C_{17}H_{22}O_5Na$ [M^+ + Na]: 329.13594, found: 329.13632.

Sugar building blocks

Trichloroacetimidate 15: Trichloroacetonitrile (0.48 mL, 4.79 mmol) and Cs_2CO_3 (85 mg, 0.26 mmol) were added to a solution of compound **14** (1.00 g, 2.62 mmol)[5] in CH_2Cl_2 (4 mL) and the resulting mixture was stirred for 15 h at ambient temperature before it was filtered through a pad of silica. The filtrate was evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 2/1) to give trichloroacetimidate **15** as a mixture of anomers (1.19 g, 86 %, α:β = 2:1). $[\alpha]_D^{20}$ = +25.9 (*c* = 0.83, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.81 (s, 1 H of β-anomer), 8.71 (s, 1 H of α-anomer), 7.37-7.35 (m, 2 H), 6.89-6.86 (m, 2 H), 6.53 (d, *J* = 3.9 Hz, 1 H of α-anomer), 6.00 (d, *J* = 7.7 Hz, 1 H of β-anomer), 5.61 (t, *J* = 9.9 Hz, 1 H of α-anomer), 5.49 (s, 1 H of α-anomer), 5.48 (s, 1 H of β-anomer), 5.35 (t, *J* = 8.8 Hz, 1 H of β-anomer), 5.26 (dd, *J* = 8.6, 7.8 Hz, 1 H of β-anomer), 5.12 (dd, *J* = 9.9, 3.9 Hz, 1H of α-anomer), 4.37 (dd, *J* = 9.8, 4.3 Hz, 1 H of β-anomer), 4.31 (dd, *J* = 10.4, 5.0 Hz, 1 H of α-anomer), 4.13-4.05 (m, 1 H), 4.88-3.72 (m, 5 H), 2.06 (s, 3 H of α-anomer), 2.04 (s, 3 H of β-anomer), 2.02 (s, 3 H of β-anomer), 2.01 (s, 3 H of α-anomer); ^{13}C NMR (100 MHz, CD_2Cl_2): α-anomer: δ = 170.4, 170.0, 161.3, 160.6, 129.7, 127.8, 113.9, 102.0, 93.9, 78.9, 70.7, 69.0, 68.7, 67.4, 65.5, 55.6, 21.0, 20.6; β-anomer: δ = 170.4, 169.4, 161.0, 160.6, 129.7, 127.9, 113.9, 102.0, 96.2, 78.3, 71.8, 71.4, 68.7, 67.4, 65.5, 55.6, 20.9, 20.7; IR (KBr): $\tilde{\nu}$ = 3348, 2940, 1754, 1676, 1616, 1589, 1519, 1236, 1071, 1033, 834; MS (EI): *m*/*z* (%): 527 (22), 365 (9), 179 (16), 137 (51), 136 (100), 135 (71), 43 (85); HRMS (EI): *m*/*z*: calcd for $C_{20}H_{22}Cl_3NO_9$ [M^+ + H]: 526.04329, found: 526.04327.

Disaccharide 16a (n = 1)**:** $BF_3{\cdot}Et_2O$ (0.25 M in Et_2O, 1.90 mL) was added to a solution of trichloroacetimidate **15** (746 mg, 1.41 mmol) and alcohol **13a** (500 mg, 1.66 mmol) in CH_2Cl_2/pentane (2.0 mL each) at −20 °C. After stirring at that temperature for 30 min, the reaction was quenched with sat. aq. $NaHCO_3$ and the mixture diluted with CH_2Cl_2. The organic layer was separated, dried over Na_2SO_4, and evaporated, and the residue purified by flash chromatography (hexanes/EtOAc, 4/1) to give disaccharide **16a** as a white solid (696 mg, 77 %). M.p. = 129-130 °C. $[\alpha]_D^{20}$ = –35.1 (*c* = 0.70, CH_2Cl_2); ^{1}H NMR (400 MHz,

[5] A. Fürstner, K. Radkowski, J. Grabowski, C. Wirtz, R. Mynott, *J. Org. Chem.* **2000**, *65*, 8758-8762.

CD_2Cl_2): δ = 7.35 (d, *J* = 8.8 Hz, 2 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 5.90 (ddt, *J* = 17.2, 10.1, 7.2 Hz, 1 H), 5.46 (s, 1 H), 5.28-5.23 (m, 1 H), 5.10-5.03 (m, 2 H), 5.01 (d, *J* = 7.6 Hz, 1 H), 4.95-4.91 (m, 1 H), 4.33 (dd, *J* = 10.4, 5.0 Hz, 1 H), 4.27 (d, *J* = 8.0 Hz, 1 H), 4.03-4.00 (m, 1 H), 3.96 (dd, *J* = 5.6, 2.1 Hz, 1 H), 3.82-3.49 (m, 9 H), 2.28-2.24 (m, 2 H), 2.05 (s, 3 H), 2.02 (s, 3 H), 1.52-1.31 (13 H), 0.92 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 170.3, 169.8, 160.6, 135.7, 130.0, 127.8, 116.8, 113.8, 110.0, 101.8, 100.6, 100.1, 80.2, 79.7, 78.7, 78.5, 76.9, 73.0, 72.3, 69.0, 68.8, 66.7, 55.6, 38.9, 37.1, 28.1, 26.4, 21.0, 20.9, 18.7, 16.7, 14.2; IR (film): $\tilde{\nu}$ = 3073, 2936, 2873, 1755, 1640, 1616, 1518, 1371, 1244, 1219, 1175, 1099, 1073, 1037, 920, 831; MS (EI): *m*/*z* (%): 43 (100), 55 (54), 57 (13), 59 (16), 97 (16), 99 (78), 100 (45), 109 (14), 121 (14), 127 (14), 135 (28), 136 (26), 137 (38), 169 (26), 179 (53), 305 (30), 365 (63), 366 (13), 551 (13); HRMS (ESI): *m*/*z*: calcd for $C_{34}H_{48}O_{13}$ [M^+ + H]: 665.31732, found: 665.31667.

Compound 16b (n = 3): Freshly activated MS 4 Å (174 mg) were added to a solution of fucoside **13b** (600 mg, 1.827 mmol) and trichloroacetimidate **15** (916 mg, 1.740 mmol) in CH_2Cl_2 (17.4 mL) and the resulting solution was stirred for 10 min before it was cooled to −30 °C. TMSOTf (31 µL, 0.174 mmol) was then added dropwise and stirring continued for 45 min at −30 °C before the reaction was quenched with Et_3N (0.5 mL). The resulting mixture was allowed to reach ambient temperature, the solvents were evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc, 10:1→4:1) to give disaccharide **16b** as a colorless solid (1.15 g, 95 %). M.p. = 134-135 °C; $[\alpha]_D^{20}$ = –27.8 (*c* = 0.77, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 8.7 Hz, 2 H), 6.74 (d, *J* = 8.8 Hz, 2 H), 6.16 (ddt, *J* = 17.3, 10.4, 7.1 Hz, 1 H), 5.61 (dd, *J* = 9.5, 8.8 Hz, 1 H), 5.44 (dd, *J* = 8.6, 7.5 Hz, 1 H), 5.28 (s, 1 H), 5.17-5.23 (m, 2 H), 5.08 (d, *J* = 7.4 Hz, 1 H), 4.27 (d, *J* = 7.7 Hz, 1 H), 4.25 (dd, *J* = 10.6, 4.7 Hz, 1 H), 3.98 (dd, *J* = 13.3, 7.6 Hz, 1 H), 3.91 (dd, *J* = 10.4, 7.0 Hz, 1 H), 3.75 (td, *J* = 10.5, 5.9 Hz, 1 H), 3.67 (t, *J* = 9.5 Hz, 1 H), 3.59 (t, *J* = 10.2 Hz, 1 H), 3.54 (dd, *J* = 5.5, 2.1 Hz, 1 H), 3.39 (td, *J* = 9.9, 5.0 Hz, 1 H), 3.24 (s, 3 H), 3.19-3.26 (m, 1 H), 2.34-2.46 (m, 2 H), 1.90 (s, 3 H), 1.74 (s, 3 H), 1.44-1.59 (m, 3 H), 1.31 (d, *J* = 6.5 Hz, 3 H), 1.24-1.29 (m, 8 H), 1.25 (s, 3 H), 0.87 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2, 169.8,

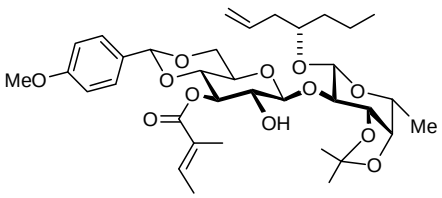
161.0, 136.2, 130.7, 128.6, 128.3, 117.3, 114.2, 110.1, 102.3, 101.2, 100.9, 80.4, 80.2, 79.1, 79.0, 77.1, 74.0, 73.1, 69.2, 68.9, 66.9, 55.1, 39.7, 35.6, 32.6, 28.4, 26.8, 25.6, 23.4, 21.0, 20.8, 17.1, 14.7; IR (film): $\tilde{\nu}$ = 2984, 2954, 2035, 2873, 1743, 1695, 1614, 1519, 1377, 1303, 1245, 1219, 1179, 1073, 1033, 996, 834, 815, 787, 681; MS (EI): *m*/*z* (%): 551 (19), 366 (20), 365 (100), 306 (12), 105 (60), 245 (11), 229 (11), 179 (78), 169 (34), 157 (10), 152 (20), 137 (45), 136 (27), 135 (32), 132 (11), 127 (18), 121 (17), 109 (18), 100 (50), 99 (81), 83 (12), 69 (22), 59 (12), 55 (17), 43 (83); HRMS (ESI): *m*/*z*: calcd for $C_{36}H_{52}O_{13}Na$: [M^+ + Na]: 715.3300, found: 715.3298.

Disaccharide 17a (n = 1): A solution of disaccaride **16a** (686 mg, 1.06 mmol) and KOMe (10 mg) in MeOH (10 mL) was stirred for 4 h before it was filtered through a pad of silica and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 2/1 $\rightarrow$ 0/1) to give disaccharide **17a** as a white solid (518 mg, 84 %). M.p. = 68-69 °C. $[\alpha]_D^{20}$ = –9.9 (*c* = 1.21, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2): δ= 7.43 (d, *J* = 8.8 Hz, 2 H), 6.92 (d, *J* = 8.8 Hz, 2 H), 5.95 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1 H), 5.52 (s, 1 H), 5.14-5.07 (m, 2 H), 4.69 (d, *J* = 7.7 Hz, 1 H), 4.35 (d, *J* = 8.2 Hz, 1 H), 4.31 (dd, *J* = 10.5, 4.9 Hz, 1 H), 4.17 (dd, *J* = 7.4, 5.5 Hz, 1 H), 4.04 (dd, *J* = 5.4, 2.1 Hz, 1 H), 3.86-3.44 (m, 12 H), 2.80 (br, 1 H), 2.32 (m, 1 H), 1.66 (br, 1 H), 1.56-1.30 (m, 13 H), 0.94 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ= 160.6, 135.4, 130.2, 127.9, 116.9, 113.8, 110.4, 104.3, 102.1, 100.2, 96.0, 81.0, 79.2, 78.6, 77.0, 76.3, 73.2, 69.0, 68.8, 67.3, 55.6, 38.6, 36.9, 28.0, 26.3, 18.5, 16.6, 14.2; IR (film): $\tilde{\nu}$ = 3459, 3072, 2935, 2872, 1640, 1615, 1589, 1518, 1382, 1250, 1075, 1034, 923, 831; MS (EI): *m*/z (%): 41 (18), 43 (20), 55 (63), 57 (25), 59 (25), 69 (14), 73 (14), 85 (14), 97 (14), 99 (100), 100 (58), 101 (11), 135 (29), 136 (37), 137 (70), 281 (78), 282 (13), 467 (35); HRMS (EI): *m*/*z*: calcd for $C_{30}H_{45}O_{11}$ [M^+ + H]: 581.29684, found: 581.29659.

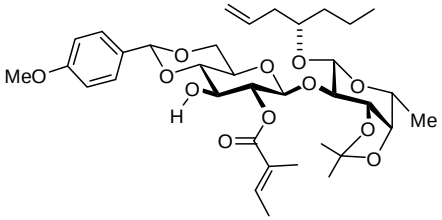
Compound 17b (n = 3): Prepared analogously from diacetate **16b** (481 mg, 0.695 mmol) as a colorless solid (316.2 mg, 76 %). $[\alpha]_D^{20}$ = +3.7 (*c* = 0.88, $CHCl_3$); ^{1}H NMR (300 MHz, C_6D_6): δ= 7.53 (m, 2 H), 6.81 (m, 2 H), 6.15 (m, 1 H), 5.28 (s, 1 H), 5.16 (d, *J* = 4.7 Hz, 1 H), 5.12 (s, 1 H), 4.80 (d, *J* = 7.4 Hz, 1 H), 4.33 (dd, *J* = 10.3, 4.6 Hz, 1 H), 4.25 (d, *J* = 7.7 Hz, 1 H),

3.88-4.03 (m, 1 H), 3.90 (dd, *J* = 15.9, 7.5 Hz, 1 H), 3.70-3.85 (m, 2 H), 3.59 (t, *J* = 9.9 Hz, 1 H), 3.35-3.50 (m, 3 H), 3.26 (s, 3 H), 3.21 (dd, *J* = 6.5, 2.1 Hz, 1 H), 2.75 (br s, 1 H), 2.39 (dd, *J* = 6.8, 5.8 Hz, 2 H), 1.48-1.75 (m, 4 H), 1.43 (s, 3 H), 1.22-1.41 (m, 9 H), 1.19 (s, 3 H), 0.88 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (75 MHz, C_6D_6): δ= 161.2, 136.3, 131.4, 128.8, 117.5, 114.3, 110.8, 105.1, 102.6 101.4, 81.8, 81.5, 79.9, 77.4, 77.3, 74.3, 69.5, 69.1, 68.0, 55.4, 39.8, 35.6, 32.8, 28.5, 26.9, 25.8, 23.6, 17.4, 14.9; IR (film): $\tilde{\nu}$ = 3468, 3076, 2978, 2934, 2871, 1615, 1519, 1457, 1379, 1303, 1248, 1173, 1070, 1030, 921, 868, 828, 787, 725, 688; HRMS (ESI): *m*/*z*: calcd for $C_{32}H_{48}O_{16}Na$ [M^+ + Na]: 631.3089, found: 631.3092.

Regioselective acylation: preparation of compound 18a (n = 1)**:** A solution of diol **17a** (690 mg, 1.19 mmol), DMAP (73.0 mg, 0.60 mmol) and DCC (293 mg, 1.42 mmol) in CH_2Cl_2 (30 mL) was stirred for 5 min prior to the addition of *(E)*-2-methylbutenoic acid (119 mg, 1.19 mmol). Stirring was continued overnight and the resulting precipitate was filtered off through a pad of silica. The insoluble residues were thoroughly washed with EtOAc and the combined filtrates were evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 4/1 $\rightarrow$ 0/1) to give disaccharide **18a** and its regioisomer (ratio ca. 9/1). Further purification was performed by preparative HPLC (Nucleodur 100-16-C18/A; MeOH/H_2O = 4/1; flow rate: 35.0 mL/min; pressure: 4.1 MPa) to give pure **18a** (432 mg, 55 %) and pure regioisomer (45 mg, 6 %), respectively. Analytical and spectroscopic data of compound **18a**: colorless solid, m.p. = 72-73 °C. $[\alpha]_D^{20}$ = –24.7 (*c* = 0.42, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2): δ= 7.33 (d, *J* = 8.8 Hz, 2 H), 6.91 (m, 1 H), 6.86 (d, *J* = 8.8 Hz, 2 H), 5.91 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1 H), 5.62 (s, 1 H), 5.24 (d, *J* = 9.4 Hz, 1 H), 5.11-5.03 (m, 2 H), 4.77 (d, *J* = 7.7 Hz, 1 H), 4.34-4.29 (m, 2 H), 4.15-4.12 (m, 1 H), 4.01 (dd, *J* = 5.4, 2.1 Hz, 1 H), 3.83-3.50 (m, 9 H), 3.36 (d, *J* = 2.7 Hz, 1 H), 2.28 (m, 2 H), 1.84-1.78 (m, 6 H), 1.53-1.33 (m, 14 H), 0.91 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ= 167.7, 160.5, 138.3, 135.4, 130.1, 128.6, 127.8, 117.0, 113.8, 110.4, 104.4, 101.9, 100.1, 81.0, 79.3, 79.2, 78.4, 77.0, 74.8, 73.5, 69.0, 68.9, 67.3, 55.6, 38.6, 36.9, 28.1, 26.3, 18.6, 16.6, 14.6, 14.2, 12.3; IR (film): $\tilde{\nu}$ = 3474, 3072, 2935, 2873, 1718, 1651, 1589, 1518, 1381, 1252, 1175, 1075, 1036, 990, 923, 829; MS (EI): *m*/*z* (%): 43 (17), 55 (65), 57 (11), 59 (13), 83



(100), 97 (12), 99 (63), 100 (33), 121 (13), 135 (20), 136 (26), 137 (32), 179 (13), 363 (24), 549 (20); HRMS (EI): *m*/*z*: calcd for $C_{35}H_{51}O_{12}$ [M^+ + H]: 663.33877, found: 663.33806.



Analytical and spectroscopic data of the regioisomer: m.p. = 67-68 °C. $[\alpha]_D^{20}$ = –7.0 (*c* = 0.83, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.39 (d, *J* = 8.8 Hz, 2 H), 6.96 (m, 1 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 5.90 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1 H), 5.51 (s, 1 H), 5.09-5.01 (m, 3 H), 4.91-4.87 (m, 1 H), 4.31 (dd, *J* = 10.4, 5.0 Hz, 1 H), 4.25 (d, *J* = 7.9 Hz, 1 H), 4.00-3.86 (m, 3 H), 3.81-3.71 (m, 4 H), 3.65-3.57 (m, 3 H), 3.48-3.40 (m, 2 H), 2.73 (d, *J* = 3.8 Hz, 1 H), 2.27 (m, 2 H), 1.86 (m, 3 H), 1.81 (m, 3 H), 1.51-1.29 (m, 13 H), 0.89 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 167.6, 160.6, 138.6, 135.7, 130.2, 128.6, 127.9, 116.8, 113.9, 109.9, 102.1, 100.3, 100.2, 81.3, 79.8, 79.3, 78.8, 76.8, 75.3, 73.1, 69.1, 68.8, 66.5, 55.6, 38.9, 37.1, 28.0, 26.3, 18.7, 16.7, 14.6, 14.2, 12.3; IR (KBr): $\tilde{\nu}$ = 3494, 3074, 2935, 2872, 1722, 1651, 1616, 1589, 1519, 1303, 1174, 921, 830; MS (EI): *m*/*z* (%): 549 (8), 363 (98), 219 (19), 209 (12), 179 (19), 137 (18), 136 (18), 135 (16), 100 (24), 99 (41), 83 (100), 55 (28); HRMS (ESI): *m*/*z*: calcd for $C_{35}H_{50}O_{12}Na$ [M^+ + Na]: 685.31945, found: 685.31954.

Compound 18b (n = 3): Prepared analogously from compound **17b** (200 mg, 0.329 mmol) as a colorless solid (167 mg, 73 %). $[\alpha]_D^{20}$ = –20.7 (*c* = 0.73, $CHCl_3$); ^{1}H NMR (300 MHz, C_6D_6): δ = 7.49 (m, 2 H), 7.00 (qq, *J* = 7.0, 1.5 Hz, 1 H), 6.69 (m, 2 H), 6.14 (m, 1 H), 5.71 (t, *J* = 9.4 Hz, 1 H), 5.26 (s, 1 H), 5.15 (d, *J* = 5.1 Hz, 1 H), 5.11 (s, 1 H), 4.82 (d, *J* = 7.5 Hz, 1 H), 4.82 (d, *J* = 7.5 Hz, 1 H), 4.31 (dd, *J* = 10.2, 4.9 Hz, 1 H), 4.24 (d, *J* = 4.2 Hz, 1 H), 3.96-4.03 (m, 1 H), 3.80 (br s, 1 H), 3.69-3.80 (m, 2 H), 3.63 (t, *J* = 10.6 Hz, 1 H), 3.58 (d, *J* = 12.3 Hz, 1 H), 3.48 (dd, *J* = 5.3, 2.1 Hz, 1 H), 3.37 (dd, *J* = 9.7, 4.8 Hz, 1 H), 3.21 (s, 3 H), 3.18 (dd, *J* = 6.4, 2.1 Hz, 2 H), 1.77 (t, *J* = 1.2 Hz, 3 H), 1.66-1.74 (m, 1 H), 1.45-1.62 (m, 4 H), 1.39 (s, 3 H), 1.31 (t, *J* = 6.5 Hz, 10 H), 1.15 (s, 3 H), 0.89 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75

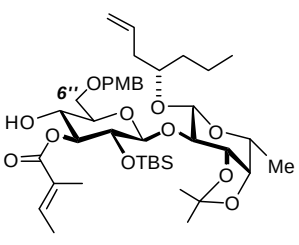
MHz, C_6D_6): δ= 168.1, 161.1, 138.0, 136.4, 131.1, 129.6, 117.5, 114.4, 110.8, 105.6, 102.4, 101.4, 81.8, 80.0, 79.9, 79.6, 77.3, 76.2, 74.6, 69.5, 69.1, 67.8, 55.3, 38.8, 35.6, 32.8, 28.5, 26.9, 25.8, 23.6, 17.4, 14.9, 14.6, 12.9; IR (film): $\tilde{\nu}$ = 3452, 3328, 3078, 3068, 2980, 2932, 2873, 2856, 1717, 1616, 1573, 1518, 1462, 1379, 1302, 1248, 1173, 1137, 1070, 1031, 921, 867, 827, 787, 729, 687; HRMS (EI): *m*/*z*: calcd for $C_{37}H_{55}O_{12}$ [M^+ + H]: 691.3688, found: 631.3693.

Compound 19a: TBSOTf (87.0 mL, 0.30 mmol) was added to a solution of compound **18a** (100 mg, 0.15 mmol) and 2,6-lutidine (69.0 mL, 0.75 mmol) in CH_2Cl_2 (2 mL) and the resulting mixture was stirred for 2 h. Evaporation of the solvent followed by purification of the residue by preparative TLC (hexanes/EtOAc, 4/1) gave product **19a** as a colorless solid (112 mg, 96 %). M.p. = 54-55 °C. $[\alpha]_D^{20}$ = –11.7 (*c* = 0.72, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2): δ= 7.20 (d, *J* = 8.8 Hz, 2 H), 6.78 (m, 1 H), 6.75 (d, *J* = 8.8 Hz, 2 H), 5.80 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1 H), 5.34 (s, 1 H), 5.15 (m, 1 H), 5.00-4.93 (m, 3 H), 4.21-4.17 (m, 2 H), 4.06 (dd, *J* = 6.8, 5.7 Hz, H), 3.89 (dd, *J* = 5.5, 2.0 Hz, 1 H), 3.73-3.66 (m, 6 H), 3.59-3.50 (m, 3 H), 3.43-3.39 (m, 1 H), 2.18 (m, 2 H), 1.71-1.66 (m, 6 H), 1.43-1.19 (m, 13 H), 0.80 (t, *J* = 5.0 Hz, 3 H), 0.73 (s, 9 H), –0.02 (s, 3 H), –0.11 (s, 3 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ= 167.2, 160.5, 138.1, 135.6, 130.3, 128.8, 127.7, 116.8, 113.8, 110.0, 101.6, 100.6, 100.0, 80.0, 79.6, 78.4, 77.0, 76.2, 74.8, 74.3, 69.1, 68.9, 66.5, 55.6, 38.8, 36.9, 28.0, 26.4, 25.9, 18.8, 18.3, 16.7, 14.5, 14.2, 12.3, –3.6, –4.8; IR (KBr): $\tilde{\nu}$ = 3073, 2958, 2934, 2859, 1724, 1653, 1616, 1519, 1252, 1181, 1085, 923, 837, 779, 671; MS (EI): *m*/*z* (%): 719 (10), 663 (12), 477 (7), 283 (13), 211 (18), 183 (18), 179 (21), 158 (10), 157 (79), 136 (17), 135 (13), 121 (35), 99 (23), 97 (19), 83 (100), 73 (29), 59 (14), 55 (79), 43 (14); HRMS (ESI): *m*/*z*: calcd for $C_{41}H_{64}O_{12}SiNa$ [M^+ + Na]: 799.40593, found: 799.40524.

Compound 19b (n = 3): Prepared analogously as a colorless syrup (143 mg, 93 %). ^{1}H NMR (400 MHz, C_6D_6): δ= 7.46 (m, 2 H), 7.01 (qq, *J* = 7.0, 1.3 Hz, 1 H), 6.65 (m, 2 H), 6.18 (m, 1 H), 5.75 (dd, *J* = 9.6, 8.6 Hz, 1 H), 5.28 (s, 1 H), 5.19 (d, *J* = 7.3 Hz, 2 H), 5.16 (s, 1 H), 4.44 (d, *J* = 7.3 Hz, 1 H), 4.20-4.28 (m, 2 H), 4.15 (dd, *J* = 10.2, 4.9 Hz, 1 H), 3.94 (dd, *J* = 8.3, 7.3

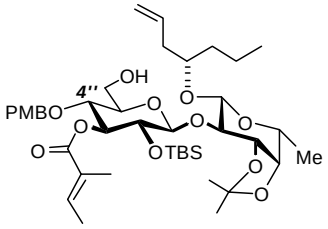
Hz, 1 H), 3.82 (quint., J = 5.7 Hz, 1 H), 3.52-3.60 (m, 3 H), 3.38-3.44 (m, 1 H), 3.33 (qq, J = 6.5, 1.9 Hz, 1 H), 3.19 (s, 3 H), 2.44-2.48 (m, 2 H), 1.85 (s, 3 H), 1.64-1.75 (m, 1 H), 1.47-1.62 (m, 4 H), 1.39 (dd, J = 7.1, 1.3 Hz, 3 H), 1.36 (d, J = 6.6 Hz, 3 H), 1.33 (s, 3 H), 1.24-1.30 (m, 4 H), 1.22 (s, 3 H), 1.06 (s, 9 H), 0.89 (s, 1 H), 0.52 (br s, 1 H), 0.34 (s, 3 H), 0.26 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6): δ = 176.4, 167.3, 161.0, 137.8, 136.5, 131.2, 129.9, 117.4, 114.3, 110.4, 102.3, 101.4, 101.0, 80.7, 80.2, 79.9, 79.0, 77.4, 76.4, 75.7, 75.6, 69.5, 69.4, 67.0, 55.2, 39.8, 35.6, 32.8, 28.4, 27.1, 26.7, 26.6, 26.5, 25.8, 23.6, 19.0, 17.5, 14.9, 14.6, 13.0, –2.8, –3.9; IR (film): $\tilde{\nu}$ = 3072, 2955, 2931, 2858, 1721, 1650, 1616, 1519, 1463, 1379, 1303, 1248, 1221, 1173, 1072, 1034, 1003, 923, 855, 834, 778, 728, 671; HRMS (ESI): *m*/*z*: calcd for $C_{43}H_{68}O_{12}SiNa$ [M^+ + Na]: 827.4372, found: 827.4372.

Compounds 20a and 21a (n = 1)**:** Disaccharide **19a** (500 mg, 0.643 mmol) was added to a suspension of freshly activated MS 4 Å (1.7 g) in CH_3CN (15 mL) and the resulting mixture was stirred for 15 min at that temperature. $NaBH_3CN$ (404 mg, 6.43 mmol) was then introduced before the suspension was cooled to 0 °C and TMSCl (0.82 mL, 6.43 mmol) was added. The mixture was quickly warmed to room temperature and stirring was continued for 3 h. The suspension was filtered through Celite, the filtrate diluted with Et_2O, the organic phase washed with sat. aq. $NaHCO_3$, dried over sodium sulfate, filtered and evaporated. The residue was purified by flash chromatography to give a mixture of the reduction products (308 mg, 62 %, **21a/20a** = 3.5/1). This mixture does not need to be further purified because compound **27** derived thereof can be isolated in pure form by conventional chromatography at the next step (see below). For analytical purposes, however, the regioisomers were separated by preparative HPLC (Nucleodur 100-16-C18/A; MeOH/H_2O = 4/1; flow rate: 35.0 mL/min; pressure: 4.1 MPa) to give product **21a** (210 mg, 42 %) and regioisomer **20a** (24 mg, 5 %), which showed the following spectroscopic and analytical properties:



Compound **21a**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.28 (d, J = 8.7 Hz, 2 H), 6.92 (m, 1 H), 6.87 (d, J = 8.7 Hz, 2 H), 5.90 (ddt, J = 17.2, 10.2, 7.1 Hz, 1 H), 5.09-4.99 (m, 3 H), 4.93 (d, J = 7.7 Hz, 1 H), 4.54 (d, J = 11.5 Hz, 1 H), 4.47 (d, J = 11.5 Hz, 1 H), 4.30 (d,

J = 8.1 Hz, 1 H), 4.14 (m, 1 H), 3.98 (dd, *J* = 5.6, 2.0 Hz, 1 H), 3.85-3.40 (m, 11 H), 2.75 (br s, 1 H), 2.28 (m, 2 H), 1.84-1.71 (m, 6 H), 1.55-1.31 (m, 13 H), 0.89 (t, *J* = 7.2 Hz, 3 H), 0.81 (s, 9 H), 0.07 (s, 3 H), –0.02 (s, 3 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 168.6, 159.7, 138.7, 135.7, 130.4, 129.9, 128.7, 116.8, 114.0, 110.0, 100.1, 99.9, 80.2, 79.3, 78.4, 77.0, 75.9, 74.7, 73.6, 73.3, 71.2, 69.5, 68.9, 55.6, 38.8, 36.9, 28.0, 26.5, 25.9, 18.8, 18.3, 16.8, 14.5, 14.1, 12.2, –3.5, –4.9. HRMS (ESI): *m*/*z*: calcd for $C_{41}H_{66}O_{12}SiNa$ [M^+ + Na]: 801.42158, found: 801.42204.



Compound **20a**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.13 (d, *J* = 8.8 Hz, 2 H), 6.90 (m, 1 H), 6.82 (d, *J* = 8.8 Hz, 2 H), 5.91 (ddt, *1* = 17.2, 10.2, 7.1 Hz, 1 H), 5.22 (t, *J* = 9.2 Hz, 1 H), 5.11-5.03 (m, 2 H), 4.95 (d, *J* = 7.6 Hz, 1 H), 4.45 (m, 2 H), 4.29 (d, *J* = 8.1 Hz, 1 H), 4.15 (dd, *J* = 6.8, 5.7 H, 1 H), 3.98 (dd, *J* = 5.6, 2.1 Hz, 1 H), 3.84-3.76 (m, 6 H), 3.71-3.65 (m, 2 H), 3.61 (t, *J* = 9.5 Hz, 1 H), 3.52 (dd, *J* = 9.0, 7.5 Hz, 1 H), 3.42-3.38 (m, 1 H), 2.28 (m, 2 H), 1.84-1.79 (m, 6 H), 1.65 (br s, 1 H), 1.55-1.32 (m, 13 H), 0.09 (t, *J* = 7.2 Hz, 3 H), 0.82 (s, 9 H), 0.07 (s, 3 H), –0.03 (s, 3 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 167.1, 159.7, 138.26, 135.6, 130.5, 130.1, 129.0, 116.8, 114.0, 110.0, 100.2, 100.1, 80.0, 78.5, 77.5, 77.0, 76.6, 76.3, 75.5, 74.3, 73.8, 69.0, 62.0, 55.5, 38.8, 36.9, 28.1, 26.3, 25.8, 18.7, 18.2, 16.7, 14.6, 14.1, 12.3, –3.6, –4.8.

The assigned regiochemistry was corroborated by acylation of both isomers. The corresponding ring proton H-6,6' (m, 2 H) in **20a** and H-4 (app. t, 1 H) in **21a** showed the expected acylation shifts.

Assembly

Compound 27: Et_3N (43 μL, 0.305 mmol) and 2,4,6-trichlorobenzoyl chloride (22 mL, 0.139 mmol) were added to a solution of acid **26** (39 mg, 0.139 mmol) in toluene (0.6 mL) and the resulting mixture was stirred for 1.5 h before a solution of the mixture of alcohols **21a** and **20a** (54 mg, 0.0693 mmol) and DMAP (8.0 mg, 0.0693 mmol) in CH_2Cl_2 (0.5 mL) was introduced. Stirring was continued for 3 h before the mixture was filtered through a pad of

silica. The filtrate was evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 6/1) to give product **27** as a colorless oil (56.8 mg, 79 %). $[\alpha]_D^{20}$ = –4.4 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49-7.46 (m, 2 H), 7.26-7.18 (m, 10 H), 6.97-6.94 (m, 2 H), 6.84-6.80 (m, 3 H), 6.31 (s, 1 H), 5.94 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1 H), 5.27 (t, *J* = 9.4 Hz, 1 H), 5.08-4.99 (m, 3 H), 4.90 (d, *J* = 7.6 Hz, 1 H), 4.41 (d, *J* = 11.6 Hz, 1 H), 4.39 (d, *J* = 11.6 Hz, 1 H), 4.31 (d, *J* = 7.7 Hz, 1 H), 4.15 (t, *J* = 6.1 Hz, 1 H), 3.97-3.90 (m, 2 H), 3.78-3.74 (m, 4 H), 3.66-3.53 (m, 3 H), 3.36-3.34 (m, 2 H), 2.29-2.26 (m, 2 H), 1.76-1.75 (m, 6 H), 1.56-1.24 (m, 11 H), 0.86 (t, *J* = 7.2 Hz, 3 H), 0.81 (s, 9 H), 0.41 (s, 3 H), 0.26 (s, 3 H), 0.04 (s, 3 H), –0.06 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 165.8, 164.8, 159.0, 144.7, 138.3, 137.9, 135.4, 133.9, 132.9, 130.3, 129.4, 128.6, 128.3, 127.8, 127.4, 126.8, 126.6, 116.5, 113.6, 109.7, 100.2, 99.8, 79.6, 78.7, 76.4, 76.0, 75.3, 73.6, 73.3, 73.1, 69.9, 68.5, 68.4, 55.2, 38.5, 36.6, 27.7, 26.3, 25.7, 18.3, 18.0, 16.7, 14.3, 14.1, 12.0, –0.8, –1.5, –3.9, –5.0; IR (film): $\tilde{\nu}$ = 3070, 2956, 2932, 2904, 2858, 1730, 1652, 1612, 1587, 1513, 1248, 1160, 1074, 915, 839, 780, 701; MS (EI): *m*/*z* (%): 83 (14), 121 (100), 157 (9), 265 (30), 565 (4), 985 (2); HRMS (ESI): *m*/*z*: calcd for $C_{58}H_{82}O_{13}Si_2Na$ [M^+ + Na]: 1065.51862, found: 1065.51779.

Compound 54: A solution of disaccharide **19** (138 mg, 0.171 mmol) in MeCN (1 mL) was added to a suspension of freshly activated MS 4 Å (466 mg) in MeCN (2.5 mL) and the resulting mixture was stirred for 10 min before $NaBH_3CN$ (108 mg, 1.71 mmol) was introduced. The resulting suspension was stirred at 0 °C for 5 min before TMSCl (220 µL, 1.71 mmol) was added. Immediately after the addition, the mixture was warmed to room temperature and stirring was continued for 1.5 h. The suspension was filtered through Celite, the filtrate was diluted with Et_2O, the organic phase was washed with sat. aq. $NaHCO_3$, dried over $MgSO_4$ and evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc, 10:1) to give a mixture of products **21b** and **20b** (n = 3, 70 mg, 51 %, ratio ca. 4:1).

NEt_3 (53 μL, 0.381 mmol) and 2,4,6-trichlorobenzoyl chloride (27 μL, 0.173 mmol) were added to a solution of acid **26** (49 mg, 0.173 mmol) in toluene (770 μL) and the mixture was stirred for 1.5 h before a solution of the isomeric alcohols **20b** and **21b** (70 mg, 0.0867 mmol) in CH_2Cl_2 (650 μL) and DMAP (10.6 mg, 0.0867 mmol) were successively added. Stirring was continued for 14 h before the mixture was filtered through a pad of silica which was carefully rinsed with EtOAc. The combined filtrates was evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 12.1) to give product **54** as a colorless oil (67 mg, 72 %); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.49-7.46 (m, 2 H), 7.25-7.20 (m, 10 H), 6.97-6.95 (m, 2 H), 6.84-6.82 (m, 3 H), 6.31 (s, 1 H), 5.99-5.92 (m, 1 H), 5.27 (t, *J* = 9.4 Hz, 1 H), 5.08-5.00 (m, 3 H), 4.91 (d, *J* = 7.6 Hz, 1 H), 4.41 (q, *J* = 11.6 Hz, 2 H), 4.31 (d, *J* = 7.7 Hz, 1 H), 4.16 (t, *J* = 6.1 Hz, 1 H), 3.97-3.91 (m, 2 H), 3.78-375 (m, 4 H), 3.65-3.53 (m, 3 H), 3.36-3.35 (m, 2 H), 2.30-2.27 (m, 2 H), 1.76-1.75 (m, 6 H), 1.54-1.24 (m, 15 H), 0.87 (t, *J* = 7.2 Hz, 3 H), 0.81 (s, 9 H), 0.42 (s, 3 H), 0.26 (s, 3 H), 0.05 (s, 3 H), –0.05 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 166.9, 165.8, 164.8, 159.0, 144.7, 138.3, 137.7, 135.4, 134.0, 132.8, 130.2, 129.4, 128.6, 127.7, 127.4, 126.7, 126.5, 116.5, 113.5, 109.7, 100.3, 99.7, 79.6, 78.7, 76.3, 76.0, 75.4, 73.6, 73.3, 73.1, 69.9, 68.5, 68.4, 55.3, 38.5, 36.5, 32.1, 27.7, 26.3, 25.7, 24.7, 22.7, 18.0, 16.6, 14.3, 14.1, 12.0, –0.8, –1.5, –3.8, –5.0; IR (film): $\tilde{\nu}$ = 2934, 2858, 1731, 1651, 1613, 1588, 1514, 1246, 1160, 1069, 921, 838, 778; HRMS (ESI): *m*/*z*: calcd for $C_{60}H_{86}O_{13}Si_2Na$ [M^+ + Na]: 1093.5507, found: 1093.5499.

Synthesis of 29: DDQ (49.0 mg, 0.216 mmol) was added to a solution of compound **27** (150 mg, 0.144 mmol) in CH_2Cl_2 (6.0 mL) and water (0.3 mL). The mixture was stirred for 16 h before it was filtered through a pad of silica which was carefully rinsed with ethyl acetate. The combined filtrates were evaporated and the residue was purified by flash chromatography (hexanes/EtOAc, 6/1) to give alcohol **28** (150 mg) which contained *p*-methoxybenzaldehyde as an inseparable impurity.

Et_3N (45 μL, 0.318 mmol) and 2,4,6-trichlorobenzoyl chloride (23 μL, 0.148 mmol) were added to a solution of 4-oxo-8-nonenoic acid (25 mg, 0.0862 mmol)[6,7] in toluene (1.0 mL) and the mixture was stirred for 1.5 h before a solution of the crude alcohol **28** (75 mg, ca. 0.074 mmol) and DMAP (9.0 mg, 0.074 mmol) in toluene (1.5 mL) was introduced. Stirring was continued for 2 h, the mixture was passed through a pad of silica which was carefully rinsed with EtOAc, the combined filtrates were evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc, 8/1) to give disaccharide **29** as a colorless syrup (61.7 mg, 78 %). $[\alpha]_D^{20} = -4.2$ ($c = 0.43$, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47-7.44 (m, 2 H), 7.28-7.18 (m, 6 H), 6.98-6.95 (m, 2 H), 6.81 (m, 1 H), 6.33 (s, 1 H), 5.93 (ddt, J = 17.1, 10.1, 7.1 Hz, 1 H), 5.77 (ddt, J = 17.0, 10.3, 6.4 Hz, 1 H), 5.27 (t, J = 9.4 Hz, 1 H), 5.08-4.96 (m, 5 H), 4.94 (d, J = 7.6 Hz, 1 H), 4.28 (d, J = 7.8 Hz, 1 H), 4.14 (t, J = 5.9 Hz, 1 H), 4.01-3.99 (m, 2 H), 3.97 (dd, J = 5.6, 2.0 Hz, 1 H), 3.89-3.85 (m, 1 H), 3.77 (m, 1 H), 3.68-3.61 (m, 2 H), 3.55 (dd, J = 9.1, 7.6 Hz, 1 H), 2.67-2.42 (m, 6 H), 2.27 (m, 2 H), 2.09-2.03 (m, 2 H), 1.77-1.75 (m, 6 H), 1.59-1.34 (m, 15 H), 0.89 (t, J = 7.2 Hz, 3 H), 0.81 (s, 9 H), 0.39 (s, 3 H), 0.27 (s, 3 H), 0.04 (s, 3 H), –0.06 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.6, 172.4, 166.9, 166.6, 164.7, 144.7, 138.2, 138.0, 135.4, 133.8, 132.6, 128.7, 128.2, 127.9, 127.6, 126.9, 126.6, 116.5, 115.3, 109.7, 100.3, 99.8, 79.7, 79.1, 77.2, 76.5, 76.0, 75.2, 73.2, 71.5, 69.4, 68.6, 63.0, 41.9, 38.6, 37.1, 36.7, 33.1, 28.0, 27.8, 26.4, 25.7, 22.8, 18.3, 18.0, 16.7, 14.4, 14.1, 12.1, –0.7, –1.4, –3.8, –4.9; IR (film): $\tilde{\nu}$ = 3071, 2956, 2933, 1732, 1651, 1588, 1248, 1157, 914, 839, 780, 730, 701; MS (EI): *m*/*z* (%): 83 (68), 157 (29), 265 (100), 393 (30), 775 (9), 793 (42), 961 (13), 1017 (7); HRMS (ESI): *m*/*z*: calcd for $C_{59}H_{86}O_{14}Si_2Na$ [M^+ + Na]: 1097.54483, found: 1097.54416.

Diene 35: Prepared analogously from 8-nonenoic acid (33 mg, 0.212 mmol) and crude alcohol **28** (112 mg, 0.106 mmol) as a colorless syrup (81 mg, 72 %). $[\alpha]_D^{20} = -10.8$ ($c = 0.32$,

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[6] Prepared by reaction of 4-pentenylmagnesium bromide with succinic anhydride, cf. G. Lhommet, S. Fréville, V. Thuy, H. Petit, J. P. Célérier, *Synth. Commun*. **1996**, *26*, 3897-3901. It was found that the reaction is cleaner in the presence of $Fe(acac)_3$ (10 mol%) in THF at −78 °C, even though the unoptimized yield was only 41 %. For iron catalyzed formations of functionalized ketones, see: B. Scheiper, M. Bonnekessel, H. Krause, A. Fürstner, *J. Org. Chem*. **2004**, *69*, 3943-3949.

[7] D. M. Hodgson, P. A. Stupple, F. Y. T. M. Pierard, A. H. Labande, C. Johnstone, *Chem. Eur. J.* **2001**, *7*, 4465-4476.

CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2): δ= 7.48-7.45 (m, 2 H), 7.29-7.19 (m, 6 H), 6.99-6.97 (m, 2 H), 6.82 (m, 1 H), 5.90 (ddt, *J* = 17.2, 10.2, 6.8 Hz, 1 H), 5.82 (ddt, *J* = 17.2, 10.2, 6.8 Hz, 1 H), 5.25 (t, *J* = 9.3 Hz, 1 H), 5.10-4.91 (m, 6 H), 4.30 (d, *J* = 8.1 Hz, 1 H), 4.16-3.98 (m, 4 H), 3.82-3.77 (m, 2 H), 3.71-3.66 (m, 2 H), 3.60 (dd, *J* = 9.0, 7.8 Hz, 1 H), 2.30-2.25 (m, 4 H), 2.07-2.02 (m, 2 H), 1.78-1.75 (m, 6 H), 1.61-1.29 (m, 22 H), 0.90 (t, *J* = 7.3 Hz, 3 H), 0.81 (s, 9 H), 0.36 (s, 3 H), 0.29 (s, 3 H), 0.07 (s, 3 H), –0.04 (s, 3 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ= 173.5, 167.1, 166.8, 165.0, 145.1, 139.6, 138.7, 138.7, 135.6, 134.2, 133.0, 129.0, 128.9, 128.6, 128.2, 127.8, 127.2, 126.9, 116.8, 114.3, 110.0, 100.1, 80.2, 78.6, 77.1, 76.4, 75.7, 73.5, 72.1, 69.5, 69.0, 62.6, 38.8, 36.9, 34.2, 34.1, 29.4, 29.2, 29.1, 28.2, 26.4, 25.8, 25.0, 18.8, 18.2, 16.7, 14.6, 14.2, 12.2, –0.7, –1.1, –3.6, –4.8; IR (film): $\tilde{\nu}$ = 2930, 2858, 1732, 1580, 1428, 1380, 1320, 1247, 1221, 1152, 1111, 1072, 1038, 911, 885, 837, 778, 730, 699; MS (EI): *m*/*z* (%): 83 (84), 99 (13), 157 (34), 211 (10), 265 (100), 379 (25), 761 (8), 779 (53), 947 (20), 1003 (12); HRMS (ESI): *m*/*z*: calcd for $C_{59}H_{88}O_{13}Si_2Na$ [M^+ + Na]: 1083.56557, found: 1083.56558.

Diene 45: DDQ (19.0 mg, 0.0830 mmol) was added to a solution of compound **27** (57.7 mg, 0.0553 mmol) in CH_2Cl_2 (2.0 mL) and water (0.1 mL), and the resulting mixture was stirred at ambient temperature for 16 h. The suspension was then filtered through a pad of silica which was rinsed with ethyl acetate, the combined filtrates were evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc, 6/1) to give alcohol **28** (45.6 mg) which contained traces of *p*-methoxybenzaldehyde.

Et_3N (26 μL, 0.185 mmol) and 2,4,6-trichlorobenzoyl chloride (13 mL, 0.0862 mmol) were added to a solution of acid **44** (19.7 mg, 0.0862 mmol) in toluene (0.5 mL). After stirring for 1.5 h at ambient temperature, a solution of the crude alcohol **28** (45.6 mg) and DMAP (5.0 mg, 0.0431 mmol) in toluene (1.0 mL) was introduced and stirring continued for 2 h. The mixture was filtered through a pad of silica which was carefully rinsed with EtOAc, the combined filtrates were evaporated and the residue was purified by flash chromatography (hexanes/EtOAc, 8/1) to give product **45** as a colorless syrup (54.6 mg, 87 % over both steps).

$[\alpha]_D^{20}$ = –3.7 (*c* = 0.40, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.47-7.45 (m, 2 H), 7.29-7.19 (m, 6 H), 7.00-6.97 (m, 2 H), 6.82 (m, 1 H), 6.33 (s, 1 H), 5.89 (ddt, *J* = 17.2, 10.2, 6.9 Hz, 1 H), 5.81 (ddt, *J* = 17.0, 10.3, 6.6 Hz, 1 H), 5.25 (t, *J* = 9.4 Hz, 1 H), 5.10-4.99 (m, 7 H), 4.30 (d, *J* = 8.1 Hz, 1 H), 4.16-4.03 (m, 3 H), 3.99 (dd, *J* = 5.5, 1.9 Hz, 1 H), 3.82-3.65 (m, 4 H), 3.60 (m, 1 H), 2.83-2.47 (m, 4 H), 2.28 (m, 2 H), 2.18-2.11 (m, 5 H), 1.96-1.74 (m, 8 H), 1.55-1.32 (m, 13 H), 0.90 (t, *J* = 7.2 Hz, 3 H), 0.81 (s, 9 H), 0.37 (s, 3 H), 0.28 (s, 3 H), 0.07 (s, 3 H), –0.04 (s, 3 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 205.8, 172.4, 170. 7, 167.1, 166.9, 165.0, 145.1, 138.7, 137.5, 135.6, 134.2, 133.0, 129.0, 128.5, 128.2, 127.9, 127.2, 126.9, 116.8, 115.9, 110.0, 100.1, 100.0, 80.2, 78.6, 78.0, 77.1, 76.4, 75.6, 73.5, 72.0, 69.6, 69.0, 63.1, 38.8, 36.9, 33.7, 33.6, 30.1, 29.6, 28.2, 27.5, 26.4, 25.8, 20.8, 18.8, 18.2, 16.7, 14.6, 14.2, 12.2, –0.7, –1.2, –3.6, –4.8; IR (film): $\tilde{\nu}$ = 3072, 2956, 2932, 2858, 1732, 1651, 1642, 1586, 1428, 1248, 1113, 916, 839, 780; MS (EI): *m*/*z* (%): 83 (63), 157 (29), 265 (100), 265 (100), 451 (32), 833 (10), 851 (49), 1019 (17), 1075 (8); HRMS (ESI): *m*/*z*: calcd for $C_{61}H_{88}O_{16}Si_2Na$ [M^+ + Na]: 1155.55032, found: 1155.54897.

Diene 50: Prepared analogously from carboxylic acid **49** (100 mg, 0.33 mmol) and crude alcohol **28** (231 mg, 0.25 mmol) as a colorless syrup (220 mg, 73 %). $[\alpha]_D^{20}$ = –6.2 (*c* = 1.01, CH_2Cl_2). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.47-7.45 (m, 2 H), 7.30-7.19 (m, 9 H), 6.99-6.92 (m, 3 H), 6.88 (m, 1 H), 6.33 (s, 1 H), 5.91 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1 H), 5.79 (ddt, *J* = 17.0, 10.3, 6.6 Hz, 1 H), 5.26 (t, *J* = 9.3 Hz, 1 H), 5.10-4.96 (m, 6 H), 4.54 (d, *J* = 11.1 Hz, 1 H), 4.35 (d, *J* = 11.1 Hz, 1 H), 4.31 (d, *J* = 8.1 Hz, 1 H), 4.16 (dd, *J* = 6.4, 5.9 Hz, 1 H), 4.08-4.05 (m, 2 H), 3.99 (dd, *J* = 5.6, 1.9 Hz, 1 H), 3.86-3.78 (m, 6 H), 3.73-3.66 (m, 2 H), 3.61 (dd, *J* = 9.0, 7.8 Hz, 1 H), 2.91-2.51 (m, 4 H), 2.31-2.28 (m, 2 H), 2.21-2.09 (m, 2 H), 1.77-1.33 (m, 21 H), 0.91 (t, *J* = 7.2 Hz, 3 H), 0.82 (s, 9 H), 0.37 (s, 3 H), 0.29 (s, 3 H), 0.08 (s, 3 H), –0.03 (s, 3 H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 211.0, 172.7, 167.2, 166.9, 165.1, 159.9, 145.2, 138.7, 138.6, 138.2, 135.7, 134.2, 133.0, 130.4, 130.0, 129.0, 128.6, 128.2, 127.9, 127.2, 127.0, 116.8, 115.5, 114.2, 110.1, 100.2, 100.1, 84.1, 80.2, 78.7, 77.1, 76.5, 75.7, 73.5, 72.4, 72.1, 69.7, 69.0, 63.2, 55.6, 38.9, 37.0, 33.1, 31.9, 29.8, 28.3, 27.6, 26.5, 25.9, 18.8, 18.3, 16.8, 14.6, 14.2, 12.2, –0.7, –1.1, –3.6, –4.8; IR (film): $\tilde{\nu}$ = 3072, 2955,

2933, 2858, 1731, 1514, 1249, 1156, 1112, 1074, 1039, 915, 839, 818, 780, 730, 701; MS (EI): *m*/*z* (%): 83 (42), 121 (100), 157 (19), 211 (6), 265 (71), 529 (10), 911 (2), 929 (8), 1097 (3); HRMS (ESI): *m*/*z*: calcd for $C_{67}H_{94}O_{16}Si_2Na$ [M^+ + Na]: 1233.59726, found: 1233.59623.

Compound 56: Prepared analogously as a colorless oil (72 mg, 83 % over both steps). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 47-7.45 (m, 2 H), 7.27-7.20 (m, 6 H), 6.98-6.96 (m, 2 H), 6.82-6.81 (m, 1 H), 6.33 (s, 1 H), 5.99-5.89 (m, 1 H), 5.82-5.72 (m, 1 H), 5.28 (t, *J* = 9.4 Hz, 1 H), 5.09-4.96 (m, 5 H), 4.94 (d, *J* = 7.6 Hz, 1 H), 4.28 (d, *J* = 7.8 Hz, 1 H), 4.15 (t, *J* = 5.9 Hz, 1 H), 4.01-3.99 (m, 2 H), 3.97 (dd, *J* = 5.6, 2.0 Hz, 1 H), 3.89-3.86 (m, 1 H), 3.80-3.75 (m, 1 H), 3.69-3.60 (m, 2 H), 3.55 (dd, *J* = 9.1, 7.6 Hz, 1 H), 2.69-2.42 (m, 6 H), 2.29-2.26 (m, 2 H), 2.09-2.03 (m, 2 H), 1.77-1.75 (m, 6 H), 1.71-1.31 (m, 19 H), 0.89 (t, *J* = 7.2 Hz, 3 H), 0.81 (s, 9 H), 0.39 (s, 3 H), 0.28 (s, 3 H), 0.05 (s, 3 H), –0.05 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.7, 172.3, 166.8, 166.5, 164.8, 144.7, 138.1, 137.9, 135.4, 133.8, 132.5, 128.6, 128.1, 127.8, 127.5, 126.8, 126.5, 116.4, 115.3, 109.8, 100.4, 99.8, 79.7, 79.6, 77.2, 76.4, 76.0, 75.2, 73.3, 71.5, 69.5, 68.5, 63.0, 41.8, 38.5, 37.2, 34.5, 33.2, 31.8, 28.0, 27.7, 26.3, 25.6, 24.7, 22.7, 22.6, 18.0, 16.7, 14.3, 14.1, 12.0, –0.6, –1.4, –3.8, –4.9; IR (film): $\tilde{\nu}$ = 2930, 2857, 1731, 1651, 1588, 1428, 1380, 1320, 1247, 1153, 1111, 1073, 1039, 913, 838, 816, 779, 730, 700; HRMS (ESI): *m*/*z*: calcd for $C_{61}H_{90}O_{14}Si_2Na$ [M^+ + Na]: 1125.5756, found: 1125.5761.

Macrocyclization/hydrogenation sequence

Compound 32: Complex **30** (5.0 mg, 0.00558 mmol) was added to a solution of diene **29** (60 mg, 0.0558 mmol) in CH_2Cl_2 (10 mL) and the resulting mixture was stirred under reflux for 4 h before the reaction was quenched with ethyl vinyl ether. Evaporation of all volatile materials followed by flash chromatography of the residue (hexanes/EtOAc, 4/1) gave the corresponding metathesis product **31** as a mixture of (*E*)- and (*Z*)-isomers.

A solution of cycloalkene **31** (42 mg, 0.0398 mmol) and $RhCl(PPh_3)_3$ (7.0 mg, 0.0076 mmol) in EtOH (0.6 mL) was stirred under an atmosphere of H_2 (1 atm) overnight. Evaporation of

the solvent and flash chromatography of the crude product (hexanes/EtOAc, 4/1) gave compound **32** as a colorless oil (34 mg, 81 %). $[\alpha]_D^{20}$ = +0.6 (*c* = 0.50, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46-7.45 (m, 2 H), 7.28-7.17 (m, 6 H), 6.97-6.95 (m, 2 H), 6.86 (m, 1 H), 6.31 (s, 1 H), 5.27 (t, *J* = 9.3 Hz, 1 H), 5.08 (t, *J* = 9.8 Hz, 1 H), 4.93 (d, *J* = 7.7 Hz, 1 H), 4.27 (d, *J* = 7.8 Hz, 1 H), 4.20-4.13 (m, 2 H), 4.00-3.97 (m, 2 H), 3.87 (dd, *J* = 7.7, 6.6 Hz, 1 H), 3.78 (m, 1 H), 3.63 (m, 1 H), 3.54 (dd, *J* = 9.0, 7.8 Hz, 1 H), 3.51 (m, 1 H), 2.81-2.73 (m, 1 H), 2.58-2.31 (m, 5 H), 1.79-1.24 (m, 29 H), 0.90 (t, *J* = 7.3 Hz, 3 H), 0.81 (s, 9 H), 0.37 (s, 3 H), 0.24 (s, 3 H), 0.05 (s, 3 H), –0.04 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.6, 171.4, 166.8, 166.3, 164.4, 144.7, 138.4, 138.2, 133.8, 132.7, 128.6, 128.2, 127.8, 127.5, 126.8, 126.6, 109.7, 101.5, 99.8, 82.0, 79.4, 76.5, 76.4, 75.6, 73.1, 71.7, 68.4, 68.3, 61.7, 42.3, 37.3, 37.0, 33.7, 28.7, 28.3, 28.0, 27.8, 26.3, 25.7, 24.0, 23.7, 18.4, 18.0, 16.8, 14.4, 14.3, 12.1, –0.5, –1.6, –3.8, –4.9; IR (film): $\tilde{\nu}$ = 3069, 2932, 2858, 1733, 1652, 1588, 1248, 1155, 1074, 839, 780, 730, 701; MS (EI): *m*/*z* (%): 83 (91), 157 (29), 265 (100), 349 (13), 767 (36), 991 (9); HRMS (ESI): *m*/*z*: calcd for $C_{57}H_{84}O_{14}Si_2Na$ [M^+ + Na]: 1071.52919, found: 1071.53009.

Compound 36: Prepared analogously from diene **35** (51 mg, 0.0484 mmol) as a colorless solid (37 mg). $[\alpha]_D^{20}$ = +3.5 (*c* = 0.52, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.48-7.46 (m, 2 H), 7.28-7.18 (m, 6 H), 6.98-6.96 (m, 2 H), 6.83 (m, 1 H), 6.32 (s, 1 H), 5.26 (t, *J* = 9.6 Hz, 1 H), 5.17 (t, *J* = 9.6 Hz, 1 H), 5.03 (d, *J* = 8.0 Hz, 1 H), 4.26-4.22 (m, 2 H), 4.18-4.13 (m, 2 H), 3.99 (dd, *J* = 2.0, 5.7 Hz, 1 H), 3.81 (dd, *J* = 6.6, 8.1 Hz, 1 H), 3.78 (m, 1 H), 3.69 (m, 1 H), 3.56 (dd, *J* = 7.8, 8.9 Hz, 1 H), 3.51-3.49 (m, 1 H), 2.27-2.22 (m, 2 H), 1.78-1.27 (m, 35 H), 0.91 (t, *J* = 7.2 Hz, 3 H), 0.82 (s, 9 H), 0.34 (s, 3 H), 0.27 (s, 3 H), 0.08 (s, 3 H), –0.03 (s, 3 H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 173.2, 167.2, 166.5, 164.6, 145.3, 138.9, 138.6, 134.3, 133.1, 128.9, 128.6, 128.2, 127.8, 127.1, 127.0, 110.0, 102.3, 100.1, 82.7, 80.2, 76.9, 76.1, 73.6, 72.3, 68.8, 61.3, 38.0, 34.6, 30.1, 29.0, 28.6, 28.3, 28.0, 27.9, 26.4, 25.8, 24.7, 24.4, 18.7, 18.3, 16.9, 14.6, 14.4, 12.2, –0.7, –1.3, –3.5, –4.8; IR (film): $\tilde{\nu}$ = 2929, 2858, 1732, 1246, 1150, 1071, 1037, 837, 778, 729, 698. MS (EI): *m*/*z* (%): 83 (90), 135 (10), 157 (32), 205 (11), 265 (100), 335 (10), 409 (7), 495 (7), 595 (6), 753 (43), 977 (11); HRMS (ESI): *m*/*z*: calcd for $C_{57}H_{86}O_{13}Si_2Na$ [M^+ + Na]: 1057.54992, found: 1057.55069.

Compound 46: Prepared analogously from diene **45** (74 mg, 0.0653 mmol) as a colorless syrup (60 mg, 83 %). $[\alpha]_D^{20}$ = +0.4 (*c* = 0.77, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46-7.44 (m, 2 H), 7.29-7.19 (m, 6 H), 6.99-6.97 (m, 2 H), 6.81 (m, 1 H), 6.31 (s, 1 H), 5.28 (t, *J* = 9.2 Hz, 1 H), 5.06-5.00 (m, 2 H), 4.94 (d, *J* = 7.7 Hz, 1 H), 4.25 (d, *J* = 7.8 Hz, 1 H), 4.13 (t, *J* = 6.0 Hz, 1 H), 4.03-4.02 (m, 1 H), 3.98 (dd, *J* = 5.8, 2.0 Hz, 1 H), 3.86 (dd, *J* = 7.8, 6.4 Hz, 1 H), 3.78 (m, 1 H), 3.65 (dt, *J* = 10.0, 2.7 Hz, 1 H), 3.54-3.48 (m, 2 H), 2.87 (dt, *J* = 18.8, 6.8 Hz, 1 H), 2.62 (dt, *J* = 18.8, 6.8 Hz, 1 H), 2.49 (m, 2 H), 2.14 (s, 3 H), 1.77-1.26 (m, 30 H), 0.09 (t, *J* = 7.3 Hz, 3 H), 0.81 (s, 9 H), 0.37 (s, 3 H), 0.23 (s, 3 H), 0.05 (s, 3 H), –0.04 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.9, 170.9, 170.6, 166.8, 166.6, 164.4, 144.6, 138.3, 138.0, 133.6, 132.5, 128.7, 128.2, 127.9, 127.6, 126.9, 126.6, 109.7, 101.3, 99.7, 81.9, 79.4, 78.4, 77.2, 76.3, 75.4, 73.1, 71.6, 68.5, 68.3, 61.8, 37.3, 33.9, 33.8, 29.9, 28.5, 28.0, 27.8, 26.3, 25.6, 24.2, 20.6, 18.3, 18.0, 16.8, 14.4, 14.3, 12.1, –0.4, –1.6, –3.8, –4.9; IR (film): $\tilde{\nu}$ = 3069, 2931, 2858, 1732, 1652, 1588, 1379, 1371, 1247, 1155, 1074, 839, 780, 731, 702; MS (EI): *m*/*z* (%): 83 (66), 157 (26), 265 (100), 567 (11), 825 (41), 1049 (9); HRMS (ESI): *m*/*z*: calcd for $C_{59}H_{86}O_{16}Si_2Na$ [M^+ + Na]: 1129.53466, found: 1129.53524.

Compound 51: Prepared analogously from diene **50** (133 mg, 0.11 mmol) as a colorless solid (99.6 mg). $[\alpha]_D^{20}$ = –3.3 (*c* = 0.89, CH_2Cl_2); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.49-7.47 (m, 2 H), 7.30-7.19 (m, 8 H), 7.00-6.97 (m, 2 H), 6.90-6.85 (m, 3 H), 6.31 (s, 1 H), 5.25 (t, *J* = 9.5 Hz, 1 H), 5.13 (t, *J* = 9.8 Hz, 1 H), 4.97 (d, *J* = 7.8 Hz, 1 H), 4.51 (d, *J* = 11.6 Hz, 1 H), 4.36 (d, *J* = 11.6 Hz, 1 H), 4.26-4.22 (m, 2 H), 4.15 (t, *J* = 6.1 Hz, 1 H), 3.98 (dd, *J* = 5.8, 2.0 Hz, 1 H), 3.80 (s, 3 H), 3.79-3.75 (m, 4 H), 3.68 (m, 1 H), 3.53 (dd, *J* = 9.0, 7.8 Hz, 1 H), 3.51-3.47 (m, 1 H), 3.04 (ddd, *J* = 19.2, 8.9, 5.6 Hz, 1 H), 2.64 (dt, *J* = 19.2, 5.7 Hz, 1 H), 2.44 (ddd, *J* = 16.6, 8.9, 5.5 Hz, 1 H), 2.17 (dt, *J* = 16.6, 5.7 Hz, 1 H), 1.77-1.25 (m, 29 H), 0.90 (t, *J* = 7.2 Hz, 3 H), 0.82 (s, 9 H), 0.38 (s, 3 H), 0.23 (s, 3 H), 0.08 (s, 3 H), –0.01 (s, 3 H); ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 211.6, 171.6, 167.1, 166.8, 164.7, 159.9, 145.3, 139.0, 138.8, 134.2, 133.1, 130.4, 129.9, 129.0, 128.6, 128.2, 127.9, 127.2, 127.0, 114.2, 110.0, 102.3, 100.4, 84.5, 82.7, 80.1, 77.3, 76.9, 76.0, 73.5, 72.3, 68.8, 68.7, 62.1, 62.1, 55.6, 37.9, 34.1, 33.4, 31.9, 29.0, 28.6, 28.0, 26.4, 25.9, 24.8, 24.6, 18.7, 18.3, 16.9, 14.6, 14.4, 12.3, –0.2, –1.6, –3.4, –

4.7; IR (film): $\tilde{\nu}$ = 2933, 2859, 1732, 1652, 1612, 1587, 1513, 1248, 1155, 1074, 1038, 839, 818, 780, 730, 701; MS (EI): *m*/*z* (%): 83 (32), 121 (100), 157 (12), 211 (1), 265 (52), 323 (2), 645 (2), 903 (5), 1127 (2); HRMS (ESI): *m*/*z*: calcd for $C_{65}H_{92}O_{16}Si_2Na$ [M^+ + Na]: 1207.58162, found: 1207.58256.

Compound 57: Prepared analogously from diene **56** (72 mg, 0.065 mmol) as a colorless solid (57 mg, 81 % over two steps). $[\alpha]_D^{20}$ = + 1.2 (*c* = 1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.47-7.45 (m, 2 H), 7.28-7.18 (m, 6 H), 6.97-6.95 (m, 2 H), 6.87-6.85 (m, 1 H), 6.31 (s, 1 H), 5.28 (t, *J* = 9.3 Hz, 1 H), 5.08 (t, *J* = 9.8 Hz, 1 H), 4.93 (d, *J* = 7.7 Hz, 1 H), 4.26 (d, *J* = 7.8 Hz, 1 H), 4.21-4.11 (m, 2 H), 4.00-3.97 (m, 2 H), 3.90-3.86 (m, 1 H), 3.80-3.77 (m, 1 H), 3.65-3.62 (m, 1 H), 3.56-3.52 (m, 1 H), 3.52-3.47 (m, 1 H), 2.82-2.74 (m, 1 H), 2.58-2.33 (m, 5 H), 1.79-1.78 (m, 6 H), 1.71-1.24 (m, 27 H), 0.89 (t, *J* = 7.3 Hz, 3 H), 0.82 (s, 9 H), 0.37 (s, 3 H), 0.24 (s, 3 H), 0.06 (s, 3 H), –0.03 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 209.5, 171.3, 166.7, 166.3, 164.3, 144.6, 138.4, 138.1, 133.7, 132.6, 128.6, 128.2, 127.8, 127.5, 126.8, 126.5, 109.6, 101.5, 99.7, 82.4, 79.4, 76.4, 76.3, 75.6, 73.1, 71.6, 68.4, 68.3, 61.6, 42.2, 36.9, 35.0, 33.7, 32.0, 28.6, 28.2, 27.9, 27.7, 26.2, 25.6, 24.7, 24.0, 23.6, 22.5, 17.9, 16.7, 14.4, 14.0, 12.1, –0.5, –1.6, –3.8, –4.9; IR (film): $\tilde{\nu}$ = 2931, 2858, 1732, 1652, 1587, 1458, 1380, 1321, 1247, 1153, 1073, 1038, 838, 816, 779, 730, 700; HRMS (ESI): *m*/z: calcd for $C_{59}H_{88}O_{14}Si_2Na$ [M^+ + Na]: 1099.5599, found: 1099.5604.

Completion of the total syntheses

Ipomoeassin B (2). A solution of TASF (79 mg, 0.286 mmol) in MeCN (2.0 mL) was added to a solution of compound **32** (30 mg, 0.0286 mmol) in wet MeCN (1.5 mL). After stirring for 4 h, the mixture was filtered through a pad of silica which was carefully rinsed with EtOAc, the combined filtrates were evaporated, and the residue was treated with trifluoroacetic acid (16 µL, 215 mmol) in CH_2Cl_2 (2.0 mL). After stirring for 3 h, the solution was neutralized with Et_3N, the solvent was evaporated, and the residue purified by flash chromatography (CH_2Cl_2/MeOH, 20/1) to afford Ipomoeassin B (**2**) as a colorless syrup which solidifies when

kept in the freezer (10 mg, 45 %). $[\alpha]_D^{25}$ = –48.0 (*c* = 0.36, EtOH); lit.[8] $[\alpha]_D^{25}$ = –39 (*c* = 0.3, EtOH); For a compilation of the ^{1}H and ^{13}C NMR data of the synthetic samples and a comparison with the data of the natural products, see Tables 5 and 6 in the Supporting Information; IR (film): $\tilde{\nu}$ = 3365, 3062, 2932, 1744, 1719, 1631, 1371, 1316, 1265, 1249, 1157, 1138, 1073; MS (EI): *m*/*z* (%): 513 (11), 467 (14), 349 (10), 241 (13), 223 (42), 131 (44), 111 (13), 83 (100), 55 (28); HRMS (ESI): *m*/*z*: calcd for $C_{40}H_{56}O_{14}Na$ [M^+ + Na]: 783.35623, found: 783.35629.

4-Deoxy-ipomoeassin B (38): Prepared analogously from compound **36** (15 mg, 0.0145 mmol) as a colorless syrup (6.1 mg, 56 % overall). $[\alpha]_D^{20}$ = –33 (*c* = 0.29, EtOH); ^{1}H NMR (400 MHz, C_6D_6): δ = 7.81 (d, *J* = 16.0 Hz, 1 H), 7.06-6.90 (m, 6 H), 6.38 (d, *J* = 16.0 Hz, 1 H), 5.77 (t, *J* = 9.8 Hz, 1 H), 5.39 (br. m, 1 H), 4.69 (br. m, 1 H), 4.52-4.46 (m, 2 H), 4.38 (d, *J* = 7.6 Hz, 1 H), 4.20 (d, *J* = 11.9 Hz, 1 H), 3.91-3.75 (m, 3 H), 3.58 (m, 1 H), 3.45 (br. s, 1 H), 3.37 (m, 1 H), 3.08 (br. q, *J* = 6.2 Hz, 1 H), 2.61-2.51 (m, 2 H), 2.39-2.33 (m, 1 H), 1.79-1.56 (m, 30 H), 0.99 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (75 MHz, C_6D_6): δ = 173.2, 168.8, 165.4, 146.2, 139.5, 134.4, 130.4, 128.9, 128.5, 128.0, 117.5, 106.5, 100.5, 84.0, 79.0, 76.8, 74.4, 74.2, 73.0, 71.6, 70.2, 67.9, 61.5, 37.4, 34.5, 34.0, 29.3, 27.7, 27.6, 27.0, 25.2, 24.6, 18.7, 16.6, 14.4, 14.1, 12.0. MS (EI): *m*/*z* (%): 55 (24), 83 (100), 131 (42), 209 (13), 335 (9), 453 (17), 499 (8), 583 (6), 629 (4); HRMS (ESI): *m*/*z*: calcd for $C_{40}H_{58}O_{13}Na$ [M^+ + Na]: 769.37696, found: 769.37677.

Ipomoeassin E (5): Prepared analogously from compound **46** (30 mg, 0.027 mmol) as a colorless syrup which solidifies when kept in the freezer (14 mg, 63 % over both steps). $[\alpha]_D^{25}$ = –32 (*c* = 0.21, EtOH); lit.[8] $[\alpha]_D^{25}$ = –24 (*c* = 0.2, EtOH); For a compilation of the ^{1}H and ^{13}C NMR data of the synthetic samples and a comparison with the data of the natural products, see Tables 11 and 12 in the Supporting Information; IR (film): $\tilde{\nu}$ = 3408, 2933, 2869, 1725, 1636, 1450, 1374, 1309, 1248, 1156, 1073, 768; MS (EI): *m*/*z* (%): 655 (5), 571 (7), 525 (7), 407 (9), 281 (40), 239 (11), 221 (19), 192 (11), 131 (58), 110 (10), 83 (100), 55

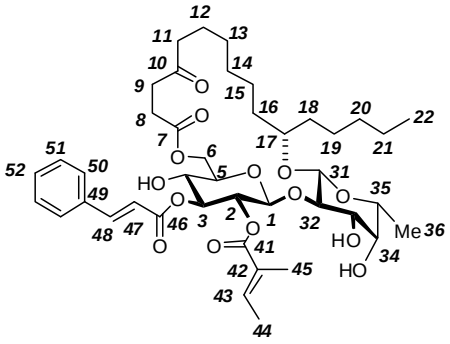
[8] S. Cao, R. C. Guza, J. H. Wisse, J. S. Miller, R. Evans, D. G. I. Kingston, *J. Nat. Prod*. **2005**, *68*, 487-492.

(20), 43 (19); HRMS (ESI): *m*/*z*: calcd for $C_{42}H_{58}O_{16}Na$ [M^+ + Na]: 841.36172, found: 841.36245.

Compound 58: A solution of compound **57** (25.6 mg, 0.025 mmol) in MeCN (1.5 mL) was added to a solution of TASF (68 mg, 0.246 mmol) in MeCN (2 mL) and water (5 μL). After stirring overnight, the solvent was evaporated and the residue purified by flash chromatography (hexanes/EtOAc, 6:1) to give product **58** as a colorless syrup (8.8 mg, 43 %). $[\alpha]_D^{20}$ = –29 (*c* = 0.11, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.61 (d, *J* = 16.2 Hz, 1 H), 7.48 – 7.50 (m, 2 H), 7.36 – 7.39 (m, 3 H), 6.84 – 6.90 (m, 1 H), 6.32 (d, *J* = 16.0 Hz, 1 H), 5.23 – 5.32 (m, 2 H), 4.64 (d, *J* = 7.6 Hz, 1 H), 4.41 (dd, *J* = 2.8, 12.4 Hz, 1 H), 4.32 (d, *J* = 8.1 Hz, 1 H), 4.20 (dd, *J* = 7.5, 5.7 Hz, 1 H), 4.11 (dd, *J* = 12.1, 2.3 Hz, 1 H), 4.01 (dd, *J* = 5.4, 2.2 Hz, 1 H), 3.80 (dd, *J* = 6.6, 2.0 Hz, 1 H), 3.72 (dt, *J* = 9.3, 2.7 Hz, 1 H), 3.64 (t, *J* = 7.9 Hz, 2 H), 3.59 (quint., *J* = 5.4 Hz, 1 H), 2.42 – 2.75 (m, 6 H), 1.75 – 1.78 (m, 3 H), 1.72 – 1.74 (m, 3 H), 1.61 – 1.68 (m, 3 H), 1.52 (s, 3 H), 1.39 – 1.51 (m, 4 H), 1.38 (d, *J* = 6.6 Hz, 3 H) 1.33 (s, 3 H), 1.21 – 1.32 (m, 12 H), 0.89 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ= 210.2, 171.7, 167.6, 165.4, 146.0, 138.6, 134.0, 130.5, 128.9, 128.3, 127.8, 116.8, 110.3, 105.1, 100.0, 82.4, 79.8, 78.5, 76.5, 74.2, 73.9, 72.3, 68.5, 68.3, 65.9, 61.9, 42.0, 37.4, 34.5, 33.2, 32.0, 29.3, 29.0, 28.5, 27.9, 26.2, 24.8, 24.6, 23.7, 22.7, 16.6, 15.3, 14.5, 14.2, 12.1.

Compound 59: A solution of compound **58** (4.3 mg, 0.0052 mmol) and trifluoroacetic acid (3.8 μL, 0.0511 mmol) in CH_2Cl_2 (1 mL) was stirred for 2 h. After neutralization with $NaHCO_3$, all volatile materials were removed under reduced pressure and the resulting crude material (8.1 mg) was used in the next step. For analytical purposes, a small sample was purified by preparative HPLC (Shimadzu LC-8A/10A, MeOH/H_2O, 85:15, 10 mL/min, 6.3 MPa), which analyzed as follows: ^{1}H NMR (400 MHz, C_6D_6): δ= 7.82 (d, *J* = 16.0 Hz, 1 H), 7.07-6.89 (m, 6 H), 6.40 (d, *J* = 16.0 Hz, 1 H), 5.73 (t, *J* = 9.7 Hz, 1 H), 5.43 (t, *J* = 9.4 Hz, 1 H), 4.66-4.63 (m, 1 H), 4.56-4.54 (m, 1 H), 4.39 (d, *J* = 7.6 Hz, 1 H), 4.19 (d, *J* = 12.4 Hz, 1 H), 3.96-3.92 (m, 1 H), 3.88-3.84 (m, 1 H), 3.73 (m, 1 H), 3.64-3.61 (m, 1 H), 3.49 (s, 1 H),

3.43-3.40 (m, 1 H), 3.13-3.08 (m, 1 H), 2.62 (ddd, J = 3.4, 7.7, 16.1 Hz, 1 H), 2.56-2.54 (m, 1 H), 2.43-2.35 (m, 1 H), 2.18-2.11 (m, 1 H), 2.08 (t, J = 6.2 Hz, 2 H), 1.72 (s, 3 H), 1.67-1.27 (m, 24 H), 0.93 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (100 MHz, C_6D_6): δ = 208.3, 171.5, 168.4, 165.6, 146.1, 139.3, 134.4, 130.3, 128.8, 128.5, 127.9, 117.6, 106.3, 100.6, 83.6, 79.3, 76.6, 74.5, 74.1, 73.1, 71.7, 70.2, 67.8, 61.4, 41.5, 37.4, 35.2, 34.4, 32.3, 29.5, 29.4, 28.6, 25.4, 25.3, 23.7, 23.1, 16.6, 14.3, 14.1, 12.0; IR (film): $\tilde{\nu}$ = 3374, 2929, 2856, 1745, 1718, 1632, 1449, 1380, 1372, 1315, 1250, 1156, 1072, 905, 864, 767, 729, 685; HRMS (ESI): *m*/*z*: calcd for $C_{42}H_{60}O_{14}Na$ [M^+ + Na]: 811.3882, found: 811.3875.



Compound 60: Prepared analogously upon stirring of **58** (62 mg, 0.075 mmol) and trifluoroacetic acid (926 µL, 12.0 mmol) in CH_2Cl_2 (9 mL) for 2 h. The mixture was neutralized with Et_3N before all volatile materials were evaporated and the residue was purified by flash chromatography (CH_2Cl_2/MeOH, 60:1) to give product **60** as a colorless syrup (32 mg, 54 %). ^{1}H NMR (600 MHz, C_6D_6): δ = 7.84 (d, J = 16.0 Hz, 1 H, H-48), 7.11 (m, 1 H, H-43); 7.01 (m, 1 H, H-50), 6.94 (m, 1 H, H-52), 6.91 (m, 1 H, H-51), 6.49 (d, J = 16.0 Hz, 1 H, H-47), 5.79 (t, J = 9.5 Hz, 1 H, H-3), 5.59 (dd, J = 9.6, 8.1 Hz, 1 H, H-2), 5.44 (d, J = 7.9 Hz, 1 H, H-1), 4.96 (d, J = 12.2 Hz, 1 H, H-6a), 4.26 (d, J = 7.6 Hz, 1 H, H-31), 4.21 (d, J = 12.6 Hz, 1 H, H-6b), 4.06 (t, J = 9.6 Hz, 1H, H-4), 3.97 (dd, J = 7.6, 9.0 Hz, 1H, H-32), 3.66 (m, 1H, H-17), 3.54-3.59 (m, 2 H, H-5, H-33), 3.42 (br. s, 1 H, H-34), 3.02 (m, 1 H, H-35), 2.45 (m, 1 H, H-8a), 2.36 (m, 1 H, H-9a), 2.24 (m, 1 H, H-8b), 2.16 (m, 1 H, H-11a), 2.09 (m, 2 H, H-9b, H-11b), 1.86 (s, 3 H, H-45), 1.26-1.78 (m, 23 H), 1.37 (d, J = 6.5 Hz, 3 H, H-44), 1.20 (d, J = 6.5 Hz, 3 H, H-36), 0.91 (t, J = 6.7 Hz, 3 H, H-22); ^{13}C NMR (150 MHz, C_6D_6): δ = 209.6 (C-10), 173.3 (C-7), 167.3 (C-41), 166.9 (C-46), 145.9 (C-48), 138.5 (C-43), 134.7 (C-49), 130.1 (C-52), 128.9 (C-51), 128.8 (C-42), 127.7 (C-50), 118.2 (C-47), 101.6 (C-31), 101.5 (C-1), 80.1 (C-17), 78.9 (C-32), 75.8 (C-3), 75.4 (C-5), 74.9 (C-33), 73.1 (C-2), 72.2 (C-34), 70.2 (C-35), 68.6 (C-4), 63.1 (C-6), 42.1 (C-11), 37.1 (C-9), 35.4 (C-16), 34.3 (C-18), 29.1 (C-8), 28.7 (C-13),

25.4 (C-15), 24.6 (C-19), 24.1 (C-12), 23.13 (C-20), 23.08 (C-14), 20.6 (C-21), 16.5 (C-36), 14.4 (C-22), 14.2 (C-44), 12.4 (C-45).

Orthoester rearrangements

Ipomoeassin A (1): Camphersulfonic acid (1.0 mg) was added to a solution of ipomoeassin B (**2**) (2.4 mg, 0.00315 mmol) in triethyl orthoacetate (0.10 mL) and the mixture was stirred for 1 h before aq. acetic acid (80 % *w*/*w*, 0.10 mL) was introduced and stirring continued for 3 h. Evaporation of the solvent and flash column chromatography of the crude material (CH_2Cl_2/MeOH, 30/1) gave ipomoeassin A as a colorless oil (2.4 mg, 95 %). For a compilation of the ^{1}H and ^{13}C NMR data of the synthetic samples and a comparison with the data of the natural products, see Tables 3 and 4 in the Supporting Information. $[\alpha]_D^{25}$ = –22 (*c* = 0.1, EtOH); lit.[8] $[\alpha]_D^{25}$ = –36 (*c* = 0.2, EtOH); MS (EI): *m*/*z* (%): 55 (22), 83 (99), 131 (100), 192 (13), 223 (29), 349 (14), 597 (15); HRMS (ESI): *m*/*z*: calcd for $C_{42}H_{58}O_{15}Na$ [M^+ + Na]: 825.36680, found: 825.36615.

Ipomoeassin C (3): Prepared analogously starting with compound **51** (29.1 mg, 0.0368 mmol) as a colorless oil (5.9 mg, 30 % overall). For a compilation of the ^{1}H and ^{13}C NMR data of the synthetic samples and a comparison with the data of the natural products, see Tables 7 and 8 in the Supporting Information. $[\alpha]_D^{25}$ = –20 (*c* = 0.3, EtOH); lit.[8] $[\alpha]_D^{25}$ = –29 (*c* = 0.4, EtOH); MS (EI): m/z (rel. intensity): 55 (18) 131 (100), 149 (6), 245 (6), 375 (20) 417 (7); HRMS (ESI): *m*/*z*: calcd for $C_{42}H_{58}O_{16}Na$ [M^+ + Na]: 841.36171, found: 841.36128.

Ipomoeassin D (4): Prepared analogously from ipomoeassin E (**5**) (13 mg, 0.0159 mmol) as a colorless oil (12.3 mg, 90 %). For a compilation of the ^{1}H and ^{13}C NMR data of the synthetic samples and a comparison with the data of the natural products, see Tables 9 and 10 in the Supporting Information. $[\alpha]_D^{25}$ = –30 (*c* = 0.2, EtOH); lit.[8] $[\alpha]_D^{25}$ = –35 (*c* = 0.2, EtOH); MS (EI): *m*/*z* (%): 83 (72), 131 (100)192 (12), 281 (26), 407 (11), 655 (6), 701 (4); HRMS (ESI): *m*/*z*: calcd for $C_{44}H_{60}O_{17}Na$ [M^+ + Na]. 883.37227, found: 883.37305.

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[8] S. Cao, R. C. Guza, J. H. Wisse, J. S. Miller, R. Evans, D. G. I. Kingston, *J. Nat. Prod*. **2005**, *68*, 487-492.

Ipomoeassin F (6): Prepared analogously as a colorless oil (4.8 mg, 96 %, overall from **58**). $[\alpha]_D^{20}$ = –33 (*c* = 0.16, EtOH); lit.[9] $[\alpha]_D^{22}$ = –54 (*c* = 0.16, EtOH); ^{1}H NMR (400 MHz, C_6D_6): δ = 7.81 (d, *J* = 16.0 Hz, 1 H), 7.06-6.90 (m, 4 H), 6.38 (d, *J* = 16.0 Hz, 1 H), 5.69 (t, *J* = 9.7 Hz, 1 H), 5.44 (t, *J* = 9.5 Hz, 1 H), 5.18-5.17 (m, 1 H), 4.70-4.66 (m, 1 H), 4.58 (d, *J* = 7.7 Hz, 1 H), 4.41 (d, *J* = 7.6 Hz, 1 H), 4.14 (d, *J* = 12.4 Hz, 1 H), 3.97-3.87 (m, 2 H), 3.78-3.69 (m, 2 H), 3.36 (d, *J* = 9.7 Hz, 1 H), 3.18-3.12 (m, 1 H), 2.66 (ddd, *J* = 16.1, 7.7, 3.4 Hz, 1 H), 2.56-2.48 (m, 1 H), 2.44-2.36 (m, 1 H), 2.20-2.12 (m, 1 H), 2.08 (t, *J* = 6.0 Hz, 2 H), 1.86 (s, 3 H), 1.72 (s, 3 H), 1.67-1.17 (m, 22 H), 1.26 (d, *J* = 17.0 Hz, 3 H), 1.12 (d, *J* = 6.4 Hz, 3 H), 0.92 (t, *J* = 6.9 Hz, 3 H); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 16.1 Hz, 1 H), 7.48 (m, 2 H), 7.37 (m, 1 H), 7.36 (m, 2 H), 6.87 (qq, *J* = 7.0, 1.4 Hz, 1 H), 6.32 (d, *J* = 16.0 Hz, 1 H), 5.29 (dd, *J* = 9.8, 9.8 Hz, 1 H), 5.12 (dd, *J* = 3.7, 0.9 Hz, 1 H), 5.11 (dd, *J* = 9.5, 9.5 Hz, 1 H), 4.59 (d, *J* = 7.8 Hz, 1 H), 4.44 (dd, *J* = 12.4, 3.5 Hz, 1 H), 4.38 (d, *J* = 7.7 Hz, 1 H), 4.12 (dd, *J* = 12.4, 2.4 Hz, 1 H), 3.89 (dd, *J* = 9.6, 3.7 Hz, 1 H), 3.72 (ddd, *J* = 9.8, 3.5, 2.4 Hz, 1 H), 3.63 – 3.68 (m, 3 H), 3.61 (t, *J* = 5.7 Hz, 1 H), 2.77 (ddd, *J* = 17.6, 9.1, 4.1 Hz, 1 H), 2.71 (ddd, *J* = 17.2, 7.3, 3.8 Hz, 1 H), 2.63 (ddd, *J* = 16.6, 7.3, 4.1 Hz, 1 H), 2.55 (ddd, *J* = 16.3, 9.0, 3.9 Hz, 1 H), 2.47 (ddd, *J* = 16.0, 8.1, 4.6 Hz, 1 H), 2.41 (ddd, *J* = 16.0, 9.0, 5.6 Hz, 1 H), 2.16 (s, 3 H), 1.70 – 1.74 (m, 6 H), 1.63 (m, 4 H), 1.49 (m, 4 H), 1.26 (m, 13 H), 1.16 (d, *J* = 6.4 Hz, 3 H), 0.86 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 210.1, 171.9, 171.7, 168.9, 165.4, 146.2, 139.9, 133.9, 130.7, 128.9, 128.3, 127.5, 116.6, 105.7, 100.1, 82.8, 79.7, 75.9, 73.9, 72.7, 72.6, 72.5, 68.8, 67.4, 61.7, 41.9, 37.6, 34.3, 33.0, 31.9, 29.1, 29.0, 28.3, 24.6, 24.5, 23.5, 22.7, 21.0, 16.4, 14.7, 14.1, 12.0; ^{13}C NMR (100 MHz, C_6D_6): δ = 208.4, 171.7, 170.9, 168.5, 165.6, 146.3, 139.2, 134.6, 130.7, 128.8, 128.5, 127.9, 117.7, 106.6, 100.8, 84.0, 79.4, 76.5, 74.8, 73.0, 72.8, 72.8, 69.0, 67.8, 61.5, 41.6, 37.4, 35.4, 34.3, 32.3, 29.7, 29.4, 28.7, 25.5, 25.2, 23.7, 23.1, 20.5, 16.6, 14.3, 14.1, 12.0; IR (film): $\tilde{\nu}$ = 3418, 2930, 2857, 1721, 1636, 1450, 1379, 1310, 1248, 1155, 1073; HRMS (ESI): *m*/*z*: calcd for $C_{44}H_{62}O_{15}Na$ [M^+ + Na]: 853.3988, found: 853.3981.

[9] S. Cao, A. Norris, J. H. Wisse, J. S. Miller, R. Evans, D. G. I. Kingston, *Nat. Prod. Res.* **2007**, *21*, 872-876.

X-ray crystal structure analysis of compound 17a: C_{30} H_{44} O_{11}, M_r = 580.65 g·mol^{-1}, colorless block, crystal size 0.26 x 0.08 x 0.02 mm, monoclinic, space group $P2_1$, a = 17.1161(5) Å, b = 5.5117(2) Å, c = 8.3107(3) Å, β = 117.278(1)°, V = 1476.85(8) Å^3, T = 100 K, Z = 2, D_{calc} = 1.306 g·cm^3, λ = 0.71073 Å, $\mu(Mo\text{-}K_\alpha)$ = 0.099 mm^{-1}, Multi-Scan absorption correction (T_{min} = 0.76, T_{max} = 0.86), Nonius KappaCCD diffractometer, 3.43 < θ < 33.21, 39545 measured reflections, 11292 independent reflections, 7390 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.056 [$I > 2\sigma(I)$], wR_2 = 0.103, absolute structure parameter = –0.2(6), 378 parameters, H atoms riding, S = 1.009, residual electron density +0.3 / –0.2 e Å^{-3}.

CCDC-732392 contains the supplementary crystallographic data of this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Bioassays

Cell culture: The L-929 cell line and the HeLa cells (ATCC Nr. CCL-2) were obtained from the German Collection of Microorganisms and Cell Cultures (DSMZ) and were cultured under conditions recommended by the depositor. Cell culture reagents were purchased from Sigma-Aldrich and plastic ware was obtained from Sarstedt AG & Co.

Cytotoxicity assays: L-929: Cells were seeded at 6·10^3 cells per well of 96-well plates in 180 µL complete medium and directly treated with varying concentrations of ipomoeassins diluted in methanol. Each ipomoeassin was tested in duplicate as well as the internal methanol control. After 5 d incubation, 20 µL of 5 mg mL^{-1} MTT (thiazolyl blue tetrazolium bromide) in PBS was added per well and it was further incubated for 2 h at 37 °C. The medium was then discarded and cells were washed with 100 µL PBS before adding 100 µL 2-propanol/10 M HCl (250:1) in order to dissolve formazan granules. The absorbance at 570 nm was measured using a microplate reader (EL808, Bio-Tek Instruments Inc.), and cell viability was expressed as percentage relative to the respective methanol control.

HeLa: Cells were seeded at $5 \cdot 10^3$ cells per well on 96-well plates in 100 µL complete medium. Cells were incubated for 18-20 h at 37 °C / 5 % CO_2 before the medium was exchanged for fresh medium containing the appropriate concentration of the compound to be tested. Compound stock solutions were prepared in DMSO at 10 mM. After incubation for 3 d at 37 °C / 5 % CO_2, 10 µL of a WST-1 ready-to-use solution (Roche) was added and the plate was kept at 37 °C for at least 30 min. Absorption was measured at 450 nm using an automatic plate reader (Tecan). Each measurement was repeated independently four times and cell viability was expressed as percentage of the mean value relative to the positive control; WST-1 = (4-[3-(4-Iodophenyl)-2-(4-nitrophenyl)-2H-5-tetrazolio]-1,3-benzene disulfonate).

Cell cycle analysis: 10^5 cells were harvested by centrifugation, washed with ice-cooled PBS, and fixed overnight with cold (−20 °C) 80 % ethanol. After fixation, ethanol was removed completely and the cell pellet was resuspended in a PBS solution containing 5 µg mL^{-1} propidium iodide and 0.1 mg mL^{-1} RNase A. The suspension was incubated for 30 min at 37 °C and samples were analyzed by a flowcytometric system (EasyCyte Plus, Guava Technologies). In total, 5000 viable cells were acquired per sample and cell cycle histograms were generated after exclusion of small cell debris using a Watson algorithm of FlowJo 7.2.5 software (TreeStar Inc.).

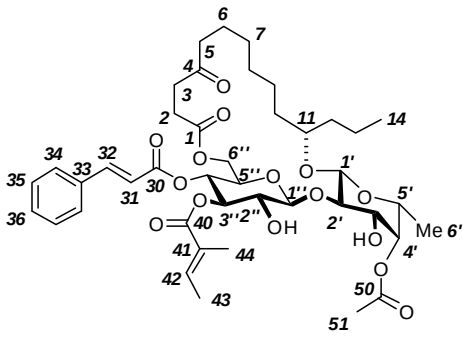

Table 3. Comparison of the published ^{1}H NMR data (C_6D_6) of Ipomoeassin A (**1**) (500 MHz) with those of the synthetic sample (600 MHz). Numbering scheme as shown in the insert.[a]

Position	Ipomoeassin A (*J* in Hz)	Synthetic Sample (*J* in Hz)
2	2.40 ddd (17.4, 9.4, 3.4)	2.38 ddd (17.4, 9.8, 3.4)
	2.14 ddd (17.4, 7.7, 3.5)	2.14 ddd (17.4, 7.5, 3.4)
3	2.65 ddd (16.1, 7.7, 3.4)	2.64 ddd (16.3, 7.5, 3.4)
	2.52 ddd (16.1, 9.4, 3.5)	2.50 ddd (16.3, 9.8, 3.4)
5	2.07 t (6.0)	2.06 t (6.0)
11	3.72 m	3.72 m
14	0.95 t (7.1)	0.95 t (6.9)
1'	4.40 d (7.7)	4.38 d (7.7)
2'	3.96 dd (9.5, 3.7)	3.86 app. t (9.2)
3'	3.72 dd (9.5, 3.7)	3.68 dd (9.6, 3.6)
4'	5.15 dd (3.7, 0.5)	5.11 brd (3.5)
5'	3.10 qd (6.4, 0.5)	3.09 brq (6.4)
6'	1.10 d (6.4)	1.09 d (6.4)
1"	4.52 d (7.9)	4.48 d (8.0)
2"	3.91 dd (9.7, 7.9)	3.92 dd (9.6, 7.8)
3"	5.39 t (9.7)	5.31 t (9.4)
4"	5.69 t (9.7)	5.67 t (9.8)
5"	3.24 ddd (9.7, 3.2, 1.6)	3.23 brd (10.3)
6"	4.66 dd (12.6, 3.2)	4.63 dd (12.6, 3.1)
	4.11 dd (12.6, 1.6)	4.11 brd (12.6)
31	6.39 d (15.9)	6.38 d (16.0)
32	7.81 d (15.9)	7.81 d (16.0)
34	6.89-7.07	6.90-7.05
35	6.89-7.07	6.90-7.05
36	6.89-7.07	6.90-7.05
42	6.95 m	6.96 m
43	1.23 d (7.1)	1.25 d (7.0)
44	1.68 brs	1.69 brs
51	1.82 s	1.82 s

[a] The protons H-6 to H-10, H-12 and H-13 appear between 1.96-1.36 ppm as a multiplet.

Table 4. Comparison of the ^{13}C NMR data (C_6D_6) of Ipomoeassin A (**1**) (125 MHz) with those of the synthetic sample (150 MHz).

Position	Ipomoeassin A	Synthetic sample
1	171.5	171.5
2	37.3	37.4
3	29.7	29.6
4	208.4	208.2
5	41.6	41.6
6	23.8	23.7
7	28.7	28.7
8	29.4	29.4
9	25.5	25.5
10	34.3	34.3
11	79.0	78.9
12	37.6	37.6
13	18.7	18.7
14	14.4	14.4
1'	100.8	100.7
2'	84.0	84.0
3'	72.7	72.8
4'	72.9	73.0
5'	69.0	69.0
6'	14.1	14.1
1"	106.6	106.5
2"	74.8	74.8
3"	76.4	76.7
4"	67.8	67.7
5"	73.0	73.0
6"	61.5	61.4
30	165.6	165.6
31	117.6	117.6
32	146.1	146.1
33	134.5	134.4
34	128.5	128.5
35	128.9	128.9
36	130.4	130.4
40	168.5	168.7
41	128.0	128.0
42	139.2	139.4
43	16.6	16.5
44	12.1	12.0
50	171.0	170.8
51	20.5	20.4

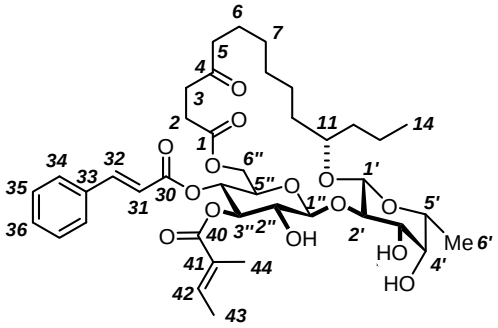

Table 5. Comparison of the published ^{1}H NMR data (C_6D_6) of Ipomoeassin B (**2**) (500 MHz) with those of the synthetic sample (300 MHz). Numbering scheme as shown in the insert.[a]

Position	Ipomoeassin B (*J* in Hz)	Synthetic sample (*J* in Hz)
2	2.38 ddd (17.4, 9.4, 3.4)	2.37 ddd (17.1, 9.3, 3.5)
	2.13 ddd (17.4, 7.7, 3.5)	2.15 ddd (17.1, 7.6, 3.3)
3	2.62 ddd (16.1, 7.7, 3.4)	2.63 ddd (16.1, 7.7, 3.3)
	2.50 ddd (16.1, 9.4, 3.5)	2.49 ddd (16.1, 9.2, 3.4)
5	2.07 t (6.2)	2.08 t (6.2)
11	3.71 m	3.73 m
14	0.96 t (7.1)	0.97 t (7.0)
1'	4.38 d (7.6)	4.39 d (7.6)
2'	3.88 dd (9.5, 7.6)	3.88 dd (9.8, 7.5)
3'	3.65 dd (9.5, 3.3)	3.65 dd (9.6, 3.3)
4'	3.53 brs	3.53 br s
5'	3.11 brq (6.4)	3.11 br q (6.3)
6'	1.29 d (6.4)	1.29 d (6.4)
1"	4.59 d (7.8)	4.61 d (7.8)
2"	3.95 dd (9.7, 7.8)	3.95 dd (9.6, 8.0)
3"	5.50 t (9.7)	5.51 t (9.6)
4"	5.72 t (9.7)	5.73 t (9.6)
5"	3.44 brd (9.7)	3.46 brm
6"	4.66 dd (12.6, 2.1)	4.64 m
	4.16 brd (12.6)	4.18 br d (12.4)
31	6.40 d (16.1)	6.41 d (16.0)
32	7.81 d (16.1)	7.82 d (16.0)
34	6.88-7.07	6.88-7.08
35	6.88-7.07	6.88-7.08
36	6.88-7.07	6.88-7.08
42	6.95 m	6.94 m
43	1.27 d (7.1)	1.29 d (7.1)
44	1.72 brs	1.73 brs

[a] The protons H-6 to H-10, H-12 and H-13 appear between δ 1.73-1.26 as a multiplet.

Table 6. Comparison of the published ^{13}C NMR data (C_6D_6) of Ipomoeassin B (**2**) (100 MHz) with those of the synthetic samples (150 MHz).

Position	Ipomoeassin B	Synthetic Sample
1	171.5	171.6
2	37.4	37.4
3	29.5	29.6
4	208.3	208.5
5	41.5	41.6
6	23.6	23.7
7	28.6	28.7
8	29.3	29.4
9	25.4	25.5
10	34.3	34.4
11	78.8	78.9
12	37.4	37.4
13	18.8	18.8
14	14.3	14.4
1'	100.6	100.6
2'	83.7	83.7
3'	74.2	74.2
4'	71.6	71.7
5'	70.2	70.2
6'	14.0	14.1
1"	106.4	106.5
2"	74.6	74.6
3"	76.3	76.4
4"	67.8	67.9
5"	73.0	73.1
6"	61.4	61.5
30	165.5	165.6
31	117.6	117.7
32	146.0	146.1
33	134.4	134.5
34	128.4	128.5
35	128.8	128.9
36	130.3	130.4
40	168.5	168.6
41	128.0	127.9
42	139.1	139.2
43	16.6	16.6
44	12.0	12.1

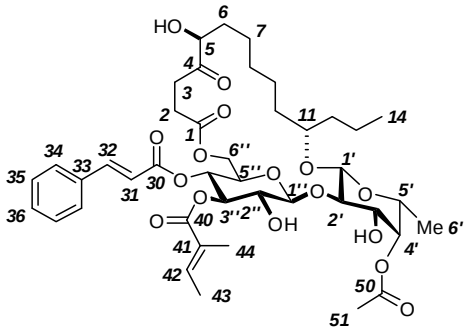

Table 7. Comparison of the published ^{1}H NMR data (C_6D_6) of Ipomoeassin C (**3**) (500 MHz) with those of the synthetic sample (400 MHz). Numbering scheme as shown in the insert.[a]

Position	Ipomoeassin C (*J* in Hz)	Synthetic sample (*J* in Hz)
2	2.65 ddd (17.9, 9.1, 4.2)	2.67 ddd (18.0, 9.2, 4.4)
	1.80 ddd (17.9, 7.8, 4.4)	1.77 m
3	3.01 ddd (16.4, 9.1, 4.4)	3.01 ddd (16.4, 9.2, 4.4)
	2.21 ddd (16.4, 7.8, 4.4)	2.24 ddt (16.4, 7.8, 4.4)
5	3.96 m	3.96 m
11	3.66 m	3.66 m
14	0.96 t (6.9)	0.97 t (6.8)
1’	4.32 d (7.6)	4.33 d (7.6)
2’	3.90 dd (9.7, 7.6)	3.89 appt (9.6)
3’	3.66 dd (9.7, 3.4)	3.66 m
4’	5.12 brd (3.4)	5.11 brm
5’	3.11 brq (6.4)	3.13 brq (6.4)
6’	1.09 d (6.4)	1.10 d (6.4)
1”	4.54 d (7.8)	4.53 brd (7.4)
2”	3.83 dd (9.7, 7.8)	3.83 appt (9.2)
3”	5.41 t (9.7)	5.39 brt (9.6)
4”	5.72 t (9.7)	5.71 t (9.6)
5”	3.26 brd (9.7)	3.27 m
6”	4.37 dd (12.4, 1.6)	4.37 brd (12.4)
	4.26 dd (12.4, 0.9)	4.25 brd (12.4)
31	6.38 d (16.0)	6.38 d (16.0)
32	7.81 d (16.0)	7.81 d (16.0)
34	6.88-7.03	6.91-7.07
35	6.88-7.03	6.91-7.07
36	6.88-7.03	6.91-7.07
42	6.95 m	6.94 m
43	1.27 d (7.1)	1.29 d (7.0)
44	1.71 brs	1.72 brs
51	1.84 s	1.84 s

[a] The protons H 6-10, H-12 and H-13 appear between 1.80-1.30 ppm as a multiplet.

Table 8. Comparison of the ^{13}C NMR data (C_6D_6) of Ipomoeassin C (**3**) (125 MHz) with those of the synthetic sample (75 MHz).

Position	Ipomoeassin C	Synthetic sample
1	171.6	171.6
2	33.0	33.0
3	28.3	28.3
4	210.7	210.6
5	76.3	76.4
6	32.7	32.8
7	22.7	22.7
8	29.9	29.9
9	25.1	25.1
10	34.1	34.2
11	78.8	78.9
12	37.6	37.7
13	18.8	18.8
14	14.4	14.4
1'	100.7	100.8
2'	83.7	83.8
3'	72.7	72.8
4'	72.6	72.7
5'	68.9	69.0
6'	14.1	14.1
1"	106.4	106.4
2"	74.7	74.8
3"	76.4	76.4
4"	67.9	67.9
5"	72.8	72.8
6"	61.6	61.6
30	165.4	165.4
31	117.5	117.6
32	146.2	146.2
33	134.4	134.5
34	128.5	128.5
35	128.9	128.9
36	130.4	130.4
40	168.5	168.6
41	128.0	128.0
42	139.3	139.3
43	16.5	16.5
44	12.1	12.0
50	171.0	170.9
51	20.5	20.5

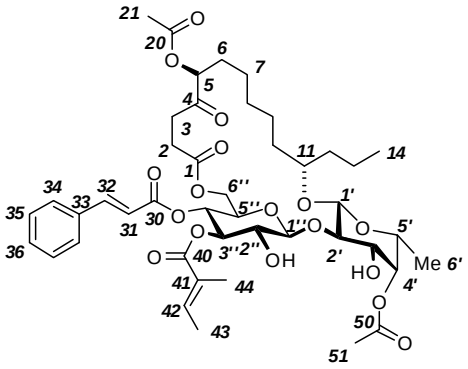

Table 9. Comparison of the published ^{1}H NMR data (C_6D_6) of Ipomoeassin D (**4**) (500 MHz) with those of the synthetic sample (400 MHz). Numbering scheme as shown in the insert.[a]

Position	Ipomoeassin D (*J* in Hz)	Synthetic Sample (*J* in Hz)
2	2.57 ddd (18.1, 9.2, 2.8)	2.59 ddd (18.0, 9.3, 2.9)
	2.38 ddd (18.1, 7.8, 3.4,)	2.40 m
3	2.83 ddd (16.3, 9.2, 3.4)	2.84 ddd (16.5, 9.2, 3.6)
	2.43 ddd (16.3, 7.8, 2.8)	2.42 brm
5	5.05 dd (6.2, 3.9)	5.07 dd (6.3, 3.8)
11	3.70 m	3.71 m
14	0.95 t (7.1)	0.96 t (7.0)
1'	4.29 d (7.6)	4.31 d (7.9)
2'	3.88 dd (9.5, 7.6)	3.88 dd (9.6, 7.8)
3'	3.62 dd (9.5, 3.7)	3.64 brm
4'	5.09 brd (3.7)	5.10 brs
5'	3.06 brq (6.4)	3.09 brq (6.2)
6'	1.08 d (6.4)	1.09 d (6.4)
1"	4.51 d (7.8)	4.50 brm
2"	3.79 dd (9.7, 7.8)	3.80 brm
3"	5.39 t (9.7)	5.39 brm
4"	5.69 t (9.7)	5.69 t (9.8)
5"	3.29 brd (9.7)	3.29 brm
6"	4.51 brd (11.5)	4.50 br d (11.7)
	4.19 brd (11.5)	4.20 brd (11.7)
21	1.70 s	1.72 s
31	6.37 d (15.8)	6.38 d (16.0)
32	7.81 d (15.8)	7.81 d (16.0)
34	6.88-7.03	6.91-7.08
35	6.88-7.03	6.91-7.08
36	6.88-7.03	6.91-7.08
42	6.95 m	6.96 m
43	1.26 d (7.1)	1.28 brm
44	1.70 brs	1.72 s
51	1.82 s	1.82 s

[a] The protons H-6 to H-10, H-12 and H-13 appear between 1.97-1.33 ppm as a multiplet.

Table 10. Comparison of the ^{13}C NMR data (C_6D_6) of Ipomoeassin D (**4**) (125 MHz) with those of the synthetic sample (75 MHz).

Position	Ipomoeassin D	Synthetic sample
1	171.3	171.3
2	34.0	34.1
3	28.3	28.3
4	205.7	205.7
5	78.4	78.5
6	30.3	30.4
7	24.0	24.0
8	30.6	30.6
9	25.2	25.2
10	34.0	34.1
11	78.5	78.5
12	37.7	37.7
13	18.9	18.9
14	14.4	14.4
1'	100.6	100.7
2'	83.9	83.9
3'	72.8	72.9
4'	72.7	72.7
5'	68.9	68.9
6'	14.1	14.1
1"	106.6	106.6
2"	75.0	75.0
3"	76.6	76.4
4"	67.6	67.8
5"	72.9	72.9
6"	61.2	61.3
50	170.9	171.0
51	20.4	20.5
20	169.8	169.8
21	20.3	20.3
40	168.8	168.6
41	128.0	128.0
42	139.4	139.2
43	16.5	16.5
44	12.0	12.1
30	165.5	165.5
31	117.6	117.6
32	146.2	146.2
33	134.4	134.5
34	128.4	128.3
35	128.8	128.9
36	130.4	130.4

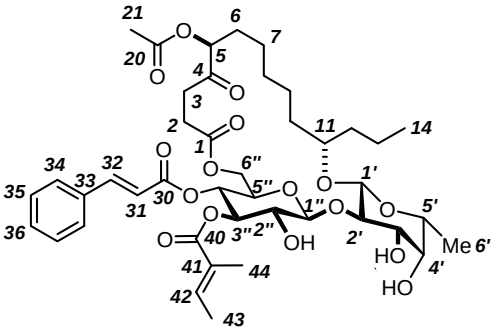

Table 11. Comparison of the ^{1}H NMR data (C_6D_6) reported for Ipomoeassin E (**5**) (500 MHz) with those of the synthetic material (400 MHz). Numbering scheme as shown in the insert.[a, b]

Position	Ipomoeassin E (*J* in Hz)	Synthetic sample (*J* in Hz)
2	2.55 ddd (18.1, 9.2, 2.8)	2.59 ddd (18.0, 9.2, 3.1)
	2.34 ddd (18.1, 7.8, 3.4)	2.46-2.36 m
3	2.81 ddd (16.3, 9.2, 3.4)	2.82 ddd (16.5, 9.2, 3.5)
	2.39 ddd (16.3, 7.8, 2.8)	2.46-2.36 m
5	5.04 dd (6.2, 3.9)	5.07 dd (6.1, 3.9)
11	3.71 m	3.74 brm
14	0.97 t (6.9)	0.99 t (7.0)
1'	4.28 d (7.6)	4.32 d (7.6)
2'	3.80 dd (9.5, 7.6)	3.82 appt (9.4)
3'	3.55 dd (9.5, 3.7)	3.59 dd (9.3, 3.2)
4'	3.44 brs	3.48 brs
5'	3.02 brq (6.4)	3.09 brq (6.4)
6'	1.25 d (6.4)	1.28 d (6.6)
1"	4.50 d (7.8)	4.55 d (8.0)
2"	3.81 dd (9.7, 7.8)	3.84 appt (9.5)
3"	5.38 t (9.7)	5.43 t (9.5)
4"	5.70 t (9.7)	5.71 t (9.7)
5"	3.36 brd (9.7)	3.43 brd (9.8)
6"	4.51 dd (11.0, 2.0)	4.52 dd (11.4, 2.2)
	4.20 brd (11.0)	4.24 brd (11.5)
21	1.67 brs	1.73 brs
31	6.40 d (16.1)	6.41 d (16.0)
32	7.81 d (16.1)	7.82 d (16.0)
34	6.88-7.03	6.91-7.09
35	6.88-7.03	6.91-7.09
36	6.88-7.03	6.91-7.09
42	6.95 m	6.95 m
43	1.25 d (7.1)	1.30 d (7.3)
44	1.67 brs	1.73 brs

[a] The chemical shifts depend on the concentration of the sample and the dryness of the C_6D_6 used; the data compiled in this Table were recorded using 3 mg of compound **2** in 0.6 mL of freshly distilled (CaH_2) C_6D_6. [b] The protons at positions H-6 to H-10, H-12 and H-13 appear between 1.96-1.36 ppm as a multiplet.

Table 12. Comparison of the ^{13}C NMR data (C_6D_6) reported for Ipomoeassin E (**5**) (125 MHz) with those of the synthetic sample (75 MHz).

Position	Ipomoeassin E	Synthetic sample
1	171.4	171.4
2	34.0	34.1
3	28.3	28.3
4	205.8	205.7
5	78.2	78.2
6	30.3	30.3
7	24.0	24.0
8	30.5	30.5
9	25.2	25.2
10	34.0	34.1
11	78.5	78.5
12	37.7	37.7
13	18.9	19.0
14	14.4	14.4
1'	100.5	100.4
2'	84.2	84.3
3'	74.0	74.0
4'	71.6	71.6
5'	70.0	70.0
6'	14.1	14.1
1"	106.7	106.7
2"	74.9	74.9
3"	76.6	76.7
4"	67.7	67.7
5"	72.9	73.0
6"	61.2	61.3
20	169.8	169.8
21	20.3	20.3
30	165.5	165.5
31	117.5	117.6
32	146.2	146.2
33	134.4	134.5
34	128.3	128.2
35	128.5	128.3
36	130.4	130.4
40	168.9	168.9
41	128.0	128.0
42	139.6	139.5
43	16.6	16.5
44	12.0	12.0