SUPPORTING INFORMATION

Total Syntheses of Ipomoeassin B and E

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General. All reactions were carried out under Ar atmosphere. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF (Mg-anthracene), CH₂Cl₂ (P₄O₁₀), MeCN, Et₃N, DMSO (CaH₂), MeOH (Mg), toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on a DPX 300, AV 400 or DMX 600 spectrometer (Bruker) 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 (calibration: CDCl₃, δ_C = 77.0, δ_H = 7.26; CD₂Cl₂, δ_C = 53.8, δ_H = 5.32). IR: Nicolet FT-7199 spectrometer, wavenumbers in cm⁻¹. MS (EI): Finnigan MAT 8200 (70 eV), HRMS: Finnigan MAT 95. Melting points: Büchi melting point apparatus (uncorrected). All commercially available compounds were used as received.

Preparation of the Building Blocks

Scheme S1. Conditions: a) EtMgCl, CuCN (10 mol%), THF, -78 → -20 °C; b) NaOH, Et₂O; c) CH₂=CHMgBr, CuCN (10 mol%), THF, -78 → 0 °C, 77% (overall), 99% ee; d) AgOTf, 2,6-di-*tert*-butylpyridine, MS 4 Å, CH₂Cl₂, 0 °C → RT, 84%; e) KOMe cat., MeOH; f) 2,2-dimethoxypropane, *p*-TsOH·H₂O cat., acetone, 98% (over both steps).

(S)-1-Hepten-4-ol (S-1). A solution of EtMgCl (2 M in THF, 16.2 mL, 32.4 mmol) was added dropwise to a solution of (S)-epichlorohydrin (2.00 g, 21.6 mmol) and CuCN (193 mg, 2.16 mmol) in THF (30 mL) at $-78\text{ }^{\circ}\text{C}$. The mixture was warmed to $-20\text{ }^{\circ}\text{C}$ over 3 h before it was poured into sat. aq. NH_4Cl . The organic layer was separated, the aqueous layer 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, which was used without further purification.

Powdered NaOH (4.80 g, 121 mmol) was added to a solution of the crude (S)-1-chloro-pentene-2-ol 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 , the combined organic phases were dried over MgSO_4 , filtered and evaporated to give (S)-2-propyloxirane, which was used without further purification.

To a stirred solution of the crude oxirane 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 $-78\text{ }^{\circ}\text{C}$ over a period of 45 min. The resulting mixture was allowed to warm to $0\text{ }^{\circ}\text{C}$ 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 on silica gel (hexanes/*tert*-butyl methyl ether, 4/1) to give (S)-1-hepten-4-ol (**S-1**) as a pale yellow oil (1.91 g, 77%). The NMR data are in full agreement with those previously reported in the literature. $[\alpha]_{\text{D}}^{20} = -12.8$ (c 0.52, CHCl_3); lit.¹ $[\alpha]_{\text{D}}^{20} = +12.7$ (c 0.54, CHCl_3) for (*R*)-enantiomer (99% *ee*).

Compound S-3. A solution of HBr in HOAc (30% w/w, 7.1 mL) was added dropwise to a cold ($0\text{ }^{\circ}\text{C}$) solution of 1,2,3,4-tetra-O-acetyl-D-fucopyranose² (2.08 g, 6.26 mmol) 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 times) to give crude glycosyl bromide **S-2** which was used in the following step without further purification.

To a suspension of activated MS 4Å in CH_2Cl_2 (50 mL) was added a solution of the

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

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

crude bromide **S-2** prepared above in CH_2Cl_2 (120 mL) and the resulting mixture was stirred at room temperature for 10 minutes before (*S*)-1-hepten-4-ol (**S-1**) (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 and the filtrate was evaporated. The residue was purified by flash chromatography on silica (hexanes/*tert*-butyl methyl ether, 6/1) to give compound **S-3** as a colorless syrup (1.36 g, 84%). $[\alpha]_{\text{D}}^{20} = -20.1$ (c 0.73, CHCl_3). IR (KAP): $\tilde{\nu} = 3076, 2961, 2937, 2873, 1752, 1641, 1368, 1250, 1223, 1074, 915$. ^1H NMR (400 MHz, CDCl_3): $\delta = 5.77$ (ddt, $J = 7.0, 10.2, 17.2$ Hz, 1 H), 5.21 (dd, $J = 1.1, 3.5$ Hz, 1H), 5.17-4.99 (m, 4H), 4.48 (d, $J = 7.9$ Hz, 1H), 3.76 (dq, $J = 1.0, 6.5$ Hz, 1H), 3.64 (m, 1H), 2.25-2.22 (m, 2H), 2.17 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H), 1.63-1.34 (m, 4H), 1.20 (d, $J = 6.7$ Hz, 3H), 0.89 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 170.8, 170.3, 169.4, 134.4, 117.1, 100.4, 79.7, 71.5, 70.4, 69.3, 68.9, 38.4, 36.6, 20.9, 20.7, 20.6, 18.3, 16.1, 14.0$. MS (EI): m/z (%): 273 (27), 157 (17), 153 (25), 115 (13), 111 (24), 83 (12), 55 (23), 43 (100). HRMS: calcd. for $\text{C}_{19}\text{H}_{30}\text{O}_8$ $[\text{Na}]^+$ 409.183143, found 409.183288.

Compound S-4. Compound **S-3** (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 $\text{TsOH} \cdot \text{H}_2\text{O}$ (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 on silica (hexanes/EtOAc, 6/1 $\rightarrow$ 4/1) to give glycoside **S-4** as a colorless syrup (1.46 g, 98%). $[\alpha]_{\text{D}}^{20} = +3.4$ (c 1.18, CHCl_3). IR (KAP): $\tilde{\nu} = 3483, 3076, 2983, 2959, 2935, 2872, 1641, 1380, 1073, 1036, 990, 918$. ^1H NMR (400 MHz, CDCl_3): $\delta = 5.83$ (ddt, $J = 7.2, 10.1, 17.1$ Hz, 1H), 5.13-5.08 (m, 2H), 4.17 (d, $J = 8.2$ Hz, 1H), 4.04-3.98 (m, 2H), 3.83 (dq, $J = 2.2, 6.6$ Hz, 1H), 3.72-3.66 (m, 1H), 3.50 (dd, $J = 7.3, 8.2$ Hz, 1H), 2.35-2.23 (m, 3H), 1.65-1.33 (m, 13H), 0.91 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 134.9, 117.6, 109.8, 101.6, 78.8, 78.7, 76.3, 73.8, 69.1, 38.7, 37.0, 28.2, 26.3, 18.4, 16.6, 14.0$. 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: calcd. for $\text{C}_{16}\text{H}_{28}\text{O}_5$ $[\text{Na}]^+$ 323.182872, found 323.182895.

Scheme S2. Conditions: a) 1-bromo-3-pentene, Mg, THF, then 2-furylcarbaldehyde, 82%; b) $\text{Ti}(\text{OiPr})_4$, D-(–)-diisopropyltartrate (DIPT), *t*-BuOOH, CH_2Cl_2 , -20°C , 47% (= 94% theoretical yield), > 99 *ee*; c) *t*-BuOOH, $\text{VO}(\text{acac})_2$ (2 mol%), CH_2Cl_2 , 71%; d) CrO_3 , H_2SO_4 , acetone, 0°C ; e) Zn, HOAc, CH_2Cl_2 , 78% (over both steps); f) (i) $\text{HO}(\text{CH}_2)_2\text{SiMe}_3$, *p*-TsOH· H_2O cat., CH_2Cl_2 ; (ii) Ac_2O , DMAP cat., CH_2Cl_2 , 93%, 97% *ee* (over both steps); g) TASF, DMF, 68%.

***dl*-5-Hydroxy-5-(2-furyl)-1-pentene (*rac*-15).** 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 added 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 2-furylcarbaldehyde (1.0 g, 10.4 mmol) was introduced at that temperature. After 2 h, the mixture was quenched with aq. HCl (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*-15 as a pale yellow oil (1.30 g, 82%). IR (KAP): $\tilde{\nu}$ = 3366, 2943, 2863, 1641, 1505, 1149, 1066, 1009, 913, 738, 599. ^1H NMR (400 MHz, CDCl_3): δ = 7.37 (dd, J = 0.8, 1.8 Hz, 1H), 6.33 (dd, J = 1.8, 3.2 Hz, 1H), 6.24 (d, J = 3.2 Hz, 1H), 5.84 (ddt, J = 6.6, 10.3, 17.0 Hz, 1H), 5.08–4.97 (m, 2H), 4.70 (t, J = 6.7 Hz, 1H), 2.20–2.12 (m, 2H), 1.98–1.92 (m, 3H). ^{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. 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: calcd. for $\text{C}_9\text{H}_{12}\text{O}_2$ 152.083577, found 152.083730.

Kinetic resolution: Preparation of (–)-15. D-(–)-DIPT (2.50 g, 11.8 mmol) was added to a solution of $\text{Ti}(\text{OiPr})_4$ (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 $-30\text{ }^{\circ}\text{C}$ and a solution of *rac*-**15** (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 $-20\text{ }^{\circ}\text{C}$. For work-up, the mixture was filtered through a short pad of silica and the filtrate was evaporated. The residue was purified by flash chromatography on silica (hexanes/EtOAc, 9/1) to give (–)-**15** as a pale yellow oil (701 mg, 47%, >99% *ee*). The *ee* was determined by chiral HPLC (Chiralcel OB-H, Hexane/*i*PrOH = 95/5). The NMR data are identical with those of the racemic sample described above. $[\alpha]_{\text{D}}^{20} = -6.6$ (c 1.12, CHCl_3).

Compound 16. To a solution of alcohol (–)-**15** (333 mg, 2.19 mmol) and $\text{VO}(\text{acac})_2$ (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 $\text{VO}(\text{acac})_2$ (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 on silica (hexanes/EtOAc, 4/1) to give compound **16** as a mixture of diastereomers (262 mg, 71 %, major/minor = 69/31). IR (KAP): $\tilde{\nu} = 3411, 3077, 2926, 1690, 1641, 1089, 1033, 916$. ^1H NMR (400 MHz, CDCl_3): $\delta = 6.94$ (dd, $J = 1.5, 10.3$ Hz, 1H of minor isomer), 6.90 (dd, $J = 3.5, 10.3$ Hz, 1H of major isomer), 6.16 (dd, $J = 1.6, 10.3$ Hz, 1H of minor isomer), 6.11 (d, $J = 10.3$ Hz, 1H of major isomer), 5.87–5.76 (m, 1H), 5.66–5.65 (m, 1H), 5.18–4.98 (m, 2H), 4.59 (dd, $J = 3.8, 8.3$ Hz, 1H of major isomer), 4.11 (ddd, $J = 1.2, 3.8, 8.6$ Hz, 1H of minor isomer), 3.34 (br, 1H of minor isomer), 3.06 (br, 1H of major isomer), 2.24–2.18 (m, 2H), 2.07–2.03 (m, 1H), 1.18–1.74 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 196.5$ (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). MS (EI): *m/z* (rel. intensity): 168 (4), 114 (20), 84 (100), 56 (28), 55 (39), 39 (10), 29 (12), 28 (12), 27 (14). HRMS: calcd. for $\text{C}_9\text{H}_{12}\text{O}_3$ 168.078643, found 168.078521.

Compound 17. Jones' reagent (1.7 mL)³ was added dropwise to an ice-cold solution of hemiacetal **16** (413 mg, 2.46 mmol) in acetone (13 mL). The resulting mixture was stirred for 3 h at room temperature. The mixture was diluted with *tert*-butyl methyl ether

³ Georgiadis, M. P.; Tsekouras, A.; Kotretsou, S. I.; Haroutounian, S. A.; Polissiou, M. G. *Synthesis* **1991**, 929.

(50 mL) and washed with water, the organic phase was dried over Na₂SO₄, filtered, and evaporated to give the crude oxidation product. To a solution of this material in CHCl₃ (26 mL) and AcOH (17 mL) was added zinc powder (1.2 g). The suspension was stirred for 3 h at room temperature before it was filtered 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 **17** as a colorless oil (324 mg, 78%). $[\alpha]_D^{20} = -246.3$ (c 1.08, CHCl₃). IR (KAP): $\tilde{\nu} = 3079, 2929, 1759, 1735, 1641, 1267, 1171, 999, 919$. ¹H NMR (400 MHz, CDCl₃): $\delta = 5.77$ (ddt, $J = 6.7, 10.3, 16.9$ Hz, 1H), 5.11-5.02 (m, 2H), 4.68 (dd, $J = 4.0, 8.2$ Hz, 1H), 2.93-2.89 (m, 2H), 2.79-2.64 (m, 2H), 2.34-2.19 (m, 2H), 2.13-2.04 (m, 1H), 1.96-1.86 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 205.4, 170.0, 136.5, 116.4, 82.2, 33.8, 29.6, 28.6, 28.2$. 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: calcd. for C₉H₁₂O₃ 168.078649, found 168.078862.

Compound 18. To a solution of ketolactone **17** (100 mg, 0.59 mmol) and 2-trimethylsilylethanol (0.17 mL, 1.18 mmol) in CH₂Cl₂ (1.0 mL) was added *p*-TsOH•H₂O (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 CH₂Cl₂ (10 mL) and treated with triethylamine (0.50 mL, 3.54 mmol), Ac₂O (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 **18** as a colorless oil (156 mg, 93%, 97% *ee*). The *ee* was determined by chiral HPLC column (Chiralcel AD, Heptane/*i*PrOH = 98/2). $[\alpha]_D^{20} = -4.3$ (c 0.62, CH₂Cl₂). IR (KAP): $\tilde{\nu} = 3079, 2954, 1732, 1642, 1249, 1235, 1063, 996, 919, 860, 839, 695$. ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 5.81$ (ddt, $J = 6.6, 10.3, 17.0$ Hz, 1H), 5.09-4.98 (m, 3H), 4.14 (m, 2H), 2.78-2.72 (m, 2H), 2.56-2.51 (m, 2H), 2.21-2.11 (m, 5H), 1.92-1.80 (m, 2H), 0.97 (m, 2H), 0.04 (s, 9H). ¹³C NMR (100 MHz, CD₂Cl₂): $\delta = 206.2, 172.7, 170.8, 137.4, 115.9, 78.0, 63.2, 33.7, 30.1, 29.6, 27.9, 20.8, 17.6, -1.5$ (3C). MS (EI): m/z (%): 43 (47), 73 (100), 117 (33), 133 (10), 173 (82). HRMS: calcd. for C₁₆H₂₈O₅Si₁ [M⁺+Na] 351.159826, found 351.159979.

Acid 19. A solution of compound **18** (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 **19** as a colorless oil (28 mg, 68%). $[\alpha]_D^{20} = -2.1$ (c 0.60, CH₂Cl₂). IR (KAP): ν (cm⁻¹) = 3079, 2928, 1741, 1731, 1713, 1642, 1237, 999, 918. ¹H NMR (400 MHz, CD₂Cl₂): δ = 5.81 (ddt, J = 6.7, 10.3, 17.0 Hz, 1H), 5.09-4.99 (m, 3H), 2.80-2.60 (m, 4H), 2.20-2.12 (m, 5H), 1.92-1.80 (m, 2H). ¹³C NMR (100 MHz, CD₂Cl₂): δ = 206.1, 177.9, 170.9, 137.4, 115.9, 78.0, 33.5, 30.0, 29.6, 27.5, 20.8. MS (EI): m/z (%): 43 (100), 85 (12), 101 (40), 114 (7), 132 (5), 174 (6). HRMS: calcd. for C₁₁H₁₆O₅ [M⁺+Na] 251.088993, found 251.089031.

Scheme S3. Conditions: a) Cl₃CCN, Cs₂CO₃ cat., CH₂Cl₂, 86%; b) compound **S-4**, BF₃·Et₂O cat., CH₂Cl₂/pentane (1:1), -20°C, 77%; c) KOMe cat., MeOH, 84%.

Trichloroacetimidate S-6. To a solution of substrate **S-5**⁴ (1.00 g, 2.62 mmol) in CH₂Cl₂ (4 mL) were added trichloroacetonitrile (0.48 mL, 4.79 mmol) and Cs₂CO₃ (85 mg, 0.26 mmol). The resulting mixture was stirred for 15 h at ambient temperature before it was filtered through a pad of silica and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 2/1) to give trichloroacetimidate **S-6** as a mixture of anomers (1.19 g, 86%, α : β = 2:1). $[\alpha]_D^{20} = +25.9$ (c 0.83, CH₂Cl₂). IR (KBr): $\tilde{\nu}$ = 3348, 2940, 1754, 1676, 1616, 1589, 1519, 1236, 1071, 1033, 834. ¹H NMR (400 MHz, CD₂Cl₂): δ = 8.81 (s, 1H of β -anomer), 8.71 (s, 1H of α -anomer), 7.37-7.35 (m, 2H), 6.89-6.86 (m, 2H), 6.53 (d, J = 3.9 Hz, 1H of α -anomer), 6.00 (d, J = 7.7 Hz, 1H of β -anomer), 5.61 (t, J = 9.9 Hz, 1H of α -anomer), 5.49 (s, 1H of α -anomer), 5.48 (s, 1H of β -anomer), 5.35 (t, J = 8.8 Hz, 1H of β -anomer), 5.26 (dd, J

⁴ Fürstner, A.; Radkowski, K.; Grabowski, J.; Wirtz, C.; Mynott, R. *J. Org. Chem.* **2000**, *65*, 8758-8762.

= 7.8, 8.6 Hz, 1H of β -anomer), 5.12 (dd, J = 3.9, 9.9 Hz, 1H of α -anomer), 4.37 (dd, J = 4.3, 9.8 Hz, 1H of β -anomer), 4.31 (dd, J = 5.0, 10.4 Hz, 1H of α -anomer), 4.13-4.05 (m, 1H), 4.88-3.72 (m, 5H), 2.06 (s, 3H of α -anomer), 2.04 (s, 3H of β -anomer), 2.02 (s, 3H of β -anomer), 2.01 (s, 3H 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 (2C), 113.9 (2C), 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 (2C), 113.9 (2C), 102.0, 96.2, 78.3, 71.8, 71.4, 68.7, 67.4, 65.5, 55.6, 20.9, 20.7. MS (EI): m/z (%): 527 (22), 365 (9), 179 (16), 137 (51), 136 (100), 135 (71), 43 (85). HRMS: calcd. for $\text{C}_{20}\text{H}_{22}\text{Cl}_3\text{N}_1\text{O}_9$ [$\text{M}^+ + \text{H}$] 526.043294, found 526.043271.

Disaccharide S-7. $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.25 M in Et_2O , 1.90 mL) was added to a solution of trichloroacetimidate **S-6** (746 mg, 1.41 mmol) and alcohol **S-4** (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 **S-7** as a white solid (696 mg, 77%). mp = $129\text{--}130^\circ\text{C}$. $[\alpha]_{\text{D}}^{20} = -35.1$ (c 0.70, CH_2Cl_2). IR (KAP): $\tilde{\nu}$ = 3073, 2936, 2873, 1755, 1640, 1616, 1518, 1371, 1244, 1219, 1175, 1099, 1073, 1037, 920, 831. ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.35 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.90 (ddt, J = 7.2, 10.1, 17.2 Hz, 1H), 5.46 (s, 1H), 5.28-5.23 (m, 1H), 5.10-5.03 (m, 2H), 5.01 (d, J = 7.6 Hz, 1H), 4.95-4.91 (m, 1H), 4.33 (dd, J = 5.0, 10.4 Hz, 1H), 4.27 (d, J = 8.0 Hz, 1H), 4.03-4.00 (m, 1H), 3.96 (dd, J = 2.1, 5.6 Hz, 1H), 3.82-3.49 (m, 9H), 2.28-2.24 (m, 2H), 2.05 (s, 3H), 2.02 (s, 3H), 1.52-1.31 (13 H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 170.3, 169.8, 160.6, 135.7, 130.0 (2C), 127.8, 116.8, 113.8 (2C), 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. 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: calcd. for $\text{C}_{34}\text{H}_{48}\text{O}_{13}$ [$\text{M}^+ + \text{H}$] 665.317321, found 665.316665.

Disaccharide 3. A solution of disaccharide **S-7** (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 **3** as a white solid (518 mg, 84%). mp = $68\text{--}69^\circ\text{C}$. $[\alpha]_{\text{D}}^{20} = -9.9$ (c 1.21, C_2HCl_2). IR (KAP): $\tilde{\nu}$ = 3459, 3072, 2935, 2872, 1640, 1615, 1589, 1518, 1382, 1250, 1075, 1034, 923, 831. ^1H NMR (400 MHz, CD_2Cl_2): δ = 7.43 (d, J =

8.8 Hz, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 5.95 (ddt, $J = 7.1, 10.2, 17.2$ Hz, 1H), 5.52 (s, 1H), 5.14-5.07 (m, 2H), 4.69 (d, $J = 7.7$ Hz, 1H), 4.35 (d, $J = 8.2$ Hz, 1H), 4.31 (dd, $J = 4.9, 10.5$ Hz, 1H), 4.17 (dd, $J = 5.5, 7.4$ Hz, 1H), 4.04 (dd, $J = 2.1, 5.4$ Hz, 1H), 3.86-3.44 (m, 12H), 2.80 (br, 1H), 2.32 (m, 1H), 1.66 (br, 1H), 1.56-1.30 (m, 13H), 0.94 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 160.6, 135.4, 130.2$ (2C), 127.9, 116.9, 113.8 (2C), 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. 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: calcd. for $\text{C}_{30}\text{H}_{45}\text{O}_{11}$ [$\text{M}^+ + \text{H}$] 581.296842, found 581.296186.

Regioselective Acylation: Preparation of Compound 4. A solution of diol **3** (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 precipitate formed 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 **4** and its regioisomer **4a** (**4**/**4a** = 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 **4** (432 mg, 55%) and pure **4a** (45 mg, 6%), respectively. Analytical and spectroscopic data of compound **4**: Colorless solid, mp = 72-73°C. $[\alpha]_{\text{D}}^{20} = -24.7$ (c

0.42, CH_2Cl_2) IR (KAP): $\tilde{\nu} = 3474, 3072, 2935, 2873, 1718, 1651, 1589, 1518, 1381, 1252, 1175, 1075, 1036, 990, 923, 829$. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 7.33$ (d, $J = 8.8$ Hz, 2H), 6.91 (m, 1H), 6.86 (d, $J = 8.8$ Hz, 2H), 5.91 (ddt, $J = 7.1,$

10.2, 17.2 Hz, 1H), 5.62 (s, 1H), 5.24 (d, $J = 9.4$ Hz, 1H), 5.11-5.03 (m, 2H), 4.77 (d, $J = 7.7$ Hz, 1H), 4.34-4.29 (m, 2H), 4.15-4.12 (m, 1H), 4.01 (dd, $J = 2.1, 5.4$ Hz, 1H), 3.83-3.50 (m, 9H), 3.36 (d, $J = 2.7$ Hz, 1H), 2.28 (m, 2H), 1.84-1.78 (m, 6H), 1.53-1.33 (m, 14H), 0.91 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 167.7, 160.5, 138.3, 135.4, 130.1, 128.6, 127.8$ (2C), 117.0, 113.8 (2C), 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. 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: calcd. for $\text{C}_{35}\text{H}_{51}\text{O}_{12}$ [$\text{M}^+ + \text{H}$] 663.338772, found 663.338055.

Analytical and spectroscopic data of compound **4a**: mp = 67-68 °C. $[\alpha]_D^{20} = -7.0$ (c 0.83, CH₂Cl₂) IR (KBr): $\tilde{\nu} = 3494, 3074, 2935, 2872, 1722, 1651, 1616, 1589, 1519,$

1303, 1174, 921, 830. ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 7.39$ (d, $J = 8.8$ Hz, 2H), 6.96 (m, 1H), 6.89 (d, $J = 8.8$ Hz, 2H), 5.90 (ddt, $J = 7.1, 10.2, 17.2$ Hz, 1H), 5.51 (s, 1H), 5.09-5.01 (m, 3H), 4.91-4.87 (m, 1H), 4.31 (dd, $J = 5.0, 10.4$ Hz, 1H), 4.25 (d, $J = 7.9$ Hz, 1H), 4.00-3.86 (m, 3H),

3.81-3.71 (m, 4H), 3.65-3.57 (m, 3H), 3.48-3.40 (m, 2H), 2.73 (d, $J = 3.8$ Hz, 1H), 2.27 (m, 2H), 1.86 (m, 3H), 1.81 (m, 3H), 1.51-1.29 (m, 13H), 0.89 (t, $J = 7.2$ Hz, 3H). ¹³C NMR (100 MHz, CD₂Cl₂): $\delta = 167.6, 160.6, 138.6, 135.7, 130.2, 128.6, 127.9$ (2C), 116.8, 113.9 (2C), 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. 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: calcd. for C₃₅H₅₀O₁₂ [$M^+ + Na$] 685.319445, found 685.319537.

Compound 5. TBSOTf (87.0 mL, 0.30 mmol) was added to a solution of compound **4** (100 mg, 0.15 mmol) and 2,6-lutidine (69.0 mL, 0.75 mmol) in CH₂Cl₂ (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 **5** as a colorless solid (112 mg, 96%). mp = 54-55 °C. $[\alpha]_D^{20}$

= -11.7 (c 0.72, CH₂Cl₂). IR (KBr): $\tilde{\nu} = 3073, 2958, 2934, 2859, 1724, 1653, 1616, 1519, 1252, 1181, 1085, 923, 837, 779, 671$. ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 7.20$ (d, $J = 8.8$ Hz, 2H), 6.78 (m, 1H), 6.75 (d, $J = 8.8$ Hz, 2H), 5.80 (ddt, $J = 7.0, 10.2, 17.2$ Hz, 1H), 5.34 (s, 1H), 5.15 (m, 1H), 5.00-4.93 (m, 3H), 4.21-4.17 (m, 2H), 4.06 (dd, $J = 5.7, 6.8$ Hz, 1H), 3.89 (dd, $J = 2.0, 5.5$ Hz, 1H), 3.73-3.66 (m, 6H), 3.59-3.50 (m, 3H), 3.43-3.39 (m, 1H), 2.18 (m, 2H), 1.71-1.66 (m, 6H), 1.43-1.19 (m, 13H), 0.80 (t, $J = 5.0$ Hz, 3H), 0.73 (s, 9H), -0.02 (s, 3H), -0.11 (s, 3H). ¹³C NMR (100 MHz, CD₂Cl₂): $\delta = 167.2, 160.5, 138.1, 135.6, 130.3, 128.8, 127.7$ (2C), 116.8, 113.8 (2C), 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 (3C), 18.8, 18.3, 16.7, 14.5, 14.2, 12.3, -3.6, -4.8. 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: calcd. for C₄₁H₆₄O₁₂Si [$M^+ + Na$] 799.405930, found 799.405236.

(Z)-3-Dimethyl(phenyl)silyl-2-propenoic Acid
as Protected Cinnamic Acid Surrogate

Scheme S4. Conditions: a) (i) $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OMe})_2$, Et_2O , then I_2 , (ii) PhMe_2SiCl , Et_3N , DMAP cat, CH_2Cl_2 , 87%, cf. ref.; b) BuLi , THF, $-78^\circ\text{C} \rightarrow \text{RT}$, 50%, cf. ref.; c) $(\text{COCl})_2$, DMSO, Et_3N , CH_2Cl_2 , -78°C ; d) NaClO_2 , 2-methyl-2-butene, NaH_2PO_4 , $t\text{BuOH}/\text{H}_2\text{O}$, 93% (over both steps).

(Z)-3-Dimethyl(phenyl)silyl-2-propenoic acid (8). 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 (5.0 mL) and the mixture was stirred for 15 min at that temperature. A solution of (Z)-3-dimethyl(phenyl)silyl-2-propene-1-ol (**S-9**)⁵ (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 reaction mixture was allowed to warm to 0°C over 1.5 h before it 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 **S-10** as a pale yellow oil which was used without further purification (239 mg, 90%). Characteristic data: IR (KAP): $\tilde{\nu} = 2839, 2739, 1677, 1489, 1428, 1254, 1111, 814, 783, 733, 701, 641, 472$. ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 9.83$ (d, $J = 8.4$ Hz, 1H), 7.61–7.58 (m, 2H), 7.42–7.30 (m, 6H), 7.16–7.13 (m, 2H), 6.51 (d, $J = 8.4$ Hz, 1H), 0.34 (s, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 192.9, 168.4, 144.6, 143.7$ (2C), 138.2, 134.1 (2C), 130.0, 128.6 (3C), 127.8, 126.7 (2C), 0.3 (2C). MS (EI): m/z (%): 135 (51), 189 (78), 251 (100), 266 (9). HRMS: calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_1\text{Si}$ [$\text{M}^+ + \text{Na}$] 289.101916, found 289.101840.

⁵ (a) Ukaji, Y.; Sada, K.; Inomata, K. *Chem. Lett.* **1993**, 1227–1230. (b) See also: Arnold, L. A.; Naasz, R.; Minnaard, A. J.; Feringa, B. L. *J. Am. Chem. Soc.* **2001**, 123, 5841–5842.

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 **S-10** (100 mg, 0.38 mmol) in *t*BuOH (3.0 mL). The mixture was stirred for 2.5 h at ambient temperature, all volatiles were evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc/AcOH, 100:10:0.1) to give acid **8** (99.8 mg, 93%) as a white solid. mp = 77-78 °C. IR (KAP): $\tilde{\nu}$ = 3022, 2954, 1694, 1589, 1489, 1410, 1313, 1251, 815, 701. ^1H NMR (400 MHz, CDCl_3): δ = 7.51-7.49 (m, 2H), 7.30-7.24 (m, 6H), 7.08-7.05 (m, 2H), 6.44 (s, 1H), 0.37 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ = 166.9, 144.8, 138.2, 133.7 (2C), 132.9, 128.7, 128.0 (2C), 127.5 (3C), 126.9, 126.4 (2C), 95.7, -0.9 (2C). MS (EI): m/z (%): 75 (20), 205 (60), 267 (100), 282 (1). HRMS: calcd. for $\text{C}_{17}\text{H}_{17}\text{O}_2\text{Si}$ 281.100333, found 281.100638.

Model Studies Defining the Conditions for the Proto-Desilylation

Nr	Reagent	Conditions	Result
1	TBAF	THF, 60°C, 3h	cleavage of tiglate ester
2	TBAF	THF/DMSO, methyl propionate, 80°C, 20 min	cleavage of tiglate ester
3	AgF	THF/MeOH, rt, 20h	no reaction
4	TASF	MeCN, rt, 6h	5a (93%)

Nr	Reagent	Conditions	Result
1	BF ₃ ·Et ₂ O	CHCl ₃ , rt, 2h	no reaction
2	AgF ⁶	THF/MeOH, rt, 5h	methyl cinnamate (32%)
3	TASF	MeCN, rt, 16h	methyl cinnamate (94%)

The model studies summarized above suggested that only TBAF would be appropriate for the final deprotection steps in the projected total syntheses of ipomoeassin B and E.

Reductive Cleavage of the 4,6-O-*p*-Methoxybenzylidene Acetal

Entry	Conditions	Product	Ref.
1	BH ₃ ·THF, Cu(OTf) ₂ (15 mol%), THF, RT, 1h	decomposition	7
2	BH ₃ ·THF, Bu ₂ BOTf (1 eq.), CH ₂ Cl ₂ , RT, 4h	decomposition	8
3	Dibal-H, CH ₂ Cl ₂ , 0°C, 5 min	reduction of ester	9
4	PMHS, AlCl ₃ , CH ₂ Cl ₂ /Et ₂ O, RT, 15h	decomposition	10
5	Et ₃ SiH, PhBCl ₂ , MS 4Å, CH ₂ Cl ₂ , -78°C, 1h	decomposition	11
6	NaBH ₃ CN, TMSCl, MS 4Å, MeCN, RT, 15h	81% (7 : 6 = 4:1)	12

⁶ (a) Fürstner, A.; Radkowski, K. *Chem. Commun.* **2002**, 2182-2183. (b) F. Lacombe, K. Radkowski, A. Fürstner, *Tetrahedron* **2004**, 60, 7315-7324.

⁷ Shie, C.-R.; Tzeng, Z.-H.; Kulkarni, S. S.; Uang, B.-J.; Hsu, C.-Y.; Hung, S.-C. *Angew. Chem., Int. Ed.* **2005**, 44, 1665-1668.

⁸ Wu, X.; Schmidt, R. R. *Eur. J. Org. Chem.* **2004**, 2826-2832.

⁹ Crich, D.; Banerjee, A. *Org. Lett.* **2005**, 7, 1395-1398.

¹⁰ Chandrasekhar, S.; Reddy, Y. R.; Reddy, C. R. *Chem. Lett.* **1998**, 1273-1274.

¹¹ Sakagami, M.; Hamana, H. *Tetrahedron Lett.* **2000**, 41, 5547-5551.

Compounds 6 and 7. Disaccharide **5** (500 mg, 0.643 mmol) was added to a suspension of freshly activated MS 4Å (1.7 g) in CH₃CN (15 mL) and the resulting mixture was stirred for 15 min at that temperature. NaBH₃CN (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 allowed to warm to room temperature and stirring was continued for 3 h. The suspension was filtered through Celite, the filtrate was diluted with Et₂O, the organic phase was washed with sat. aq. NaHCO₃, 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%, **7/6** = 3.5/1). *This mixture does not need to be further purified because compound 9 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/H₂O = 4/1; flow rate: 35.0 mL/min; pressure: 4.1 MPa) to give product **7** (210 mg, 42%) and regioisomer **6** (24 mg, 5%) which showed the following spectroscopic and analytical properties:

Compound 7: ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.28 (d, *J* = 8.7 Hz, 2H), 6.92 (m, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.90 (ddt, *J* = 7.1, 10.2, 17.2 Hz, 1H), 5.09-4.99 (m, 3H), 4.93 (d, *J* = 7.7 Hz, 1H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.47 (d, *J* = 11.5 Hz, 1H), 4.30 (d, *J* = 8.1 Hz, 1H), 4.14 (m, 1H), 3.98 (dd, *J* = 2.0, 5.6 Hz, 1H), 3.85-3.40 (m, 11H), 2.75 (br s, 1H), 2.28 (m, 2H), 1.84-1.71 (m, 6H), 1.55-1.31 (m, 13 H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.81 (s, 9H), 0.07 (s, 3H), -0.02 (s, 3H). ¹³C NMR (100 MHz, CD₂Cl₂): δ = 168.6, 159.7, 138.7, 135.7, 130.4, 129.9 (2C), 128.7, 116.8, 114.0 (2C), 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 (3C), 18.8, 18.3, 16.8, 14.5, 14.1, 12.2, -3.5, -4.9. HRMS: calcd. for C₄₁H₆₆O₁₂Si₁ [M⁺+Na] 801.421577, found 801.422035.

Compound 6: ¹H NMR (400 MHz, CD₂Cl₂): δ = 7.13 (d, *J* = 8.8 Hz, 2H), 6.90 (m, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.91 (ddt, *J* = 7.1, 10.2, 17.2 Hz, 1H), 5.22 (t, *J* = 9.2 Hz, 1H), 5.11-5.03 (m, 2H), 4.95 (d, *J* = 7.6 Hz, 1H), 4.45 (m, 2H), 4.29 (d, *J* = 8.1 Hz, 1H), 4.15 (dd, *J* = 5.7, 6.8 Hz, 1H), 3.98 (dd, *J* = 2.1, 5.6 Hz, 1H), 3.84-3.76 (m, 6H), 3.71-3.65 (m, 2H), 3.61 (t, *J* = 9.5 Hz, 1H), 3.52 (dd, *J* = 7.5, 9.0, 1H), 3.42-3.38 (m, 1H),

¹² Johansson, R.; Samuelsson, B. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2371-2374.

2.28 (m, 2H), 1.84-1.79 (m, 6H), 1.65 (br s, 1H), 1.55-1.32 (m, 13 H), 0.09 (t, $J = 7.2$ Hz, 3H), 0.82 (s, 9H), 0.07 (s, 3H), -0.03 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 167.1, 159.7, 138.26, 135.6, 130.5, 130.1$ (2C), $129.0, 116.8, 114.0$ (2C), $110.0, 100.2, 100.1, 80.0, 78.5, 77.5, 77.0, 76.6, 76.3, 75.5, 74.3, 73.8, 69.0, 62.0, 55.5, 38.8, 36.9, 28.1, 26.3, 25.8$ (3C), $18.7, 18.2, 16.7, 14.6, 14.1, 12.3, -3.6, -4.8$.

The assigned regiochemistry was further corroborated by acylation of both isomers. The corresponding ring proton H-6,6' (m, 2H) in **6** and H-4 (app. t, 1H) in **7** showed the expected acylation shifts.

Model Studies on Selective Hydrogenation

Conditions	Product Distribution (NMR)			
	S-11	S-12	S-13	S-14
H_2 (1 atm), $\text{RhCl}(\text{PPh}_3)_3$ (3 mol%), benzene, RT, 4h	15%	52%	7%	26%
$\text{KOOCN}=\text{NCOOK}$ (2 eq.), AcOH, MeOH, RT, 15h	44%	14%	33%	9%

Total Synthesis of Ipomoeassin B

Compound 9. Et₃N (43 μ L, 0.305 mmol) and 2,4,6-trichlorobenzoyl chloride (22 mL, 0.139 mmol) were added to a solution of acid **8**

(39 mg, 0.139 mmol) in toluene (0.6 mL) and the resulting mixture was stirred for 1.5 h at ambient temperature before a solution of the mixture of alcohols **7** and **6** (54 mg, 0.0693 mmol) and DMAP (8.0 mg, 0.0693 mmol) in CH₂Cl₂ (0.5

mL) was introduced. After stirring for 3 h, the mixture was filtered through a pad of silica, the filtrate was evaporated and the residue was purified by flash chromatography (hexanes/EtOAc, 6/1) to give product **9** as a colorless oil (56.8 mg, 79%). $[\alpha]_D^{20} = -4.4$ (c 0.5, CHCl₃). IR (KAP): $\tilde{\nu} = 3070, 2956, 2932, 2904, 2858, 1730, 1652, 1612, 1587, 1513, 1248, 1160, 1074, 915, 839, 780, 701$. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.49\text{--}7.46$ (m, 2H), 7.26–7.18 (m, 10 H), 6.97–6.94 (m, 2H), 6.84–6.80 (m, 3H), 6.31 (s, 1H), 5.94 (ddt, $J = 7.1, 10.2, 17.2$ Hz, 1H), 5.27 (t, $J = 9.4$ Hz, 1H), 5.08–4.99 (m, 3H), 4.90 (d, $J = 7.6$ Hz, 1H), 4.41 (d, $J = 11.6$, 1H), 4.39 (d, $J = 11.6$, 1H), 4.31 (d, $J = 7.7$ Hz, 1H), 4.15 (t, $J = 6.1$ Hz, 1H), 3.97–3.90 (m, 2H), 3.78–3.74 (m, 4H), 3.66–3.53 (m, 3H), 3.36–3.34 (m, 2H), 2.29–2.26 (m, 2H), 1.76–1.75 (m, 6H), 1.56–1.24 (m, 11H), 0.86 (t, $J = 7.2$ Hz, 3H), 0.81 (s, 9H), 0.41 (s, 3H), 0.26 (s, 3H), 0.04 (s, 3H), –0.06 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 166.9, 165.8, 164.8, 159.0, 144.7, 138.3, 137.9, 135.4, 133.9$ (3C), 132.9, 130.3, 129.4 (2C), 128.6, 128.3, 127.8 (2C), 127.4 (2C), 126.8, 126.6 (2C), 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 (3C), 18.3, 18.0, 16.7, 14.3, 14.1, 12.0, –0.8, –1.5, –3.9, –5.0. MS (EI): m/z (%): 83 (14), 121 (100), 157 (9), 265 (30), 565 (4), 985 (2). HRMS: calcd. for C₅₈H₈₂O₁₃Si₂ [$M^+ + Na$] 1065.518622, found 1065.517790.

Synthesis of 11. DDQ (49.0 mg, 0.216 mmol) was added to a solution of compound **9** (150 mg, 0.144 mmol) in CH₂Cl₂ (6.0 mL) and water (0.3 mL). The mixture was stirred at room temperature 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 **10** (150 mg)

which contained *p*-methoxybenzaldehyde as an inseparable impurity.

Et₃N (45 μ L, 0.318 mmol) and 2,4,6-trichlorobenzoyl chloride (23 μ L, 0.148 mmol) were added to a solution of 4-oxo-8-nonenoic acid¹³ (25 mg, 0.0862 mmol) in toluene (1.0 mL) and the mixture was stirred for 1.5 h before a solution of the crude alcohol **10** (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 **11** as a colorless syrup (61.7 mg, 78%). $[\alpha]_D^{20} = -4.2$ (c 0.43, CH₂Cl₂). IR (KAP): $\tilde{\nu} = 3071, 2956, 2933, 1732, 1651, 1588, 1248, 1157, 914, 839, 780, 730, 701$. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.47\text{--}7.44$ (m, 2H), 7.28–7.18 (m, 6H), 6.98–6.95 (m, 2H), 6.81 (m, 1H), 6.33 (s, 1H), 5.93 (ddt, $J = 7.1, 10.1, 17.1$ Hz, 1H), 5.77 (ddt, $J = 6.4, 10.3, 17.0$ Hz, 1H), 5.27 (t, $J = 9.4$ Hz, 1H), 5.08–4.96 (m, 5H), 4.94 (d, $J = 7.6$ Hz, 1H), 4.28 (d, $J = 7.8$ Hz, 1H), 4.14 (t, $J = 5.9$ Hz, 1H), 4.01–3.99 (m, 2H), 3.97 (dd, $J = 2.0, 5.6$ Hz, 1H), 3.89–3.85 (m, 1H), 3.77 (m, 1H), 3.68–3.61 (m, 2H), 3.55 (dd, $J = 7.6, 9.1$ Hz, 1H), 2.67–2.42 (m, 6H), 2.27 (m, 2H), 2.09–2.03 (m, 2H), 1.77–1.75 (m, 6H), 1.59–1.34 (m, 15 H), 0.89 (t, $J = 7.2$ Hz, 3H), 0.81 (s, 9H), 0.39 (s, 3H), 0.27 (s, 3H), 0.04 (s, 3H), –0.06 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 208.6, 172.4, 166.9, 166.6, 164.7, 144.7, 138.2, 138.0, 135.4, 133.8$ (2C), 132.6, 128.7, 128.2, 127.9 (2C), 127.6 (2C), 126.9, 126.6 (2C), 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 (3C), 22.8, 18.3, 18.0, 16.7, 14.4, 14.1, 12.1, –0.7, –1.4, –3.8, –4.9. MS (EI): m/z (%): 83 (68), 157 (29), 265 (100), 393 (30), 775 (9), 793 (42), 961 (13), 1017 (7). HRMS: calcd. for C₅₉H₈₆O₁₄Si₂ [M⁺+Na] 1097.544832, found 1097.544163.

Compound 14. The ruthenium carbene complex **12** (5.0 mg, 0.00558 mmol) was added

to a solution of diene **11** (60 mg, 0.0558 mmol) in CH₂Cl₂ (10 mL) and the resulting mixture was refluxed 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 **13** as a mixture

of (*E*)- and (*Z*)-isomers.

¹³ Hodgson, D. M.; Stupple, P. A.; Pierard, F. Y. T. M.; Labande, A. H.; Johnstone, C. *Chem. Eur. J.* **2001**, 7, 4465.

A solution of cycloalkene **13** thus obtained (42 mg, 0.0398 mmol) and $\text{RhCl}(\text{PPh}_3)_3$ (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 **14** as a colorless oil (34 mg, 81%). $[\alpha]_{\text{D}}^{20} = +0.6$ (c 0.50, CH_2Cl_2). IR (KAP): $\tilde{\nu} = 3069, 2932, 2858, 1733, 1652, 1588, 1248, 1155, 1074, 839, 780, 730, 701$. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.46\text{--}7.45$ (m, 2H), 7.28–7.17 (m, 6H), 6.97–6.95 (m, 2H), 6.86 (m, 1H), 6.31 (s, 1H), 5.27 (t, $J = 9.3$ Hz, 1H), 5.08 (t, $J = 9.8$ Hz, 1H), 4.93 (d, $J = 7.7$ Hz, 1H), 4.27 (d, $J = 7.8$ Hz, 1H), 4.20–4.13 (m, 2H), 4.00–3.97 (m, 2H), 3.87 (dd, $J = 6.6, 7.7$ Hz, 1H), 3.78 (m, 1H), 3.63 (m, 1H), 3.54 (dd, $J = 7.8, 9.0$ Hz, 1H), 3.51 (m, 1H), 2.81–2.73 (m, 1H), 2.58–2.31 (m, 5H), 1.79–1.24 (m, 29H), 0.90 (t, $J = 7.3$ Hz, 3H), 0.81 (s, 9H), 0.37 (s, 3H), 0.24 (s, 3H), 0.05 (s, 3H), -0.04 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 209.6, 171.4, 166.8, 166.3, 164.4, 144.7, 138.4, 138.2, 133.8$ (2C), 132.7, 128.6, 128.2, 127.8 (2C), 127.5 (2C), 126.8, 126.6 (2C), 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 (3C), 24.0, 23.7, 18.4, 18.0, 16.8, 14.4, 14.3, 12.1, $-0.5, -1.6, -3.8, -4.9$. MS (EI): m/z (%): 83 (91), 157 (29), 265 (100), 349 (13), 767 (36), 991 (9). HRMS: calcd. for $\text{C}_{57}\text{H}_{84}\text{O}_{14}\text{Si}_2$ [$\text{M}^+ + \text{Na}$] 1071.529187, found 1071.530087.

Synthesis of Ipomoeassin B (1). A solution of TASF (79 mg, 0.286 mmol) in MeCN (2.0 mL) was added to a solution of compound **14** (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 ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, 20/1) to afford Ipomoeassin B (**1**) as a colorless syrup which solidifies when kept in the freezer (10 mg, 45%). $[\alpha]_{\text{D}}^{25} = -48.0$ (c 0.36, EtOH); lit.¹⁴ $[\alpha]_{\text{D}}^{25} = -39$ (c 0.3, EtOH). IR (KAP): $\tilde{\nu} = 3365, 3062, 2932, 1744, 1719, 1631, 1371, 1316, 1265, 1249, 1157, 1138, 1073$. ^1H NMR (400 MHz, C_6D_6) and ^{13}C NMR (100 MHz, C_6D_6) data, see Table S1 and S2, respectively. MS (EI): m/z (%): 513 (11), 467 (14), 349 (10), 241 (13), 223 (42), 131 (44), 111 (13), 83 (100), 55 (28). HRMS: calcd. for $\text{C}_{40}\text{H}_{56}\text{O}_{14}$ [$\text{M}^+ + \text{Na}$] 783.356230, found 783.356291.

¹⁴ Cao, S.; Guza, R. C.; Wisse J. H.; Miller, J. S.; Evans, R.; Kingston, D. G. I. *J. Nat. Prod.* **2005**, 68, 487.

Table S1. Comparison of the published ^1H NMR data (C_6D_6) of Ipomoeassin B (**1**) (500 MHz) with those of the synthetic sample (Bruker dpx300, 300 MHz). Numbering scheme as shown in the insert.

Position	Ipomoeassin B (<i>J</i> in Hz)	Synthetic Sample (<i>J</i> in Hz) ^a
2	2.38 ddd (17.4, 9.4, 3.4) 2.13 ddd (17.4, 7.7, 3.5)	2.37 ddd (17.1, 9.3, 3.5) 2.15 ddd (17.1, 7.6, 3.3)
3	2.62 ddd (16.1, 7.7, 3.4) 2.50 ddd (16.1, 9.4, 3.5)	2.63 ddd (16.1, 7.7, 3.3) 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) 4.16 brd (12.6)	4.64 m 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 at positions 6-10, 12 and 13 appear between δ 1.73-1.26 as complicated multiplet.

Table S2. Comparison of the published ^{13}C NMR data (C_6D_6) of Ipomoeassin B (**1**) (100 MHz) with those of the synthetic samples (Bruker DMX-600, 150 MHz).

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

¹H NMR spectra of Ipomoeassin B in C₆D₆: (a) natural product reported in literature (500 MHz, Kingston et al. *J. Nat. Prod.* **2005**, 68, 487); (b) sample prepared by us (400 MHz).

C609535

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 PROCNO: 1
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 SOLVENT: CDCl3
 NS: 6425
 DS: 200
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 FIDRES: 0.573645 Hz
 AQ: 0.8716891 sec
 RG: 4096
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 DE: 5.50 usec
 TE: 303.0 K
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 SFO33: 400.1464010 MHz
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 P34: 16.00 usec
 PL34: 0.00 dB
 SFO34: 400.1464010 MHz
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 NUC35: 1H
 P35: 16.00 usec
 PL35: 0.00 dB
 SFO35: 400.1464010 MHz
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 NUC36: 1H
 P36: 16.00 usec
 PL36: 0.00 dB
 SFO36: 400.1464010 MHz
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 NUC37: 1H
 P37: 16.00 usec
 PL37: 0.00 dB
 SFO37: 400.1464010 MHz
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 NUC38: 1H
 P38: 16.00 usec
 PL38: 0.00 dB
 SFO38: 400.1464010 MHz
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 P39: 16.00 usec
 PL39: 0.00 dB
 SFO39: 400.1464010 MHz
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 P40: 16.00 usec
 PL40: 0.00 dB
 SFO40: 400.1464010 MHz
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 P41: 16.00 usec
 PL41: 0.00 dB
 SFO41: 400.1464010 MHz
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 NUC42: 1H
 P42: 16.00 usec
 PL42: 0.00 dB
 SFO42: 400.1464010 MHz
 ===== CHANNEL f43 =====
 NUC43: 1H
 P43: 16.00 usec
 PL43: 0.00 dB
 SFO43: 400.1464010 MHz
 ===== CHANNEL f44 =====
 NUC44: 1H
 P44: 16.00 usec
 PL44: 0.00 dB
 SFO44: 400.1464010 MHz
 ===== CHANNEL f45 =====
 NUC45: 1H
 P45: 16.00 usec
 PL45: 0.00 dB
 SFO45: 400.1464010 MHz
 ===== CHANNEL f46 =====
 NUC46: 1H
 P46: 16.00 usec
 PL46: 0.00 dB
 SFO46: 400.1464010 MHz
 ===== CHANNEL f47 =====
 NUC47: 1H
 P47: 16.00 usec
 PL47: 0.00 dB
 SFO47: 400.1464010 MHz
 ===== CHANNEL f48 =====
 NUC48: 1H
 P48: 16.00 usec
 PL48: 0.00 dB
 SFO48: 400.1464010 MHz
 ===== CHANNEL f49 =====
 NUC49: 1H
 P49: 16.00 usec
 PL49: 0.00 dB
 SFO49: 400.1464010 MHz
 ===== CHANNEL f50 =====
 NUC50: 1H
 P50: 16.00 usec
 PL50: 0.00 dB
 SFO50: 400.1464010 MHz
 ===== CHANNEL f51 =====
 NUC51: 1H
 P51: 16.00 usec
 PL51: 0.00 dB
 SFO51: 400.1464010 MHz
 ===== CHANNEL f52 =====
 NUC52: 1H
 P52: 16.00 usec
 PL52: 0.00 dB
 SFO52: 400.1464010 MHz
 ===== CHANNEL f53 =====
 NUC53: 1H
 P53: 16.00 usec
 PL53: 0.00 dB
 SFO53: 400.1464010 MHz
 ===== CHANNEL f54 =====
 NUC54: 1H
 P54: 16.00 usec
 PL54: 0.00 dB
 SFO54: 400.1464010 MHz
 ===== CHANNEL f55 =====
 NUC55: 1H
 P55: 16.00 usec
 PL55: 0.00 dB
 SFO55: 400.1464010 MHz
 ===== CHANNEL f56 =====
 NUC56: 1H
 P56: 16.00 usec
 PL56: 0.00 dB
 SFO56: 400.1464010 MHz
 ===== CHANNEL f57 =====
 NUC57: 1H
 P57: 16.00 usec
 PL57: 0.00 dB
 SFO57: 400.1464010 MHz
 ===== CHANNEL f58 =====
 NUC58: 1H
 P58: 16.00 usec
 PL58: 0.00 dB
 SFO58: 400.1464010 MHz
 ===== CHANNEL f59 =====
 NUC59: 1H
 P59: 16.00 usec
 PL59: 0.00 dB
 SFO59: 400.1464010 MHz
 ===== CHANNEL f60 =====
 NUC60: 1H
 P60: 16.00 usec
 PL60: 0.00 dB
 SFO60: 400.1464010 MHz
 ===== CHANNEL f61 =====
 NUC61: 1H
 P61: 16.00 usec
 PL61: 0.00 dB
 SFO61: 400.1464010 MHz
 ===== CHANNEL f62 =====
 NUC62: 1H
 P62: 16.00 usec
 PL62: 0.00 dB
 SFO62: 400.1464010 MHz
 ===== CHANNEL f63 =====
 NUC63: 1H
 P63: 16.00 usec
 PL63: 0.00 dB
 SFO63: 400.1464010 MHz
 ===== CHANNEL f64 =====
 NUC64: 1H
 P64: 16.00 usec
 PL64: 0.00 dB
 SFO64: 400.1464010 MHz
 ===== CHANNEL f65 =====
 NUC65: 1H
 P65: 16.00 usec
 PL65: 0.00 dB
 SFO65: 400.1464010 MHz
 ===== CHANNEL f66 =====
 NUC66: 1H
 P66: 16.00 usec
 PL66: 0.00 dB
 SFO66: 400.1464010 MHz
 ===== CHANNEL f67 =====
 NUC67: 1H
 P67: 16.00 usec
 PL67: 0.00 dB
 SFO67: 400.1464010 MHz
 ===== CHANNEL f68 =====
 NUC68: 1H
 P68: 16.00 usec
 PL68: 0.00 dB
 SFO68: 400.1464010 MHz
 ===== CHANNEL f69 =====
 NUC69: 1H
 P69: 16.00 usec
 PL69: 0.00 dB
 SFO69: 400.1464010 MHz
 ===== CHANNEL f70 =====
 NUC70: 1H
 P70: 16.00 usec
 PL70: 0.00 dB
 SFO70: 400.1464010 MHz
 ===== CHANNEL f71 =====
 NUC71: 1H
 P71: 16.00 usec
 PL71: 0.00 dB
 SFO71: 400.1464010 MHz
 ===== CHANNEL f72 =====
 NUC72: 1H
 P72: 16.00 usec
 PL72: 0.00 dB
 SFO72: 400.1464010 MHz
 ===== CHANNEL f73 =====
 NUC73: 1H
 P73: 16.00 usec
 PL73: 0.00 dB
 SFO73: 400.1464010 MHz
 ===== CHANNEL f74 =====
 NUC74: 1H
 P74: 16.00 usec
 PL74: 0.00 dB
 SFO74: 400.1464010 MHz
 ===== CHANNEL f75 =====
 NUC75: 1H
 P75: 16.00 usec
 PL75: 0.00 dB
 SFO75: 400.1464010 MHz
 ===== CHANNEL f76 =====
 NUC76: 1H
 P76: 16.00 usec
 PL76: 0.00 dB
 SFO76: 400.1464010 MHz
 ===== CHANNEL f77 =====
 NUC77: 1H
 P77: 16.00 usec
 PL77: 0.00 dB
 SFO77: 400.1464010 MHz
 ===== CHANNEL f78 =====
 NUC78: 1H
 P78: 16.00 usec
 PL78: 0.00 dB
 SFO78: 400.1464010 MHz
 ===== CHANNEL f79 =====
 NUC79: 1H
 P79: 16.00 usec
 PL79: 0.00 dB
 SFO79: 400.1464010 MHz
 ===== CHANNEL f80 =====
 NUC80: 1H
 P80: 16.00 usec
 PL80: 0.00 dB
 SFO80: 400.1464010 MHz
 ===== CHANNEL f81 =====
 NUC81: 1H
 P81: 16.00 usec
 PL81: 0.00 dB
 SFO81: 400.1464010 MHz
 ===== CHANNEL f82 =====
 NUC82: 1H
 P82: 16.00 usec
 PL82: 0.00 dB
 SFO82: 400.1464010 MHz
 ===== CHANNEL f83 =====
 NUC83: 1H
 P83: 16.00 usec
 PL83: 0.00 dB
 SFO83: 400.1464010 MHz
 ===== CHANNEL f84 =====
 NUC84: 1H
 P84: 16.00 usec
 PL84: 0.00 dB
 SFO84: 400.1464010 MHz
 ===== CHANNEL f85 =====
 NUC85: 1H
 P85: 16.00 usec
 PL85: 0.00 dB
 SFO85: 400.1464010 MHz
 ===== CHANNEL f86 =====
 NUC86: 1H
 P86: 16.00 usec
 PL86: 0.00 dB
 SFO86: 400.1464010 MHz
 ===== CHANNEL f87 =====
 NUC87: 1H
 P87: 16.00 usec
 PL87: 0.00 dB
 SFO87: 400.1464010 MHz
 ===== CHANNEL f88 =====
 NUC88: 1H
 P88: 16.00 usec
 PL88: 0.00 dB
 SFO88: 400.1464010 MHz
 ===== CHANNEL f89 =====
 NUC89: 1H
 P89: 16.00 usec
 PL89: 0.00 dB
 SFO89: 400.1464010 MHz
 ===== CHANNEL f90 =====
 NUC90: 1H
 P90: 16.00 usec
 PL90: 0.00 dB
 SFO90: 400.1464010 MHz
 ===== CHANNEL f91 =====
 NUC91: 1H
 P91: 16.00 usec
 PL91: 0.00 dB
 SFO91: 400.1464010 MHz
 ===== CHANNEL f92 =====
 NUC92: 1H
 P92: 16.00 usec
 PL92: 0.00 dB
 SFO92: 400.1464010 MHz
 ===== CHANNEL f93 =====
 NUC93: 1H
 P93: 16.00 usec
 PL93: 0.00 dB
 SFO93: 400.1464010 MHz
 ===== CHANNEL f94 =====
 NUC94: 1H
 P94: 16.00 usec
 PL94: 0.00 dB
 SFO94: 400.1464010 MHz
 ===== CHANNEL f95 =====
 NUC95: 1H
 P95: 16.00 usec
 PL95: 0.00 dB
 SFO95: 400.1464010 MHz
 ===== CHANNEL f96 =====
 NUC96: 1H
 P96: 16.00 usec
 PL96: 0.00 dB
 SFO96: 400.1464010 MHz
 ===== CHANNEL f97 =====
 NUC97: 1H
 P97: 16.00 usec
 PL97: 0.00 dB
 SFO97: 400.1464010 MHz
 ===== CHANNEL f98 =====
 NUC98: 1H
 P98: 16.00 usec
 PL98: 0.00 dB
 SFO98: 400.1464010 MHz
 ===== CHANNEL f99 =====
 NUC99: 1H
 P99: 16.00 usec
 PL99: 0.00 dB
 SFO99: 400.1464010 MHz
 ===== CHANNEL f100 =====
 NUC100: 1H
 P100: 16.00 usec
 PL100: 0.00 dB
 SFO100: 400.1464010 MHz
 ===== CHANNEL f101 =====
 NUC101: 1H
 P101: 16.00 usec
 PL101: 0.00 dB
 SFO101: 400.1464010 MHz
 ===== CHANNEL f102 =====
 NUC102: 1H
 P102: 16.00 usec
 PL102: 0.00 dB
 SFO102: 400.1464010 MHz
 ===== CHANNEL f103 =====
 NUC103: 1H
 P103: 16.00 usec
 PL103: 0.00 dB
 SFO103: 400.1464010 MHz
 ===== CHANNEL f104 =====
 NUC104: 1H
 P104: 16.00 usec
 PL104: 0.00 dB
 SFO104: 400.1464010 MHz
 ===== CHANNEL f105 =====
 NUC105: 1H
 P105: 16.00 usec
 PL105: 0.00 dB
 SFO105: 400.1464010 MHz
 ===== CHANNEL f106 =====
 NUC106: 1H
 P106: 16.00 usec
 PL106: 0.00 dB
 SFO106: 400.1464010 MHz
 ===== CHANNEL f107 =====
 NUC107: 1H
 P107: 16.00 usec
 PL107: 0.00 dB
 SFO107: 400.1464010 MHz
 ===== CHANNEL f108 =====
 NUC108: 1H
 P108: 16.00 usec
 PL108: 0.00 dB
 SFO108: 400.1464010 MHz
 ===== CHANNEL f109 =====
 NUC109: 1H
 P109: 16.00 usec
 PL109: 0.00 dB
 SFO109: 400.1464010 MHz
 ===== CHANNEL f110 =====
 NUC110: 1H
 P110: 16.00 usec
 PL110: 0.00 dB
 SFO110: 400.1464010 MHz
 ===== CHANNEL f111 =====
 NUC111: 1H
 P111: 16.00 usec
 PL111: 0.00 dB
 SFO111: 400.1464010 MHz
 ===== CHANNEL f112 =====
 NUC112: 1H
 P112: 16.00 usec
 PL112: 0.00 dB
 SFO112: 400.1464010 MHz
 ===== CHANNEL f113 =====
 NUC113: 1H
 P113: 16.00 usec
 PL113: 0.00 dB
 SFO113: 400.1464010 MHz
 ===== CHANNEL f114 =====
 NUC114: 1H
 P114: 16.00 usec
 PL114: 0.00 dB
 SFO114: 400.1464010 MHz
 ===== CHANNEL f115 =====
 NUC115: 1H
 P115: 16.00 usec
 PL115: 0.00 dB
 SFO115: 400.1464010 MHz
 ===== CHANNEL f116 =====
 NUC116: 1H
 P116: 16.00 usec
 PL116: 0.00 dB
 SFO116: 400.1464010 MHz
 ===== CHANNEL f117 =====
 NUC117: 1H
 P117: 16.00 usec
 PL117: 0.00 dB
 SFO117: 400.1464010 MHz
 ===== CHANNEL f118 =====
 NUC118: 1H
 P118: 16.00 usec
 PL118: 0.00 dB
 SFO118: 400.1464010 MHz
 ===== CHANNEL f119 =====
 NUC119: 1H
 P119: 16.00 usec
 PL119: 0.00 dB
 SFO119: 400.1464010 MHz
 ===== CHANNEL f120 =====
 NUC120: 1H
 P120: 16.00 usec
 PL120: 0.00 dB
 SFO120: 400.1464010 MHz
 ===== CHANNEL f121 =====
 NUC121: 1H
 P121: 16.00 usec
 PL121: 0.00 dB
 SFO121: 400.1464010 MHz
 ===== CHANNEL f122 =====
 NUC122: 1H
 P122: 16.00 usec
 PL122: 0.00 dB
 SFO122: 400.1464010 MHz
 ===== CHANNEL f123 =====
 NUC123: 1H
 P123: 16.00 usec
 PL123: 0.00 dB
 SFO123: 400.1464010 MHz
 ===== CHANNEL f124 =====
 NUC124: 1H
 P124: 16.00 usec
 PL124: 0.00 dB
 SFO124: 400.1464010 MHz
 ===== CHANNEL f125 =====
 NUC125: 1H
 P125: 16.00 usec
 PL125: 0.00 dB
 SFO125: 400.1464010 MHz
 ===== CHANNEL f126 =====
 NUC126: 1H
 P126: 16.00 usec
 PL126: 0.00 dB
 SFO126: 400.1464010 MHz
 ===== CHANNEL f127 =====
 NUC127: 1H
 P127: 16.00 usec
 PL127: 0.00 dB
 SFO127: 400.1464010 MHz
 ===== CHANNEL f128 =====
 NUC128: 1H
 P128: 16.00 usec
 PL128: 0.00 dB
 SFO128: 400.1464010 MHz
 ===== CHANNEL f129 =====
 NUC129: 1H
 P129: 16.00 usec
 PL129: 0.00 dB
 SFO129: 400.1464010 MHz
 ===== CHANNEL f130 =====
 NUC130: 1H
 P130: 16.00 usec
 PL130: 0.00 dB
 SFO130: 400.1464010 MHz
 ===== CHANNEL f131 =====
 NUC131: 1H
 P131: 16.00 usec
 PL131: 0.00 dB
 SFO131: 400.1464010 MHz
 ===== CHANNEL f132 =====
 NUC132: 1H
 P132: 16.00 usec
 PL132: 0.00 dB
 SFO132: 400.1464010 MHz
 ===== CHANNEL f133 =====
 NUC133: 1H
 P133: 16.00 usec
 PL133: 0.00 dB
 SFO133: 400.1464010 MHz
 ===== CHANNEL f134 =====
 NUC134: 1H
 P134: 16.00 usec
 PL134: 0.00 dB
 SFO134: 400.1464010 MHz
 ===== CHANNEL f135 =====
 NUC135: 1H
 P135: 16.00 usec
 PL135: 0.00 dB
 SFO135: 400.1464010 MHz
 ===== CHANNEL f136 =====
 NUC136: 1H
 P136: 16.00 usec
 PL136: 0.00 dB
 SFO136: 400.1464010 MHz
 ===== CHANNEL f137 =====
 NUC137: 1H
 P137: 16.00 usec
 PL137: 0.00 dB
 SFO137: 400.1464010 MHz
 ===== CHANNEL f138 =====
 NUC138: 1H
 P138: 16.00 usec
 PL138: 0.00 dB
 SFO138: 400.1464010 MHz
 ===== CHANNEL f139 =====
 NUC139: 1H
 P139: 16.00 usec
 PL139: 0.00 dB
 SFO139: 400.1464010 MHz
 ===== CHANNEL f140 =====
 NUC140: 1H
 P140: 16.00 usec
 PL140: 0.00 dB
 SFO140: 400.1464010 MHz
 ===== CHANNEL f141 =====
 NUC141: 1H
 P141: 16.00 usec
 PL141: 0.00 dB
 SFO141: 400.1464010 MHz
 ===== CHANNEL f142 =====
 NUC142: 1H
 P142: 16.00 usec
 PL142: 0.00 dB
 SFO142: 400.1464010 MHz
 ===== CHANNEL f143 =====
 NUC143: 1H
 P143: 16.00 usec
 PL143: 0.00 dB
 SFO143: 400.1464010 MHz
 ===== CHANNEL f144 =====
 NUC144: 1H
 P144: 16.00 usec
 PL144: 0.00 dB
 SFO144: 400.1464010 MHz
 ===== CHANNEL f145 =====
 NUC145: 1H
 P145: 16.00 usec
 PL145: 0.00 dB
 SFO145: 400.1464010 MHz
 ===== CHANNEL f146 =====
 NUC146: 1H
 P146: 16.00 usec
 PL146: 0.00 dB
 SFO146: 400.1464010 MHz
 ===== CHANNEL f147 =====

Total Synthesis of Ipomoeassin E

Disaccharide 20. DDQ (19.0 mg, 0.0830 mmol) was added to a solution of compound **9** (57.7 mg, 0.0553 mmol) in CH₂Cl₂ (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 **10** (45.6 mg) which contained traces of *p*-methoxybenzaldehyde.

Et₃N (26 μL, 0.185 mmol) and 2,4,6-trichlorobenzoyl chloride (13 mL, 0.0862 mmol) were added to a solution of carboxylic acid **19** (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 **10** (45.6 mg) and DMAP (5.0 mg, 0.0431 mmol) in toluene (1.0 mL) was introduced and stirring was continued for 2 h. The mixture was then 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 **20** as a colorless syrup (54.6 mg, 87% over both steps). $[\alpha]_D^{20} = -3.7$ (c 0.40, CH₂Cl₂). IR (KAP): $\tilde{\nu} = 3072, 2956, 2932, 2858, 1732, 1651, 1642, 1586, 1428, 1248, 1113, 916, 839, 780$. ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 7.47\text{--}7.45$ (m, 2H), 7.29–7.19 (m, 6H), 7.00–6.97 (m, 2H), 6.82 (m, 1H), 6.33 (s, 1H), 5.89 (ddt, *J* = 6.9, 10.2, 17.2 Hz, 1H), 5.81 (ddt, *J* = 6.6, 10.3, 17.0 Hz, 1H), 5.25 (t, *J* = 9.4 Hz, 1H), 5.10–4.99 (m, 7H), 4.30 (d, *J* = 8.1 Hz, 1H), 4.16–4.03 (m, 3H), 3.99 (dd, *J* = 1.9, 5.5 Hz, 1H), 3.82–3.65 (m, 4H), 3.60 (m, 1H), 2.83–2.47 (m, 4H), 2.28 (m, 2H), 2.18–2.11 (m, 5H), 1.96–1.74 (m, 8H), 1.55–1.32 (m, 13 H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.81 (s, 9H), 0.37 (s, 3H), 0.28 (s, 3H), 0.07 (s, 3H), –0.04 (s, 3H). ¹³C NMR (100 MHz, CD₂Cl₂): $\delta = 205.8, 172.4, 170.7, 167.1, 166.9, 165.0, 145.1, 138.7, 137.5, 135.6, 134.2$ (2C), 133.0, 129.0, 128.5, 128.2 (2C), 127.9 (2C), 127.2, 126.9 (2C), 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 (3C), 20.8, 18.8, 18.2, 16.7, 14.6, 14.2, 12.2, –0.7, –1.2, –3.6, –4.8. MS (EI): *m/z* (%): 83 (63), 157 (29), 265 (100), 265 (100), 451 (32), 833 (10), 851 (49), 1019 (17), 1075 (8). HRMS: calcd. for C₆₁H₈₈O₁₆Si₂ [*M*⁺+Na] 1155.550316, found 1155.548973.

Product 21. The ruthenium carbene complex **12** (6.0 mg, 0.00653 mmol) was added to

a solution of compound **20** (74 mg, 0.0653 mmol) in CH₂Cl₂ (15 mL) and the resulting mixture was refluxed 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 cycloalkene (*E,Z*-mixture). This product was dissolved in EtOH (1.0 mL) and

stirred overnight in the presence RhCl(PPh₃)₃ (12 mg, 0.0125 mmol) under an atmosphere of H₂ (1 atm). The catalyst was filtered off through a pad of silica, the filtrate was evaporated and the residue was purified by flash chromatography (hexanes/EtOAc, 4/1) to give compound **21** as a colorless syrup (60 mg, 83% over both steps). $[\alpha]_D^{20} = +0.4$ (c 0.77, CH₂Cl₂). IR (KAP): $\tilde{\nu} = 3069, 2931, 2858, 1732, 1652, 1588, 1379, 1371, 1247, 1155, 1074, 839, 780, 731, 702$. ¹H NMR (400 MHz, CDCl₃): $\delta = 7.46\text{--}7.44$ (m, 2H), 7.29–7.19 (m, 6H), 6.99–6.97 (m, 2H), 6.81 (m, 1H), 6.31 (s, 1H), 5.28 (t, *J* = 9.2 Hz, 1H), 5.06–5.00 (m, 2H), 4.94 (d, *J* = 7.7 Hz, 1H), 4.25 (d, *J* = 7.8 Hz, 1H), 4.13 (t, *J* = 6.0 Hz, 1H), 4.03–4.02 (m, 1H), 3.98 (dd, *J* = 2.0, 5.8 Hz, 1H), 3.86 (dd, *J* = 6.4, 7.8 Hz, 1H), 3.78 (m, 1H), 3.65 (dt, *J* = 2.7, 10.0 Hz, 1H), 3.54–3.48 (m, 2H), 2.87 (dt, *J* = 6.8, 18.8 Hz, 1H), 2.62 (dt, *J* = 6.8, 18.8 Hz, 1H), 2.49 (m, 2H), 2.14 (s, 3H), 1.77–1.26 (m, 30 H), 0.09 (t, *J* = 7.3 Hz, 3H), 0.81 (s, 9H), 0.37 (s, 3H), 0.23 (s, 3H), 0.05 (s, 3H), –0.04 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): $\delta = 205.9, 170.9, 170.6, 166.8, 166.6, 164.4, 144.6, 138.3, 138.0, 133.6$ (2C), 132.5, 128.7, 128.2, 127.9 (2C), 127.6 (2C), 126.9, 126.6 (2C), 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 (3C), 24.2 (2C), 20.6, 18.3, 18.0, 16.8, 14.4, 14.3, 12.1, –0.4, –1.6, –3.8, –4.9. MS (EI): *m/z* (%): 83 (66), 157 (26), 265 (100), 567 (11), 825 (41), 1049 (9). HRMS: calcd. for C₅₉H₈₆O₁₆Si₂ [M⁺+Na] 1129.534663, found 1129.535235.

Ipomoeassin E (2). A solution of TASF (75 mg, 0.27 mmol) in MeCN (1.0 mL) was added to a solution of compound **21** (30 mg, 0.027 mmol) in wet MeCN (1.0 mL) and the resulting mixture was stirred for 5 h before it 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 (36 μ L, 0.49 mmol) in CH₂Cl₂ (3.0 mL) for 3 h at ambient temperature. The mixture was neutralized with triethylamine and concentrated in vacuo, and the crude product was purified by preparative HPLC (YMC-PACK ODS A, 5 μ m 12 nm; MeOH/H₂O = 70/30; flow rate: 10 mL/min;

pressure: 3.6 MPa) to afford Ipomoeassin E (**2**) as a colorless syrup which solidifies when kept in the freezer (14 mg, 63% over both steps). $[\alpha]_{\text{D}}^{25} = -32$ (c 0.21, EtOH); lit. $[\alpha]_{\text{D}}^{25} = -24$ (c 0.2, EtOH). IR (KAP): $\tilde{\nu} = 3408, 2933, 2869, 1725, 1636, 1450, 1374, 1309, 1248, 1156, 1073, 768$. ^1H NMR (400 MHz, C_6D_6) and ^{13}C NMR (75 MHz, C_6D_6) data, see Table S3 and S4, respectively. 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 (20), 43 (19). HRMS: calcd. for $\text{C}_{42}\text{H}_{58}\text{O}_{16}$ [$\text{M}^+ + \text{Na}$] 841.36172, found 841.362452.

Table S3. Comparison of the ^1H NMR data (C_6D_6) reported for Ipomoeassin E (**2**) (500 MHz) with those of the synthetic material recorded on a Bruker av400 spectrometer (400 MHz). Numbering scheme as shown in the insert.

Position	Ipomoeassin E (<i>J</i> in Hz)	Synthetic Sample (<i>J</i> in Hz) ^{a,b}
2	2.55 ddd (18.1, 9.2, 2.8) 2.34 ddd (18.1, 7.8, 3.4)	2.59 ddd (18.0, 9.2, 3.1) 2.46-2.36 m
3	2.81 ddd (16.3, 9.2, 3.4) 2.39 ddd (16.3, 7.8, 2.8)	2.82 ddd (16.5, 9.2, 3.5) 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) 4.20 brd (11.0)	4.52 dd (11.4, 2.2) 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; see below; 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 6-10, 12 and 13 appear between δ 1.96-1.36 as complicated multiplet.

Table S4. Comparison of the ^{13}C NMR data (C_6D_6) reported for Ipomoeassin E (**2**) (125 MHz) with those of the synthetic sample (Bruker AMX-300 spectrometer, 75 MHz).

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

¹H NMR spectra of Ipomoecassin E in C₆D₆: (a) natural product reported in literature (500 MHz, Kingston et al. *J. Nat. Prod.* **2005**, 68, 487); (b) sample prepared by us (400 MHz).

¹H NMR spectra of Compound 1 at different concentrations showed remarkable change of chemical shift. (a) 14 mg in 0.6 mL of nondistilled C₆D₆; (b) 4 mg in 0.6 mL of nondistilled C₆D₆; (c) 6 mg in 0.6 mL of distilled C₆D₆; (d) 3 mg in 0.6 mL of distilled C₆D₆.

Spectra of New Compounds

Current Data Parameters
NAME dr12052
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20051213
Time 0.31

INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TO 65536
SOLVENT CDCl3
NS 1500
DS 2

SWH 33132.582 Hz
FIDRES 0.505258 Hz
AQ 0.986435 sec
RG 16384
DM 15.100 usec
DE 6.00 usec
TE 303.0 K
D1 0.03000000 sec
d11 0.03000000 sec

***** CHANNEL f1 *****
NUC1 13C
P1 10.94 usec
PL1 5.00 dB
SFO1 100.6242789 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 19.76 dB
SFO2 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 100.6127662 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 230.000 ppm
F1 20153.19 Hz
F2P -30.000 ppm
F2 -3018.38 Hz
PPMCM 12.72727 ppm/cm
HZCM 1280.35612 Hz/cm

NAG-NA-134-01

Current Data Parameters
NAME n21011
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20051121
Time 12.00
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TO 65536
SOLVENT CDCl3
NS 32
DS 8
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.958443 sec
RG 114
DM 60.400 usec
DE 6.30 usec
TE 303.0 K
D1 0.00300000 sec

***** CHANNEL f1 *****
NUC1 1H
P1 9.29 usec
PL1 0.00 dB
SFO1 400.1364710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300558 MHz
KCM CM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00

10 MHz plot parameters
CX 22.00 cm
CY 15.00 cm
FIDP 9.500 ppm
F1 3801.24 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPOCM 0.45455 ppm/cm
HZCM 181.87227 Hz/cm

NAG-NA-106-02

Current Data Parameters
NAME m21011
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20001121
Time 12:29
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1000
DS 2
SWH 33112.582 Hz
FIDRES 0.5802268 Hz
AQ 0.5880436 sec
RG 18190.4
DM 15.100 usec
DE 8.00 usec
TE 303.0 K
D1 0.03000000 sec
d11 0.03000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 10.54 usec
PL1 5.00 dB
SFO1 100.6242789 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 19.75 dB
SFO2 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 100.6128045 MHz
KON EN
SGB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 250.000 ppm
F1 25153.20 Hz
F2P -30.000 ppm
F2 -3018.38 Hz
PNUCK 12.72727 ppm/cm
HZCK 1280.52651 Hz/cm

NAG-NA-106-02

Current Data Parameters
 NAME: 0701010
 EXPNO: 10
 PROCNO: 1

F2 - Acquisition Parameters
 Date_: 20051201
 Time: 11.51
 INSTRUM: av400
 PROBRD: 5 mm BBO 1H
 PULPROG: zg30
 TO: 65536
 SOLVENT: CDCl3
 NS: 32
 DS: 8
 SWH: 8278.146 Hz
 FIDRES: 0.126314 Hz
 AQ: 3.5984241 sec
 RG: 114
 BM: 60.400 ussec
 DE: 6.50 ussec
 TE: 303.0 K
 D1: 0.00300000 sec

***** CHANNEL f1 *****
 NUC1: 1H
 P1: 9.25 ussec
 PL1: 0.00 dB
 SF01: 400.1324710 MHz

F2 - Processing parameters
 SI: 32768
 SF: 400.130093 MHz
 WHW: FM
 SSB: 0
 LB: 0.30 Hz
 GB: 0
 RB: 2.00
 PC: 2.00

10 NMR plot parameters
 CX: 22.00 cm
 CY: 15.00 cm
 F1P: 9.500 DDM
 F1: 3801.24 Hz
 F2P: -200.07 Hz
 F2: 0.45455 ppm/cm
 PPMCM: 181.87727 Hz/cm
 HZCM:

NAG-NA-120-03

Current Data Parameters
NAME dr01010
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20051201
Time 12.20
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1500
DS 2
SWH 33112.582 MHz
FIDRES 0.506526 Hz
AQ 0.9696436 sec
RG 16390.4
DW 15.100 usec
DE 0.00 usec
TE 303.0 K
D1 0.03000000 sec
d11 0.03000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 10.04 usec
PL1 5.00 dB
SFO1 100.6242189 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 19.76 dB
SFO2 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 100.6127622 MHz
WDM 0
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

10 NMR plot parameters
CX 22.00 cm
CY 15.00 cm
FIP 250.000 ppm
F1 25153.19 Hz
F2P -30.000 ppm
F2 -3018.38 Hz
PWCN 12.72727 000/cm
HZCN 1280.52612 Hz/cm

NAG-NA-120-03

Current Data Parameters
NAME j123018
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080123
Time 14.23
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 181
DM 60.400 usec
DE 6.50 usec
TE 303.0 K
D1 0.00300000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 9.25 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.130070 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 9.500 ppm
F1 3801.24 Hz
F2P -200.07 Hz
F2 -200.07 Hz
FPMCH 0.46655 ppm/cm
HZCM 181.81727 Hz/cm

NAG-NA-157-01

Current Data Parameters
NAME JF23018
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060123

Time 14.54
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1500
DS 2
SWH 33112.582 Hz
FIDRES 0.505258 Hz
AQ 0.5895436 sec
RG 16384
RW 15.100 usec
DE 8.00 usec
TE 303.0 K
D1 0.03000000 sec
d11 0.03000000 sec

----- CHANNEL f1 -----
NUC1 ¹³C
P1 10.94 usec
PL1 5.00 dB
SFO1 100.6242789 MHz

----- CHANNEL f2 -----
CPOPRG2 waltz16
NUC2 ¹H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 19.76 dB
SFO2 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 100.6127672 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

10 NMR plot parameters
CX 22.00 cm
CY 15.00 cm
FIP 250.000 ppm
F1 25153.19 Hz
F2 -30.000 ppm
F2 -3018.38 Hz
PPH2 12.72727 ppm/cm
HZCM 1280.56412 Hz/cm

NAG-NA-157-01

Current Data Parameters
 NAME JY25046
 EXNO 10
 PRUNO 1

F2 - Acquisition Parameters
 Date_ 20060126
 Time 14.25
 INSTRUM av400
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 32
 DS 8
 SM 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 114
 DK 60.400 usec
 DE 6.50 usec
 TE 303.0 K
 D1 0.00300000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 9.25 usec
 PL1 0.00 dB
 SF01 400.1324710 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1300028 MHz
 KW EN
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 2.00

10 MHz plot parameters
 CX 22.00 cm
 CY 15.00 cm
 F1P 9.500 ppm
 F1 3801.24 Hz
 F2P -0.500 ppm
 F2 -200.07 Hz
 FWHM 0.45455 ppm/cm
 HZCM 181.87727 Hz/cm

NAG-NA-160-01

Current Data Parameters

NAME	Jr25046
EXPNO	11
PROCNO	1

F2 - Acquisition Parameters

Date_	20060126
Time	14.34
INSTRUM	av400
PROBHD	5 mm BBO BB-1H
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
RG	1500
DS	2
SWH	33112.582 Hz
FIDRES	0.500258 Hz
AQ	0.9896436 sec
RG	16384
DM	15.100 usec
DE	8.00 usec
TE	303.0 K
D1	0.03000000 sec
d11	0.03000000 sec

===== CHANNEL f1 =====

NUC1	13C
P1	10.34 usec
PL1	0.00 dB
SFO1	100.624789 MHz

===== CHANNEL f2 =====

CPDPRG2	mol2115
NUC2	1H
PCPD2	90.00 usec
PL2	0.00 dB
PL12	19.75 dB
SFO2	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	100.6127663 MHz
WDM	EN
SSB	0
LB	1.00 Hz
GB	0
PC	2.00

1D NMR plot parameters

CX	22.00 cm
CY	15.00 cm
FLP	250.000 ppm
F1	25153.19 Hz
F2P	-30.000 ppm
F2	-3016.38 Hz
PRMCK	12.72727 ppm/cm
HZCM	1280.52612 Hz/cm

NAG-NA-160-01

Current Data Parameters

NAME	1102019
EXPNO	10
PROCNO	1

F2 - Acquisition Parameters

Date_	20060502
Time	14.15
INSTRUM	dp3300
PROBHD	5 mm QNP 1H/
PULPROG	zgpg30
TD	32768
SOLVENT	CDCl3
NS	32
DS	0
SWH	6172.839 Hz
FIDRES	0.180360 Hz
AQ	2.6542580 sec
RG	455.1
DW	81.000 usec
DE	4.50 usec
TE	300.0 K
D1	2.00000000 sec

===== CHANNEL f1 =====

NUC1	1H
P1	7.56 usec
PL1	-6.00 dB
SFO1	300.1318534 MHz

F2 - Processing parameters

SI	16384
SF	300.1360224 MHz
KOM	EM
SSB	0
LB	0.30 Hz
GB	0
PC	2.00

1D NMR plot parameters

CX	22.00 cm
CY	15.00 cm
F1P	9.500 ppm
F1	2851.24 Hz
F2P	-0.500 ppm
F2	-150.07 Hz
PPMCM	0.45455 ppm/cm
HZCM	136.42274 Hz/cm

NAG-NA-004-02

Current Data Parameters
NAME: J002019
EXPNO: 11
PROCNO: 1

F2 - Acquisition Parameters
Date_: 20060502
Time: 14.47

INSTRUM: dpv300
PROBHD: 5 mm QNP 1H/
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl₃
NS: 1200
DS: 2
SWH: 21231.422 Hz
F1TONE: 0.323666 Hz
AQ: 1.5414228 sec
RG: 4097.6
DM: 23.550 usec
DE: 4.50 usec
TE: 300.0 K
D1: 0.03000000 sec
D11: 0.03000000 sec

===== CHANNEL f1 =====
NUC1: ¹³C
P1: 6.91 usec
PL1: -6.00 dB
SFO1: 75.4760670 MHz

===== CHANNEL f2 =====
CPDPRG2: waltz16
NUC2: ¹H
PCPD2: 80.00 usec
PL2: -6.00 dB
PL12: 14.49 dB
SFO2: 300.1312005 MHz

F2 - Processing parameters
SI: 32768
SF: 75.4676044 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 0
PC: 1.40

10 MHz plot parameters
CX: 22.00 cm
CY: 15.00 cm
F1P: 250.000 ppm
F1: 18866.90 Hz
F2P: -30.000 ppm
F2: -2264.03 Hz
PPMCK: 12.7272 ppm/cm
HZCK: 960.49813 Hz/cm

MAG-NA-004-02

NAG-NB-035-01

Current Data Parameters
NAME j114004
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060714
Time 9:57
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 32
DS 8
SWH 8278.145 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 181
DW 60.400 usec
DE 6.50 usec
TE 303.0 K
D1 0.00300000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 9.25 usec
PL1 0.00 dB
SFO1 400.1364710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300078 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00

10 NMR plot parameters
CX 22.00 cm
CY 15.00 cm
FIP 9.500 ppm
F1 3801.24 Hz
F2 -200.07 Hz
PPH0 0.45455 ppm/cm
H2C0 181.87227 Hz/cm

Current Data Parameters
NAME JY14004
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060714

Time 10.26
INSTRUM 8x400
PROBHD 5 mm 800 BBI-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1500
DS 2
SWH 33112.582 Hz
FIDRES 0.506256 Hz
AQ 0.9956436 sec
RG 10390.4
DM 15.100 usec
DE 8.00 usec
TE 303.0 K
D1 0.03000000 sec
d11 0.03000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 10.34 usec
PL1 5.00 dB
SF01 100.6242789 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 19.76 dB
SF02 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 100.6127656 MHz
KCM EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 250.000 ppm
F1 20153.19 Hz
F2P -30.000 ppm
F2 -3018.38 Hz
PPHOM 12.72727 ppm/cm
HZCM 1280.50612 Hz/cm

NA6-NB-035-01

Current Data Parameters
 NAME JY23039
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20060106
 Time 12.15
 INSTRUM av400
 PROBHD 5 mm BBO BB-JH
 PULPROG zg30
 TO 65536
 SOLVENT CDCl3
 NS 32
 DS 8
 SWH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 114
 DW 80.400 usec
 DE 6.50 usec
 TE 303.0 K
 D1 0.00300000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 9.25 usec
 PL1 0.00 dB
 SF01 400.1324710 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1300482 MHz
 KW 0
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 2.00

10 MHz plot parameters
 CX 22.00 cm
 CY 15.00 cm
 F1P 9.500 DPM
 F1 3801.24 Hz
 F2P -0.500 DPM
 F2 -200.07 Hz
 PPMCM 0.45455 DPM/CM
 HCM 181.87729 Hz/CM

NAG-NA-146-01

Current Data Parameters
 NAME J125039
 EXPNO 11
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20060126
 Time 12.43
 INSTRUM av400
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg30
 TO 65536
 SOLVENT CDCl3
 NS 1500
 DS 2
 SWH 33112.582 Hz
 FIDRES 0.500258 Hz
 AQ 0.5895436 sec
 RG 16384
 DW 15.100 usec
 DE 8.00 usec
 TE 303.0 K
 D1 0.03000000 sec
 d11 0.03000000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.94 usec
 PL1 5.00 dB
 SFO1 100.624289 MHz

===== CHANNEL f2 =====
 CPROGR2 waltz16
 NUC2 1H
 PCPO2 90.00 usec
 PL2 0.00 dB
 PL12 19.75 dB
 SFO2 400.1324710 MHz

F2 - Processing parameters
 SI 32768
 SF 100.6126888 MHz
 KW EN
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 2.00

1D NMR plot parameters
 CX 22.00 cm
 CY 15.00 cm
 F1P 250.000 ppm
 F1 25153.17 Hz
 F2P -30.000 ppm
 F2 -3018.38 Hz
 PPHC 12.72727 ppm/cm
 HZCM 1280.55315 Hz/cm

NAG-NA-146-01

Current Data Parameters
 NAME m10101
 EXPNO 20
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20051111
 Time 22.31
 INSTRUM av400
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TO 65536
 SOLVENT CDCl3
 NS 32
 DS 8
 SM 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 114
 DW 60.400 usec
 DE 6.50 usec
 TE 303.0 K
 D1 0.00300000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 9.25 usec
 PL1 0.00 dB
 SF01 400.1324710 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1300000 MHz
 KW EN
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 2.00

1D NMR plot parameters
 CX 22.00 cm
 CY 15.00 cm
 F1P 9.50000 MHz
 F1 300.124 MHz
 F2P -0.50000 MHz
 F2 -200.07 Hz
 PPMCH 0.45655 ppm/cm
 HZCH 181.87727 Hz/cm

NAG-NA-110-01

MAG-NA-110-01

Current Data Parameters
 NAME: 3-0-acylated?
 EXPNO: 10
 PROCNO: 1

F2 - Acquisition Parameters
 Date_: 20051207
 Time: 15.13
 INSTRUM: v4400
 PROBHD: 5 mm BBO BB-1H
 PULPROG: zg30
 TO: 69536
 SOLVENT: CDCl3
 NS: 32
 DS: 8
 SMH: 8278.146 Hz
 FIDRES: 0.126314 Hz
 AQ: 3.9584043 sec
 RG: 114
 BE: 60.400 uSFC
 DE: 6.50 uSFC
 TE: 303.0 K
 D1: 0.00300000 sec

===== CHANNEL f1 =====
 NUC1: 1H
 P1: 9.25 uSFC
 PL1: 0.00 dB
 SFO1: 400.1324710 MHz

F2 - Processing parameters
 SI: 32768
 SF: 400.1300000 MHz
 WDW: EM
 SSB: 0
 LB: 0.30 Hz
 GB: 0
 PC: 2.00

1D NMR plot parameters:
 CX: 32.00 cm
 CY: 15.00 cm
 F1P: 9.500 ppm
 F1: 3801.24 Hz
 F2P: -10.500 ppm
 F2: -200.07 Hz
 PPMCK: 0.45405 ppm/cm
 HZCM: 181.87727 Hz/cm

NAG-NA-127-03
 3-0-acylated?

Current Data Parameters
NAME dr07036
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20051207
Time 20.26
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TO 65536
SOLVENT CDCL3
NS 1500
DS 2
SWH 33112.582 Hz
FIDRES 0.500238 Hz
AQ 0.9895435 sec
RG 16384
DM 15.100 usec
DE 8.00 usec
TE 303.0 K
D1 0.03000000 sec
d11 0.03000000 sec

***** CHANNEL f1 *****
NUC1 13C
P1 10.94 usec
PL1 5.00 dB
SFO1 100.6262789 MHz

***** CHANNEL f2 *****
CPDPRG2 waltz16
NUC2 1H
PCPD2 50.00 usec
PL2 0.00 dB
PL12 19.75 dB
SFO2 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 100.6126888 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 250.000 ppm
F1 25153.17 Hz
F2P -30.000 ppm
F2 -3018.38 Hz
PPOCK 12.72727 DM/cm
HZCH 1280.92515 Hz/cm

NAG-NA-127-03
3-O-acetyl?

Current Data Parameters

NAME 0709010

EXPNO 11

PROCNO 1

F2 - Acquisition Parameters

Date_ 20051209

Time 12.31

INSTRUM av400

PROBHD 5 mm BBO BB-1H

PULPROG zgpg30

TD 65536

SOLVENT CDCl3

NS 1500

DS 2

SWH 33112.502 Hz

FIDRES 0.565258 Hz

AQ 0.9895436 sec

RG 16384

DM 15.100 usec

DE 8.00 usec

TE 303.0 K

D1 0.03000000 sec

d11 0.03000000 sec

***** CHANNEL f1 *****

NUC1 13C

P1 10.94 usec

PL1 5.00 dB

SFO1 100.626269 MHz

***** CHANNEL f2 *****

OPPRG2 waltz16

NUC2 1H

PCPD2 90.00 usec

PL2 0.00 dB

PL12 19.76 dB

SFO2 400.1324710 MHz

F2 - Processing parameters

SI 32768

SF 100.6126988 MHz

WDW EM

SSB 0

LB 1.00 Hz

GB 0

PC 2.00

10 NMR plot parameters

CX 22.00 cm

CY 15.00 cm

FIP 250.000 ppm

F1 25153.17 Hz

F2P -30.000 ppm

F2 -3018.38 Hz

PRNCH 12.72727 ppm/cm

H2CH 1280.52515 Hz/cm

NAG-NA-133-01

Current Data Parameters

NAME	0707013
EXPNO	10
PROCNO	1

F2 - Acquisition Parameters

Date_	20051207
Time	15.05
INSTRUM	av400
PROBHD	5 mm BBO BB-1H
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	32
DS	B
SWH	8278.146 Hz
FIDRES	0.126314 Hz
AQ	3.958423 sec
RG	114
DW	60.400 usec
DE	6.50 usec
TE	303.0 K
DT	0.00300000 sec

===== CHANNEL f1 =====

NUC1	1H
P1	9.25 usec
PL1	0.00 dB
SFO1	400.1324710 MHz

F2 - Processing parameters

SI	32768
SF	400.1300000 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	2.00

1D NMR plot parameters

CY	22.00 cm
CV	15.00 cm
F1P	0.500 ppm
F1	3801.24 Hz
F2P	-0.500 ppm
F2	-200.07 Hz
PPM0H	0.45435 ppm/cm
HZ0H	181.87727 Hz/cm

NAG-NA-127-02
2-0-acetylated?

```
Current Data Parameters
NAME          df07035
EXPNO         10
PROCNO        1
```

F2 - Acquisition Parameters
Date_ 20051207

Time	19.54
INSTRUM	av400

PROBHD	5 mm BBD BB-1M
PULPROG	Zgdc30

TO	65536
SQ WENT	002012

NS	1500
NS	3

3312.582 Hz

FILES	0.509258 Hz
AD	0.9895436 sec

PAS	16384
OM	15.100 use

```
OE      8.00 use
TE     303.0 K
```

d1	0.03000000 sec
d11	0.03000000 sec

CHANNEL 11

NUC1	13C
P1	10 GA

PL1	5.00 dB
SE01	100.6343780 MHz

CUSTOMER NO	TOTAL
	100,0642/89 MWK

```
===== CHANNEL 12 =====
CPDPAGE2      waitz16
```

	1H
NUC2	
PCPD2	90.00 use

PL2	0.00 dB
PL12	19.76 dB

SF02 400.1324710 MHz

F2 - Processing parameters
51 32758

SF 100.6126888 MHz
MTW FM

0 0 0

1.00 Hz
0
GB

PC 2.00

```
1D NMR plot parameters
CX      22.00 cm
```

CY	15.00 cm
F1P	250.000 ppm

F1	25153.17 Hz
F2P	-30.000 ppm

F2 -3018.38 Hz
PQMC 12.72727 DDT

1280.52515 Hz/cm H₂O

MIAC NIA 407 00

NAAG-NA-127-02

2-0-acyl?

NAG-NB-032-01

Current Data Parameters
NAME 1Y11031
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060712
Time 1.23

INSTRUM 5 mm BBO BB-1H
PROBHD zgpg30
PULPROG zgpg30
TO 65536
SOLVENT CDCl₃
NS 1500
DS 2
SWH 33112.582 Hz
FIDRES 0.505258 Hz
AQ 0.5896435 sec
RG 18390.4
DM 15.100 usec
DE 8.00 usec
TE 303.0 K
D1 0.03000000 sec
d11 0.03000000 sec

----- CHANNEL f1 -----
NUC1 13C
P1 10.94 usec
PL1 5.00 dB
SFO1 100.624789 MHz

----- CHANNEL f2 -----
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 19.76 dB
SFO2 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 100.6127604 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 250.000 DDM
F1 25553.19 Hz
F2P -30.000 DDM
F2 -3018.38 Hz
PPMCM 12.72727 DDM/cm
HZCM 1280.55512 Hz/cm

NAG-NB-032-01

Current Data Parameters
NAME J145072
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters

Date_ 20060713
Time 10.38
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 32
DS 8
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9564243 sec
RG 114
DE 60.400 usec
TE 303.0 K
D1 0.00300000 sec

===== CHANNEL f1 =====

NUC1 1H
P1 9.25 usec
PL1 0.00 dB
SFO1 400.1364710 MHz

F2 - Processing parameters

SI 32768
SF 400.1360649 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00

10 NMR plot parameters

CX 22.00 cm
CY 15.00 cm
F1P 9.500 ppm
F1 3801.24 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PRNCH 0.45655 ppm/cm
HCDM 181.87732 Hz/cm

NAG-NB-033-01

Current Data Parameters
NAME jyl2072
EXNO 11
PROCNO 1

F2 - Acquisition Parameters

Date_ 20060713
Time 11.06
INSTRUM av400
PROBHD 5 mm BBO DB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl₃
NS 1500
DS 2
SWH 33112.582 Hz
FIDRES 0.505258 Hz
AQ 0.3896436 sec
RG 18390.4
DW 15.100 usec
DE 8.00 usec
TE 303.0 K
D1 0.03000000 sec
d11 0.03000000 sec

----- CHANNEL f1 -----

NUC1 ¹³C
P1 10.94 usec
PL1 5.00 dB
SFO1 100.6242789 MHz

----- CHANNEL f2 -----

CPRPG2 waltz16
NUC2 ¹H
PCPRG2 90.00 usec
PL2 0.00 dB
PL12 19.76 dB
SFO2 400.1324710 MHz

F2 - Processing parameters

SF 32768
F 100.6126390 MHz
MCW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

10 NMR plot parameters

CX 22.00 cm
CY 15.00 cm
FIP 250.000 ppm
F1 25153.17 Hz
F2 -30.000 ppm
F2 -3018.38 Hz
FREQ 12.72727 ppm/cm
HZCM 1280.52466 Hz/cm

NAG-NB-033-01

Current Data Parameters
NAME mp02025
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20090508
Time 14.16
INSTRUM spect
PROBHD 5 mm BBO BB-4H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 32
DS 8
SWH 8278.145 Hz
FIDRES 0.126314 Hz
AQ 3.9564243 sec
RG 322.5
OW 60.400 usec
OE 6.50 usec
TE 303.0 K
D1 0.00300000 sec

***** CHANNEL f1 *****
NUC1 1H
P1 9.25 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300599 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00

10 NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 9.500 ppm
F1 3801.24 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPOW 0.48455 ppm/cm
H2O 181.8727 Hz/cm

NAG-NA-229-02

Current Data Parameters
 NAME 1Y19027
 EXPNO 10
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20060719
 Time 22.29
 INSTRUM 3000
 PROBHD 5 mm BBO-1H
 PULPROG zgpg30
 TO 65536
 SOLVENT CDCl3
 NS 32
 DS 8
 SWH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9594243 sec
 RG 191
 DM 60.400 usec
 DE 6.50 usec
 TE 303.2 K
 D1 0.00300000 sec

***** CHANNEL f1 *****
 NUC1 1H
 P1 9.25 usec
 PL1 0.00 dB
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1300933 MHz
 MDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 2.00

10 NMR plot parameters
 CX 22.00 cm
 CY 15.00 cm
 FLIP 9.000 ppm
 F1 3901.24 Hz
 F2 -200.07 Hz
 FWHM 0.45455 ppm/cm
 HZCM 181.8777 Hz/cm

NAG-NB-040-01

Current Data Parameters
NAME 1V19027
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060719
Time 22:57

INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1500
DS 2
SWH 33112.582 Hz
FIDRES 0.505258 Hz
AQ 0.9806436 sec
RG 16384
DM 15.100 usec
DE 8.00 usec
TE 303.0 K
D1 0.03000000 sec
d11 0.03000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 10.94 usec
PL1 5.00 dB
SFO1 100.6262709 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 19.76 dB
SFO2 400.1324710 MHz

F2 - Processing parameters
S1 32768
SF 100.6127664 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 250.000 ppm
F1 25153.19 Hz
F2P -30.000 ppm
F2 -3018.38 Hz
PPMCH 12.7272 ppm/cm
HZCM 1280.52612 Hz/cm

NAG-NB-040-01

Current Data Parameters
 NAME 1j2024
 EXPNO 11
 PROCNO 1
 F2 - Acquisition Parameters
 Date_ 20060725
 Time 15.37
 INSTRUM av400
 PROBR0 5 mm BBO BB-H1
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1500
 DS 2
 SMH 33112.582 Hz
 FIDRES 0.505258 Hz
 AQ 0.9896436 sec
 RG 18390.4
 DN 15.100 usec
 DE 8.00 usec
 TE 303.0 K
 O1 0.03000000 sec
 d11 0.03000000 sec
 ===== CHANNEL f1 =====
 NUC1 13C
 P1 10.94 usec
 PL1 5.00 dB
 SFO1 100.6242789 MHz
 ===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCP02 90.00 usec
 PL2 0.00 dB
 PL12 19.75 dB
 SFO2 400.1324710 MHz
 F2 - Processing parameters
 SI 32768
 SF 100.6127654 MHz
 KW EN
 MW EN
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 2.00
 10 NMR plot parameters
 CX 22.00 cm
 CY 15.00 cm
 F1P 250.000 ppm
 F1 25153.19 Hz
 F2P -30.000 ppm
 F2 -3016.38 Hz
 PRNCH 12.72727 ppm/cm
 HZCM 1280.52612 Hz/cm

NAG-NB-049-01
 IP0B H2 column

Current Data Parameters
 NAME 1717020
 EXNO 10
 PRDNO 1

F2 - Acquisition Parameters
 Date_ 20060717
 Time 16.01
 INSTRUM 5 mm BBO BB-4H
 PROBH 5 mm BBO BB-4H
 PULPROG zg30
 TO 65536
 SOLVENT CDCl3
 NS 32
 DS 8
 SWH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9984243 sec
 RG 114
 DW 60.400 usec
 DE 5.50 usec
 TE 303.0 K
 D1 0.00300000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 9.25 usec
 PL1 0.00 dB
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1300000 MHz
 KW 512
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 2.00

10 NMR plot parameters
 CX 22.00 cm
 CY 15.00 cm
 F1P 0.500 B0M
 F1 3801.24 Hz
 F2P -0.500 B0M
 F2 -200.07 Hz
 FREQM 0.43455 B0M/cm
 HZCM 181.87727 Hz/cm

NAG-NB-038-02

Current Data Parameters
NAME 1717020
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060717
Time 16.29

INSTRUM av400
PROBHD 5 mm BBO BB-4H
PULPROG zgpg30

TO 65536
SOLVENT CDCl₃
NS 1500

DS 2
SH 33112.582 Hz
FIDRES 0.505258 Hz

AQ 0.5895436 sec
RG 16384

DM 15.100 usec
DE 8.00 usec

TE 303.0 K
D1 0.03000000 sec
d11 0.03000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 10.94 usec
PL1 5.00 dB
SFO1 100.6242789 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 50.00 usec
PL2 0.00 dB
PL12 19.76 dB
SFO2 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 100.6126571 MHz
KHZ CM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

10 NMR plot parameters
CX 22.00 cm
CY 15.00 cm
FIP 250.000 ppm
F1 25153.17 Hz
F2P -30.000 ppm
F2 -3018.38 Hz
PPMCH 12.7272 ppm/cm
HZCM 1280.52465 Hz/cm

NAG-NB-038-02

Current Data Parameters
 NAME jn26997
 EXPRNO 10
 PRGNO 1

F2 - Acquisition Parameters
 Date_ 20060628
 Time 0.07
 INSTRUM av400
 PROBRD 5 mm BBO BB-5H
 PULPROG zg30
 TO 65536
 SOLVENT CDCl3
 NS 32
 DS 8
 SHL 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9984243 sec
 RG 114
 DW 60.400 usec
 DE 6.50 usec
 TE 303.0 K
 D1 0.00300000 sec

----- CHANNEL f1 -----
 NUC1 1H
 P1 9.25 usec
 PL1 0.00 dB
 SF01 400.1324710 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1299915 MHz
 KW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 2.00

10 NMR plot parameters
 CX 22.00 cm
 CY 15.00 cm
 F1P 9.590 ppm
 F1 3801.24 Hz
 F2P -200.07 Hz
 F2 0.45455 ppm/cm
 PRGCM HZCM
 HZCM 181.87727 Hz/cm

NAG-NB-015-02