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Supporting Information

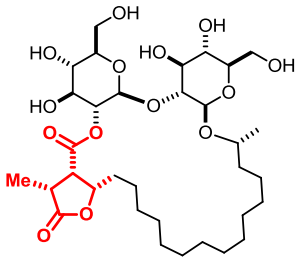
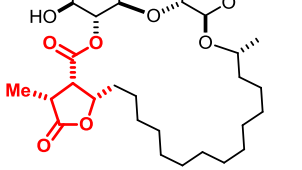
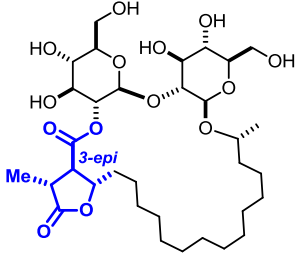
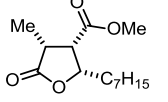
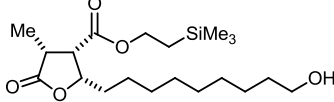
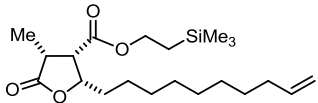
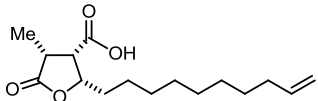
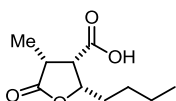
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Total Synthesis of Nominal Gobienine A

Azusa Kondoh, Alexander Arlt, Barbara Gabor, and Alois Fürstner*^[a]

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Table S1. Comparison of the ^1H NMR signals of the butanolide ring of the gobienine A aglycone with those of the all-*cis* configured paraconic acid derivatives prepared during our synthetic study and literature data.

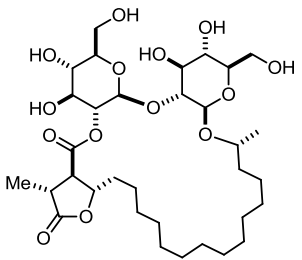
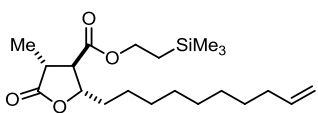
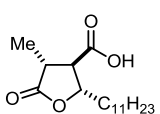
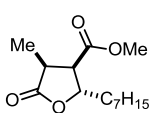
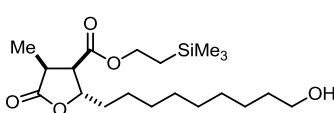
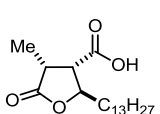
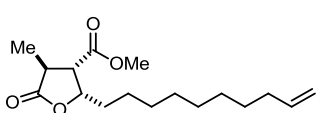
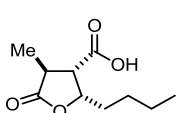
Compound	Solvent	H2	H3	H4	Ref
Gobienine A aglycone	[a]	2.88 dq (7.5, 7.0)	3.24 dd (8.0, 7.0)	4.57 ddd (8.0, 8.0, 5.0)	1
	[a]	3.04 quint (7.0)	3.49 dd (6.9, 5.1)	4.47 td (7.0, 5.2)	
	CDCl_3	2.96 quint (≈ 7) ^b	3.37 dd (≈ 7 , ≈ 5) ^b	4.45 td (≈ 9 , ≈ 5) ^b	
	CDCl_3	2.84 quint. (7.2)	3.20 dd (7.5, 5.1)	4.30 ddd (9.4, 5.2, 4.2)	
	CDCl_3	2.87 dq (7.4, 7.1)	3.29 dd (7.6, 5.2)	4.38 dt (8.6, 5.1)	
	CDCl_3	2.86 dq (7.2, 7.1)	3.23 dd (7.5, 5.2)	4.37 dt (8.5, 5.1)	
	CDCl_3	2.85 dq (7.2, 7.1)	3.23 dd (7.5, 5.2)	4.37 dt (8.4, 5.2)	
	CDCl_3	2.92 dq (7.2, 7.1)	3.30 dd (7.3, 5.2)	4.40 dt (8.7, 5.0)	
	CDCl_3	2.95 dq (7.2, 7.2)	3.33 dd (7.2, 5.2)	4.44 m	2

[a] $[\text{D}_4]\text{-MeOH}/[\text{D}_5]\text{-pyridine}$ (1:1, v/v); ^b because of the very poor solubility of synthetic **1** in CDCl_3 , the resolution of the spectra does not allow the coupling constants to be determined with an accuracy of more than ± 0.3 Hz.

¹ T. Řezanka, I. A. Guschina, *Phytochemistry* **2001**, *58*, 1281-1287

² M. Amador, X. Ariza, J. Garcia, J. Ortiz, *J. Org. Chem.* **2004**, *69*, 8172-8175

Table S2. Comparison of the ^1H NMR signals of the butanolide ring of the gobienine A aglycone with those of other diastomeric paraconic acid derivatives prepared during our synthetic study as well as with literature data.

Compound	Solvent	H2	H3	H4	Ref
Gobienine A aglycone	<i>a</i>	2.88 dq (7.5, 7.0)	3.24 dd (8.0, 7.0)	4.57 ddd (8.0, 8.0, 5.0)	1
	[a]	3.16 dq (11.4, 7.1)	2.87 dd (11.4, 9.4)	4.94 td (9.1, 3.4)	
	CDCl_3	2.92 dq (11.4, 7.1)	2.59 dd (11.4, 9.5)	4.42 ddd (9.4, 8.1, 4.3)	
	CDCl_3	2.96 dq (11.6, 7.0)	2.68 dd (11.3, 9.4)	4.47 dt (9.1, 4.0)	3
	CDCl_3	2.95 dq (9.3, 7.5)	3.09 dd (9.3, 6.4)	4.68 dt (6.8, 6.3)	
	CDCl_3	2.95 dq (9.3, 7.4)	3.04 dd (9.2, 6.4)	4.67 q (6.4)	
	CDCl_3	3.02 dq (8.5, 7.4)	3.14 dd (8.5, 6.2)	4.67 ddd (6.3, 6.3, 6.2)	4
	CDCl_3	3.03 (10.0, 7.0)	3.15 (10.0, 8.2)	4.58-4.66 (m)	b
	CDCl_3	3.04 dq (10.0, 7.1)	3.22 dd (10.0, 8.2)	4.69 m	2

[a] $[\text{D}_4]\text{-MeOH}/[\text{D}_5]\text{-pyridine}$ (1:1, v/v); ^b this isomer was a by-product in the attempted synthesis of alkene **22b** by the Wittig olefination mentioned in the text.

³ M. P. Sibi, P. Liu, J. Ji, S. Hajra and J. Chen, *J. Org. Chem.* **2002**, *67*, 1738-1745.

⁴ T. Martín, C. M. Rodríguez, V. S. Martín, *J. Org. Chem.* **1996**, *61*, 6450-6453

General. Unless stated otherwise, all reactions were carried out in flame-dried glassware under Argon. All solvents were purified by distillation over the indicated drying agents and were stored and transferred under Argon: THF (Mg-anthracene), Et₂O (Mg-anthracene), CH₂Cl₂, CHCl₃ (CaH₂), MeOH (Mg), hexanes, pentanes (Na/K), toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). IR: Nicolet FT-7199 spectrometer, wavenumbers in cm⁻¹. MS (EI): Finnigan MAT 8200, MS (CI): Finnigan MAT 95, MS (ESI) ESQ 3000, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). NMR: Spectra were recorded on a Bruker DPX 300, AV 400, AV 500 or AV 600 spectrometer in the solvents indicated; ¹H and ¹³C chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references (CDCl₃: δ_H = 7.24 ppm, δ_C = 77.00 ppm; C₆D₆: δ_H = 7.15 ppm, δ_C = 128.0 ppm, [D₄]-MeOH: δ_H = 3.30 ppm, δ_C = 49.0 ppm) and the chemical shifts converted to the TMS scale. All commercially available compounds (ABCR, Acros, Aldrich, Fluka, Lancaster, Strem) were used as received.

10-(Benzyloxy)decan-1-ol. 1,10-Decanediol (4.4 g, 25 mmol) was slowly added to a suspension of NaH (0.60 g, 25 mmol) in THF/DMF (1:1, 50 mL) at 0 °C and the resulting mixture stirred at that temperature for 4 h until the evolution of gas had ceased. Benzyl bromide (4.6 g, 27 mmol) was then introduced and the resulting mixture stirred overnight at ambient temperature. The reaction was carefully quenched with H₂O and the product extracted with hexane/EtOAc (5:1), the combined organic layers were dried over Na₂SO₄ and evaporated, and the residue purified by flash chromatography (hexane/EtOAc, 5:1) to afford the title compound as a colorless oil (3.2 g, 49%). ¹H NMR (400 MHz, CDCl₃): δ = 7.36-7.24 (m, 5H), 4.48 (s, 2H), 3.61 (t, *J* = 6.6 Hz, 2H), 3.44 (t, *J* = 6.7 Hz, 2H), 1.64-1.46 (m, 5H), 1.40-1.20 ppm (m, 12H); ¹³C NMR (100 MHz, CDCl₃): δ = 138.7, 128.3, 127.6, 127.4, 72.8, 70.5, 63.1, 32.8, 29.7, 29.50, 29.48, 29.4, 29.3, 26.2, 25.7 ppm; IR (film): $\tilde{\nu}$ = 3372, 3030, 2926, 2853, 1454, 1362, 1204, 1100, 1075, 1028, 734, 697 cm⁻¹; MS (EI): *m/z* (%): 264 (18) [M]⁺, 246 (2), 107 (95), 91 (100), 81 (11), 69 (9), 55 (14), 41 (11); HRMS (ESI⁺): calcd for C₁₇H₂₈O₂+Na⁺: 287.1981 [M+Na]⁺; found: 287.1984.

Aldehyde 14. A mixture of PCC (3.4 g, 15.7 mmol) and silica (3.4 g) was added to a solution of 10-(benzyloxy)decan-1-ol (3.2 g, 12.2 mmol) in CH₂Cl₂ (30 mL), and the resulting mixture was stirred for 3 h. Filtration of the suspension through a pad of Celite, evaporation of the filtrate, followed by flash chromatographic purification of the residue (hexane/EtOAc, 5:1) provided aldehyde **14** as a colorless oil (2.4 g, 75%). ¹H NMR (300 MHz, CDCl₃): δ = 9.74 (t, *J* = 1.8 Hz, 1H), 7.36-7.24 (m, 5H), 4.48 (s, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 2.39 (td, *J* = 7.3, 1.8 Hz, 2H), 1.70-1.50 (m, 4H), 1.40-1.20 ppm (m, 10H); ¹³C NMR (100 MHz, CDCl₃): δ = 202.9, 138.7, 128.3, 127.6, 127.4, 72.8, 70.5, 43.9, 29.7, 29.4, 29.3, 29.2, 29.1, 26.1, 22.1 ppm; IR (film): $\tilde{\nu}$ = 2927, 2854, 1724, 1454, 1362, 1205, 1101, 736, 697 cm⁻¹; MS (EI): *m/z* (%): 262 (1) [M]⁺, 107 (100), 91 (88), 79 (7); HRMS (ESI⁺): calcd for C₁₇H₂₆O₂+Na⁺: 285.1825 [M+Na]⁺; found: 285.1826.

Cyanohydrin 6. TMSCN (0.60 g, 6.0 mmol) was added to a solution of octanal (0.64 g, 5.0 mmol) and Yb(OTf)₃·*n* H₂O (0.16 g, 0.25 mmol) in CH₂Cl₂ (10 mL). The resulting mixture was stirred for 2.5 h before CH₃CN (7 mL) and aq. HCl (1 M, 7 mL) were added. After stirring for 30 min, the product was extracted with EtOAc, the combined extracts were dried over Na₂SO₄ and evaporated, and the residue purified by flash chromatography (hexane/EtOAc, 10:1) to give product **6** as a colorless oil (0.41 g, 52%). ¹H NMR (400 MHz, CDCl₃): δ = 4.45 (dt, *J* = 6.6, 6.5 Hz, 1H), 2.50 (brs, 1H), 1.86-1.79 (m, 2H), 1.53-1.43 (m, 2H), 1.38-1.20 (m, 8H), 0.86 ppm (t, *J* = 6.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 119.9, 61.4, 35.2, 31.6, 29.0, 28.9, 24.5, 22.6, 14.0 ppm; IR (film): $\tilde{\nu}$ = 3433, 2927, 2857, 1466, 1126, 1072, 724 cm⁻¹; MS (EI): *m/z* (%): 155 (< 1) [M]⁺, 110 (6), 95 (11), 84 (39), 71 (13), 69 (30), 57 (80), 43 (100), 41 (81), 29 (49), 27 (65); HRMS (CI, *i*-butane): calcd for C₉H₁₈NO⁺: 156.1388 [M+H]⁺; found: 156.1390.

(S)-Cyanohydrin 15. A solution of Ti(*Oi*-Pr)₄ in CH₂Cl₂ (0.10 M, 2.0 mL, 0.20 mmol) was added to a suspension of ligand **24** (74 mg, 0.21 mmol) in CH₂Cl₂ (8 mL). The mixture was stirred for 1 h before it was cooled to -40 °C and TMSCN (0.57 g, 6.0 mmol) was introduced. After stirring for 20 min, a solution of aldehyde **14** (0.53 g, 2.0 mmol) in CH₂Cl₂ (2 mL) was added dropwise and the resulting mixture stirred for 48 h at this temperature. aq. HCl (2 M, 12 mL) and EtOAc (12 mL) were then sequentially added, the mixture was allowed to reach ambient temperature and stirring continued for 5 h. After extraction with EtOAc, the combined organic layers were dried over Na₂SO₄ and evaporated, and the residue purified by flash chromatography (hexane/EtOAc, 5:1) to give cyanohydrin **15** as a colorless oil (0.51 g, 88%, 89% ee). $[\alpha]_D^{20} = -3$ (c = 0.17, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ = 7.35-7.24 (m, 5H), 4.48 (s, 2H), 4.44 (dt, *J* = 6.6, 6.6 Hz, 1H), 3.45 (t, *J* = 6.6 Hz, 2H), 2.31 (d, *J* = 6.6 Hz, 1H), 1.86-1.78 (m, 2H), 1.64-1.42 (m, 4H), 1.40-1.20 ppm (m, 10H); ¹³C NMR (100 MHz, CDCl₃): δ = 138.5, 128.4, 127.7, 127.5, 119.9, 72.9, 70.5, 61.3, 35.2, 29.7, 29.3 (2C), 29.2, 28.8, 26.1, 24.5 ppm; IR (film): $\tilde{\nu}$ = 3445, 2928, 2855, 1455, 1365, 1075, 739, 698 cm⁻¹; MS (EI): *m/z* (%): 289 (5) [M]⁺, 262 (6), 135 (2), 107 (76), 91 (100), 79 (10), 65 (10), 55 (12), 41 (14); HRMS (EI): calcd for C₁₈H₂₇NO₂⁺: 289.2042 [M]⁺; found: 289.2039.

The enantiomeric excess was determined by HPLC (Chiralpak IC-3 Nr IC30CD-OD004, 3 μm, Ø 4.6 mm, *n*-heptane/2-propanol = 80:20 (*v/v*), 1 mL·min⁻¹, 298 K, UV detection @ 210 nm: *t*_R = 6.73 and 9.43 min) after transformation of the cyanohydrin into the corresponding acetate (Ac₂O, Et₃N, CH₂Cl₂), using a racemic sample for comparison. The acetate analyzed as follows: $[\alpha]_D^{20} = -32$ (c = 0.13, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ = 7.34-7.24 (m, 5H), 5.29 (t, *J* = 6.8 Hz, 1H), 4.48 (s, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 2.12 (s, 3H), 1.91-1.83 (m, 2H), 1.64-1.55 (m, 2H), 1.50-1.40 (m, 2H), 1.40-1.20 ppm (m, 10H); ¹³C NMR (100 MHz, CDCl₃): δ = 169.2, 138.7, 128.3, 127.6, 127.4, 116.9, 72.8, 70.4, 61.1, 32.2, 29.7, 29.3 (2C), 29.1, 28.7, 26.1, 24.5, 20.4 ppm; IR (film): $\tilde{\nu}$ = 2929, 2855, 1753, 1454, 1372, 1218, 1101, 1029, 737, 698 cm⁻¹; MS (EI): *m/z*

(%): 331 (9) $[M]^+$, 174 (1), 135 (1), 107 (100), 91 (82), 43 (28); HRMS (ESI⁺): calcd for $C_{20}H_{29}NO_3+Na^+$: 354.2040 $[M+Na]^+$; found: 354.2037.

Ester 7. Et₃N (0.91 g, 9.0 mmol) and 2-bromopropionyl bromide (1.8 g, 8.2 mmol) were sequentially added to a solution of cyanohydrin **6** (0.98 g, 6.3 mmol) in CH₂Cl₂ (20 mL) at 0 °C. The mixture was warmed to ambient temperature and stirred for 2.5 h before the reaction was quenched with H₂O. The product was extracted with CH₂Cl₂, the combined organic layers were dried over Na₂SO₄ and evaporated, and the residue was purified by flash chromatography (hexane/EtOAc, 10:1) to give ester **7** as a mixture of diastereomers (1.8 g, 96%). ¹H NMR (400 MHz, CDCl₃): δ = 5.35 (t, *J* = 6.7 Hz, 1H), 5.34 (t, *J* = 6.7 Hz, 1H), 4.38 (q, *J* = 6.9 Hz, 1H), 4.37 (q, *J* = 6.9 Hz, 1H), 1.97-1.89 (m, 2H×2), 1.84 (d, *J* = 6.9 Hz, 3H), 1.83 (d, *J* = 6.9 Hz, 3H), 1.55-1.45 (m, 2H×2), 1.40-1.20 (m, 8H×2), 0.87 ppm (t, *J* = 6.6, 6.7 Hz, 3H×2); ¹³C NMR (100 MHz, CDCl₃): δ = 168.5 (×2), 116.4, 116.1, 62.5, 62.3, 38.5, 38.2, 32.1 (×2), 31.6 (×2), 28.9 (×2), 28.7, 28.6, 24.4, 24.3, 22.5 (×2), 21.3, 21.2, 14.0 (×2) ppm; IR (film): $\tilde{\nu}$ = 2956, 2928, 2857, 1753, 1446, 1379, 1334, 1247, 1211, 1147, 1095, 1074, 1052, 993, 969 cm⁻¹; MS (EI): *m/z* (%): 290 (< 1) $[M]^+$, 262 (1), 248 (< 1), 233 (< 1), 210 (14), 182 (2), 168 (3), 154 (27), 137 (31), 122 (17), 109 (72), 95 (65), 81 (86), 69 (71), 56 (85), 43 (100); HRMS (ESI⁺): calcd for $C_{12}H_{20}NO_2Br+Na^+$: 312.0570 $[M+Na]^+$; found: 312.0570.

Ester 16. Prepared analogously from cyanohydrin **15** (0.49 g, 1.7 mmol) and 2-bromopropionyl bromide (0.43 g, 2.0 mmol) as a mixture of diastereomers (0.69 g, 97%). $[\alpha]_D^{20} = -23$ (c = 0.13, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ = 7.34-7.24 (m, 5H×2), 5.35 (t, *J* = 6.6 Hz, 1H), 5.33 (t, *J* = 6.6 Hz, 1H), 4.48 (s, 2H×2), 4.38 (q, *J* = 6.9 Hz, 1H), 4.37 (q, *J* = 6.9 Hz, 1H), 3.44 (t, *J* = 6.6 Hz, 2H×2), 1.96-1.89 (m, 2H×2), 1.84 (d, *J* = 6.9 Hz, 3H), 1.83 (d, *J* = 6.9 Hz, 3H), 1.64-1.44 (m, 4H×2), 1.40-1.20 ppm (m, 10H×2); ¹³C NMR (100 MHz, CDCl₃): δ = 168.7, 168.5, 138.7 (×2), 128.3 (×2), 127.6 (×2), 127.5 (×2), 116.4, 116.1, 72.9 (×2), 70.4 (×2), 62.5, 62.3, 38.5, 38.2, 32.1 (×2), 29.7 (×2), 29.3 (×2), 29.2 (×2), 29.1 (×2), 28.7, 28.6, 26.1 (×2), 24.4, 24.3, 21.3, 21.1 ppm; IR (film): $\tilde{\nu}$ = 2929, 2855, 1754, 1453, 1360, 1246, 1211, 1147, 1097, 1075, 737, 698 cm⁻¹; MS (EI): *m/z* (%): 423 (2) $[M]^+$, 288 (< 1), 244 (< 1), 135 (3), 107 (100), 91 (82), 79 (6), 55 (6), 41 (6); HRMS (ESI⁺): calcd for $C_{21}H_{30}NO_3Br+Na^+$: 446.1301 $[M+Na]^+$; found: 446.1306.

Alkenyltriflate 9. Methanesulfonic acid (3.9 μL, 0.060 mmol) was added to a suspension of Zn dust (0.59 g, 9.0 mmol) in THF (6 mL) and the mixture stirred at reflux temperature for 15 min. A solution of compound **7** (1.8 g, 6.0 mmol) in THF (12 mL) was added dropwise to the refluxing suspension and stirring continued for 3 h. After reaching ambient temperature, aq. HCl (2.0 M, 60 mL) was introduced and the mixture stirred at 90 °C (bath temperature) overnight. For work up, the

mixture was allowed to cool, the product was extracted with EtOAc, and the combined extracts were dried over Na₂SO₄ and evaporated.

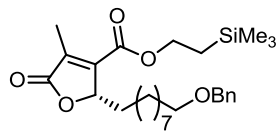
Et₃N (0.91 g, 9.0 mmol) and Tf₂O (2.5 g, 9.0 mmol) were sequentially added to a solution of the crude product **8** thus formed in CH₂Cl₂ (25 mL) at 0 °C, and the resulting mixture stirred at that temperature for 2 h. The reaction was quenched with H₂O, the product was extracted with CH₂Cl₂, the combined organic layers were dried over Na₂SO₄ and evaporated, and the residue purified by flash chromatography (hexane/EtOAc, 20:1) to provide alkenyl triflate **9** as a pale yellow oil (1.4 g, 69% over 2 steps). ¹H NMR (400 MHz, CDCl₃): δ = 5.05-4.98 (m, 1H), 2.00-1.90 (m, 1H), 1.92 (d, *J* = 1.9 Hz, 3H), 1.65-1.55 (m, 1H), 1.46-1.18 (m, 10H), 0.86 ppm (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 169.8, 162.7, 118.4 (q, *J* = 319 Hz), 118.1, 78.3, 31.6, 31.4, 28.9, 28.8, 24.1, 22.5, 14.0, 7.7 ppm; IR (film): $\tilde{\nu}$ = 2933, 1782, 1708, 1436, 1219, 1137, 811, 764 cm⁻¹; MS (EI): *m/z* (%): 344 (4) [M]⁺, 315 (2), 288 (5), 259 (18), 246 (47), 211 (9), 195 (79), 165 (11), 149 (17), 137 (5), 127 (21), 95 (7), 83 (43), 69 (29), 57 (100), 43 (43); HRMS (ESI⁺): calcd for C₁₃H₁₉O₅F₃S+Na⁺: 367.0798 [M+Na]⁺; found: 367.0798.

Alkenyltriflate 17. Prepared analogously from substrate **16** (1.3 g, 3.1 mmol) as a pale yellow oil (1.1 g, 77% over both steps). $[\alpha]_D^{20}$ = +10 (c = 0.11, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ = 7.36-7.24 (m, 5H), 5.04-4.98 (m, 1H), 4.48 (s, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 2.00-1.90 (m, 1H), 1.92 (d, *J* = 1.8 Hz, 3H), 1.65-1.53 (m, 3H), 1.48-1.20 ppm (m, 12H); ¹³C NMR (100 MHz, CDCl₃): δ = 169.8, 162.6, 138.7, 128.3, 127.6, 127.4, 118.4 (q, *J* = 319 Hz), 118.2, 78.3, 72.8, 70.5, 31.4, 29.7, 29.3 (2C), 29.2, 28.9, 26.1, 24.1, 7.7 ppm; IR (film): $\tilde{\nu}$ = 2930, 2856, 1779, 1707, 1433, 1242, 1218, 1137, 1105, 930, 810, 764, 736, 698 cm⁻¹; MS (EI): *m/z* (%): 478 (3) [M]⁺, 460 (4), 387 (4), 345 (8), 259 (6), 223 (41), 180 (3), 107 (22), 91 (100), 69 (12), 55 (11); HRMS (ESI⁺): calcd for C₂₂H₂₉O₆F₃S+Na⁺: 501.1529 [M+Na]⁺; found: 501.1534.

Methyl Ester 10. Pd(OCOCF₃)₂ (20 mg, 60 μmol) and DPEphos (32 mg, 60 μmol) were dissolved in CH₃CN (3 mL) and the mixture stirred for 5 min before a solution of alkenyltriflate **9** (0.21 g, 0.60 mmol) in CH₃CN (3 mL), followed by MeOH (1.2 mL) and *i*-Pr₂NEt (0.16 g, 1.2 mmol) were added. The resulting mixture was stirred under CO atmosphere (balloon) for 18 h before the reaction was quenched with aq. sat. NH₄Cl. The product was extracted with EtOAc, the combined organic layers were dried over Na₂SO₄ and evaporated, and the residue purified by flash chromatography (hexane/EtOAc, 10:1) to give ester **10** as a pale yellow oil (140 mg, 89%). ¹H NMR (300 MHz, CDCl₃): δ = 5.13-5.03 (m, 1H), 3.87 (s, 3H), 2.17 (d, *J* = 2.1 Hz, 3H), 2.13-1.98 (m, 1H), 1.60-1.45 (m, 1H), 1.45-1.18 (m, 10H), 0.85 ppm (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 172.9, 162.6, 147.6, 137.4, 81.4, 52.3, 32.8, 31.7, 29.1, 29.0, 24.7, 22.6, 14.0, 10.8 ppm; IR (film): $\tilde{\nu}$ = 2955, 2926, 2857, 1764, 1724, 1438, 1337, 1220, 1098, 1036, 966, 776, 759 cm⁻¹; MS (EI): *m/z* (%): 254 (1) [M]⁺, 239 (< 1), 225 (38), 195

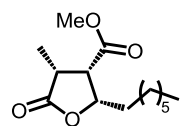
(17), 169 (14), 156 (100), 127 (49), 109 (9), 95 (16), 81 (5), 67 (45), 57 (98), 43 (54), 29 (27); HRMS (ESI⁺): calcd for C₁₄H₂₂O₄+Na⁺: 277.1410 [M+Na]⁺; found: 277.1410.

Compound 18. A solution of Pd(OCOCF₃)₂ (40 mg, 0.12 mmol) and DPEphos (65 mg, 0.12 mmol) in CH₃CN (5 mL) was stirred for 5 min before a solution of alkenyltriflate **17** (0.57 g, 1.2 mmol) in CH₃CN (5 mL), followed by 2-trimethylsilylethanol (0.71 g, 6.0 mmol) and *i*-Pr₂NEt (0.19 g, 1.5 mmol) were added. The mixture was stirred under CO atmosphere (1 atm, balloon) for 14 h. The reaction was then quenched with aq. sat. NH₄Cl and the product extracted with EtOAc. The combined organic layers were dried over Na₂SO₄ and evaporated, and the crude material was purified by flash chromatography (hexane/EtOAc, 20:1) to give ester **18** as a pale yellow oil (0.46 g, 82%).

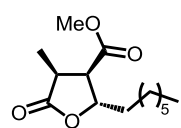


[α]_D²⁰ = -20 (c = 0.25, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ = 7.35-7.24 (m, 5H), 5.10-5.04 (m, 1H), 4.48 (s, 2H), 4.40-4.27 (m, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 2.17 (d, *J* = 2.0 Hz, 3H), 2.10-2.00 (m, 1H), 1.64-1.47 (m, 3H), 1.40-1.20 (m, 12H), 1.10-1.04 (m, 2H), 0.05 ppm (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ = 173.1, 162.4, 148.1, 138.7, 136.9, 128.3, 127.6, 127.4, 81.4, 72.8, 70.5, 64.1, 32.7, 29.7, 29.5, 29.4, 29.3, 29.2, 26.1, 24.7, 17.5, 10.8, -1.6 ppm; IR (film): $\tilde{\nu}$ = 2927, 2855, 1765, 1717, 1454, 1329, 1250, 1222, 1099, 936, 858, 837, 735, 697 cm⁻¹; MS (EI): *m/z* (%): 428 (1), 368 (12), 340 (4), 295 (3), 267 (8), 223 (58), 91 (100), 73 (46); HRMS (ESI⁺): calcd for C₂₇H₄₂O₅Si+Na⁺: 497.2694 [M+Na]⁺; found: 497.2696.

Ester 11 and Diastereomer 12. A mixture of compound **10** (25 mg, 0.10 mmol) and Rh/Al₂O₃ (5% w/w, 5 mg) in EtOAc (2 mL) was stirred in an autoclave under H₂ atmosphere (15 bar) for 22 h. The catalyst was then filtered off through a pad of Celite, the filtrate was evaporated and the residue purified by flash chromatography (hexane/EtOAc, 5:1) to provide product **11** (22 mg, 87%) along with a fraction containing the isomeric product **12** (2.3 mg, 9%).

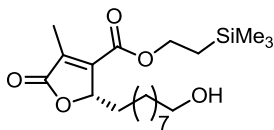


Spectral data of compound 11: ¹H NMR (500 MHz, CDCl₃): δ = 4.38 (dt, *J* = 8.6, 5.1 Hz, 1H), 3.71 (s, 3H), 3.29 (dd, *J* = 7.6, 5.2 Hz, 1H), 2.87 (dq, *J* = 7.4, 7.1 Hz, 1H), 1.76-1.68 (m, 1H), 1.60-1.44 (m, 2H), 1.40-1.18 (m, 9H), 1.22 (d, *J* = 7.1 Hz, 3H), 0.85 ppm (t, *J* = 6.8 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ = 177.1, 170.0, 79.0, 51.7, 50.7, 39.1, 31.6, 30.9, 29.2, 29.0, 25.8, 22.6, 14.0, 10.3 ppm; IR (film): $\tilde{\nu}$ = 2927, 2857, 1778, 1735, 1459, 1438, 1378, 1343, 1172, 1128, 980, 797 cm⁻¹; MS (EI): *m/z* (%): 256 (5) [M]⁺, 238 (4), 225 (11), 212 (16), 197 (50), 183 (19), 168 (9), 157 (22), 141 (12), 128 (46), 115 (33), 101 (53), 81 (20), 69 (100), 59 (39), 41 (53), 29 (24); HRMS (ESI⁺): calcd for C₁₄H₂₄O₄+Na⁺: 279.1567 [M+Na]⁺; found: 279.1568.



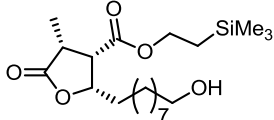
Spectral data of Isomer 12: ¹H NMR (500 MHz, CDCl₃): δ = 4.68 (dt, *J* = 6.8, 6.3 Hz, 1H), 3.73 (s, 3H), 3.09 (dd, *J* = 9.3, 6.4 Hz, 1H), 2.95 (dq, *J* = 9.3, 7.5 Hz, 1H), 1.67-1.60 (m, 2H), 1.52-1.42 (m, 1H), 1.42-1.18 (m, 9H), 1.20 (d, *J* = 7.5 Hz, 3H), 0.86 ppm (t, *J* = 6.7 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ = 177.3, 170.6, 79.5, 52.2, 50.0, 37.2, 34.7, 31.7, 29.2, 29.0, 25.3, 22.6, 14.1, 11.9 ppm.

Ester 19. A mixture of compound **18** (0.16 g, 0.34 mmol) and Pd/C (10%, 20 mg) in EtOH (10 mL) was stirred overnight under H₂ atmosphere (1 atm). The

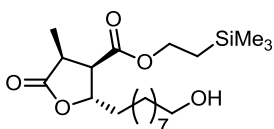


catalyst was then filtered off through a pad of Celite, the filtrate was evaporated and the residue purified by flash chromatography (hexane/EtOAc, 3:1) to yield compound **19** as a colorless oil (0.10 g, 79%). $[\alpha]_D^{20} = -27$ (c = 0.10, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ = 5.11-5.03 (m, 1H), 4.42-4.26 (m, 2H), 3.61 (t, *J* = 6.6 Hz, 2H), 2.16 (d, *J* = 2.0 Hz, 3H), 2.10-1.98 (m, 1H), 1.60-1.20 (m, 16H), 1.12-1.04 (m, 2H), 0.05 ppm (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ = 173.1, 162.4, 148.1, 136.9, 81.4, 64.1, 63.0, 32.8, 32.7, 29.4, 29.3, 29.2, 29.1, 25.7, 24.7, 17.5, 10.8, -1.6 ppm; IR (film): $\tilde{\nu} = 3422, 2928, 2856, 1766, 1717, 1393, 1331, 1250, 1224, 1180, 1042, 936, 859, 837, 760, 697$ cm⁻¹; MS (EI): *m/z* (%): 341 (11), 323 (23), 211 (26), 185 (8), 169 (8), 139 (6), 81 (7), 73 (100), 55 (24), 41 (16); HRMS (ESI⁺): calcd for C₂₀H₃₆O₅Si+Na⁺: 407.2224 [M+Na]⁺; found: 407.2224.

Ester 20. A mixture of compound **19** (93 mg, 0.24 mmol) and Rh/Al₂O₃ (5% w/w, 13 mg) in EtOAc (5 mL) was stirred in an autoclave under H₂ pressure (11 bar)

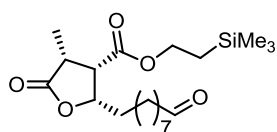


for 17 h. For work up, the autoclave was vented, the catalyst was filtered off through a pad of Celite, the filtrate was evaporated and the residue purified by flash chromatography (hexane/EtOAc, 2:1) to provide product **20** (75 mg, 81%) as a colorless oil. A second fraction was also collected, which consisted of the diastereomer **21** (13 mg, 13%). *Analytical and spectral data of 20:* $[\alpha]_D^{20} = -37$ (c = 0.1, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ = 4.37 (dt, *J* = 8.5, 5.1 Hz, 1H), 4.27-4.15 (m, 2H), 3.62 (t, *J* = 6.6 Hz, 2H), 3.23 (dd, *J* = 7.5, 5.2 Hz, 1H), 2.86 (dq, *J* = 7.2, 7.1 Hz, 1H), 1.82-1.70 (m, 1H), 1.64-1.20 (m, 16H), 1.24 (d, *J* = 7.1 Hz, 3H), 1.04-0.97 (m, 2H), 0.03 ppm (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ = 177.2, 169.7, 79.1, 63.4, 63.0, 50.7, 39.2, 32.7, 30.8, 29.4, 29.3, 29.2, 29.1, 25.8, 25.7, 17.7, 10.3, -1.6 ppm; IR (film): $\tilde{\nu} = 3438, 2927, 2855, 1777, 1729, 1462, 1402, 1341, 1250, 1173, 1039, 978, 860, 838, 760, 695$ cm⁻¹; MS (EI): *m/z* (%): 356 (1), 343 (3), 325 (5), 313 (3), 283 (3), 253 (7), 224 (4), 211 (9), 186 (6), 143 (9), 95 (13), 73 (100), 55 (14), 41 (11); HRMS (ESI⁺): calcd for C₂₀H₃₈O₅Si+Na⁺: 409.2381 [M+Na]⁺; found: 409.2383.



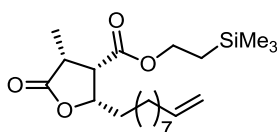
Analytical and spectral data of isomer 21: ¹H NMR (400 MHz, CDCl₃): δ = 4.67 (q, *J* = 6.4, 1H), 4.24-4.17 (m, 2H), 3.61 (t, *J* = 6.6 Hz, 2H), 3.04 (dd, *J* = 9.2, 6.4 Hz, 1H), 2.95 (dq, *J* = 9.3, 7.4 Hz, 1H), 1.70-1.24 (m, 17H), 1.21 (d, *J* = 7.4 Hz, 3H), 1.03-0.95 (m, 2H), 0.03 ppm (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ = 177.4, 170.2, 79.5, 63.7, 63.0, 50.2, 37.2, 34.7, 32.8, 29.4, 29.3, 29.2, 29.1, 25.7, 25.3, 17.6, 11.9, -1.6 ppm; IR (film): $\tilde{\nu} = 3487, 2928, 2856, 1777, 1731, 1460, 1383, 1357, 1250, 1175, 1043, 978, 859, 838, 760, 695$ cm⁻¹; MS (EI): *m/z* (%): 371 (< 1), 343 (3), 325 (5), 313 (8), 283 (5), 253 (7), 223 (5), 211 (27), 143 (12), 95 (11), 73 (100), 41 (7); HRMS (ESI⁺): calcd for C₂₀H₃₈O₅Si+Na⁺: 409.2381 [M+Na]⁺; found: 409.2383.

Compound 22. TEMPO (3.3 mg, 21 μmol) and $\text{PhI}(\text{OAc})_2$ (74 mg, 0.23 mmol) were added



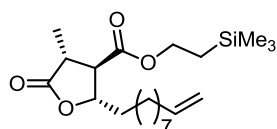
to a solution of **20** (80 mg, 0.21 mmol) in CH_2Cl_2 (2 mL). The mixture was stirred for 2 h before the reaction was quenched with aq. sat. $\text{Na}_2\text{S}_2\text{O}_3$. The product was extracted with CH_2Cl_2 , the combined organic layers were dried over Na_2SO_4 and evaporated, and the

residue was purified by flash chromatography (hexane/EtOAc, 4:1) to provide the corresponding aldehyde as a pale yellow oil (67 mg, 84%), which analyzed as follows: $[\alpha]_D^{20} = -36$ ($c = 0.11$, CH_2Cl_2); $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 9.73$ (t, $J = 1.6$ Hz, 1H), 4.36 (ddd, $J = 8.6, 5.0, 5.0$ Hz, 1H), 4.25-4.14 (m, 2H), 3.22 (dd, $J = 7.5, 5.2$ Hz, 1H), 2.85 (dq, $J = 7.2, 7.1$ Hz, 1H), 2.39 (td, $J = 7.4, 1.7$ Hz, 2H), 1.80-1.70 (m, 1H), 1.65-1.20 (m, 13H), 1.23 (d, $J = 7.1$ Hz, 3H), 1.03-0.96 (m, 2H), 0.02 ppm (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 202.8, 177.1, 169.7, 79.1, 63.4, 50.7, 43.8, 39.2, 30.8, 29.2, 29.1$ (2C), 29.0, 25.8, 21.9, 17.7, 10.3, -1.6 ppm; IR (film): $\tilde{\nu} = 2930, 2856, 2714, 1778, 1725, 1456, 1403, 1341, 1250, 1171, 1123, 1038, 976, 859, 837, 758, 695$ cm^{-1} ; MS (EI): m/z (%): 357 (1), 341 (7), 313 (7), 295 (4), 283 (7), 267 (2), 255 (5), 239 (2), 222 (3), 211 (9), 186 (5), 129 (16), 95 (9), 81 (12), 73 (100), 55 (11), 41 (11); HRMS (ESI $^+$): calcd for $\text{C}_{20}\text{H}_{36}\text{O}_5\text{Si}+\text{Na}^+$: 407.2224 $[\text{M}+\text{Na}]^+$; found: 407.2220.



A solution of this aldehyde (0.13 g, 0.34 mmol) in THF (2 mL) and CH_2I_2 (61 μL , 0.76 mmol) were sequentially added to a suspension of Cp_2ZrCl_2 (0.12 g, 0.42 mmol) and Zn dust (0.18 g, 2.8 mmol) in THF (5 mL). The resulting mixture was vigorously stirred for 5 h before the

reaction was quenched with H_2O . The product was extracted with a mixture of EtOAc and hexane, the combined extracts were dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (hexane/EtOAc, 10:1) to give compound **22** as a colorless oil (0.094 g, 71%). $[\alpha]_D^{20} = -30$ ($c = 0.13$, CH_2Cl_2); $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 5.78$ (ddt, $J = 17.0, 10.2, 6.7$ Hz, 1H), 5.01-4.88 (m, 2H), 4.37 (dt, $J = 8.4, 5.2$ Hz, 1H), 4.27-4.14 (m, 2H), 3.23 (dd, $J = 7.5, 5.2$ Hz, 1H), 2.85 (dq, $J = 7.2, 7.1$ Hz, 1H), 2.06-1.97 (m, 2H), 1.82-1.70 (m, 1H), 1.64-1.20 (m, 13H), 1.23 (d, $J = 7.1$ Hz, 3H), 1.03-0.96 (m, 2H), 0.02 ppm (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 177.2, 169.7, 139.1, 114.2, 79.1, 63.4, 50.7, 39.2, 33.8, 30.8, 29.3$ (2C), 29.2, 29.1, 28.9, 25.8, 17.7, 10.3, -1.6 ppm; IR (film): $\tilde{\nu} = 2926, 2855, 1781, 1731, 1640, 1463, 1402, 1341, 1250, 1173, 1038, 971, 909, 859, 838, 759, 696$ cm^{-1} ; MS (EI): m/z (%): 367 (5), 354 (3), 339 (5), 321 (< 1), 309 (10), 264 (2), 243 (3), 204 (11), 186 (8), 143 (10), 95 (7), 73 (100), 55 (11), 41 (11); HRMS (ESI $^+$): calcd for $\text{C}_{21}\text{H}_{38}\text{O}_4\text{Si}+\text{Na}^+$: 405.2432 $[\text{M}+\text{Na}]^+$; found: 405.2434.



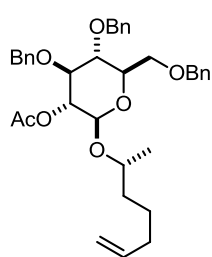
A second fraction was collected which consisted of an epimeric compound, which analyzed as follows: $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 5.79$ (ddt, $J = 17.0, 10.2, 6.7$ Hz, 1H), 5.01-4.87 (m, 2H), 4.42 (ddd, $J = 9.4, 8.1, 4.3$ Hz, 1H), 4.26-4.19 (m, 2H), 2.92 (dq, $J = 11.4, 7.1$ Hz, 1H), 2.59 (dd, $J = 11.4, 9.5$ Hz, 1H), 2.06-1.97 (m, 2H), 1.82-1.60 (m, 2H), 1.53-1.20

(m, 13H), 1.23 (d, $J = 7.1$ Hz, 3H), 1.03-0.96 (m, 2H), 0.02 ppm (s, 9H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 177.2, 169.7, 139.1, 114.2, 79.1, 63.4, 50.7, 39.2, 33.8, 30.8, 29.3$ (2C), 29.2, 29.1, 28.9, 25.8, 17.7, 10.3, -1.6 ppm; IR (film): $\tilde{\nu} = 2926, 2855, 1781, 1731, 1640, 1463, 1402, 1341, 1250, 1173, 1038, 971, 909, 859, 838, 759, 696$ cm^{-1} ; MS (EI): m/z (%): 367 (5), 354 (3), 339 (5), 321 (< 1), 309 (10), 264 (2), 243 (3), 204 (11), 186 (8), 143 (10), 95 (7), 73 (100), 55 (11), 41 (11); HRMS (ESI $^+$): calcd for $\text{C}_{21}\text{H}_{38}\text{O}_4\text{Si}+\text{Na}^+$: 405.2432 $[\text{M}+\text{Na}]^+$; found: 405.2434.

(m, 12H), 1.30 (d, $J = 7.1$ Hz, 3H), 1.04-0.96 (m, 2H), 0.04 ppm (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 176.9, 170.9, 139.1, 114.2, 79.6, 64.0, 54.6, 39.9, 34.9, 33.8, 29.3$ (2C), 29.2, 29.1, 28.9, 25.2, 17.5, 14.5, -1.5 ppm.

Acid 23. A solution of TBAF (1 M in THF, 0.60 mL, 0.6 mmol) was added to a solution of compound **22** (76 mg, 0.20 mmol) in THF (2 mL) at 0 °C and the resulting mixture stirred at that temperature for 1 h. The reaction was quenched with H_2O , the product was extracted with EtOAc, the combined organic layers were dried over Na_2SO_4 and evaporated, and the residue was purified by flash chromatography (hexane/EtOAc, 1:1 + 0.1% HOAc) to give acid **23** as a white solid (52 mg, 92%). Mp: 110-111 °C; $[\alpha]_D^{20} = -49$ ($c = 0.12$, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3): $\delta = 9.01$ (brs, 1H), 5.78 (ddt, $J = 17.0, 10.3, 6.7$ Hz, 1H), 5.00-4.87 (m, 2H), 4.40 (dt, $J = 8.7, 5.0$ Hz, 1H), 3.30 (dd, $J = 7.3, 5.2$ Hz, 1H), 2.92 (dq, $J = 7.2, 7.1$ Hz, 1H), 2.04-1.97 (m, 2H), 1.86-1.74 (m, 1H), 1.70-1.58 (m, 1H), 1.56-1.20 (m, 12H), 1.28 ppm (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 177.0, 175.0, 139.1, 114.1, 78.8, 50.3, 39.1, 33.7, 30.8, 29.3$ (2C), 29.2, 29.0, 28.9, 25.8, 10.2 ppm; IR (film): $\tilde{\nu} = 2926, 2855, 1766, 1713, 1694, 1640, 1439, 1381, 1353, 1192, 996, 961, 908, 732$ cm^{-1} ; MS (EI): m/z (%): 264 (10), 246 (18), 209 (12), 191 (10), 177 (7), 163 (13), 150 (100), 109 (31), 95 (48), 81 (62), 67 (56), 55 (81), 41 (98); HRMS (ESI⁺): calcd for $\text{C}_{16}\text{H}_{26}\text{O}_4 + \text{Na}^+$: 305.1723 $[\text{M} + \text{Na}]^+$; found: 305.1723.

(R)-Hept-6-en-2-ol. A solution of 3-butenylmagnesium bromide (1.0 M in THF, 10 mL, 10 mmol) was added dropwise to a suspension of (*R*)-propylene oxide (0.44 g, 7.5 mmol) and CuCN (67 mg, 0.75 mmol) in THF (15 mL) at -78 °C. The stirred mixture was allowed to warm to ambient temperature over 16 h. The reaction was quenched with aq. sat. NH_4Cl , the product extracted with EtOAc, and the combined organic layers were dried over Na_2SO_4 and evaporated. Purification of the residue by flash chromatography (hexane/EtOAc, 10 : 1) provided the title compound as a colorless oil (0.72 g, 84 %). $[\alpha]_D^{20} = -14$ ($c = 0.12$, CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3): $\delta = 5.79$ (ddt, $J = 17.0, 10.3, 6.7$ Hz, 1H), 5.05-4.89 (m, 2H), 3.90-3.70 (m, 1H), 2.12-2.00 (m, 2H), 1.56-1.30 (m, 5H), 1.17 ppm (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 138.7, 114.6, 68.0, 38.7, 33.7, 25.0, 23.5$ ppm; IR (film): $\tilde{\nu} = 3341, 3080, 2968, 2932, 1641, 1459, 1373, 1121, 996, 910$ cm^{-1} ; MS (EI): m/z (%): 113 (< 1), 96 (9), 79 (4), 71 (27), 67 (13), 57 (9), 54 (65), 45 (100), 42 (22); HRMS (CI, *i*-butane): calcd for $\text{C}_7\text{H}_{15}\text{O}^+$: 115.1123 $[\text{M} + \text{H}]^+$; found: 115.1123.

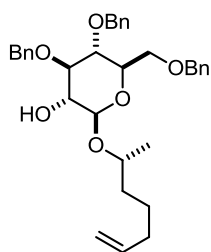


Monosaccharide 26. A solution of imidate **25** (1.3 g, 2.0 mmol)⁵ and (*R*)-hept-6-en-2-ol (**8**, 0.21 g, 1.8 mmol) in a mixture of CH_2Cl_2 and pentane (1:1, 15 mL) was cooled to -20 °C. A solution of $\text{BF}_3 \cdot \text{OEt}_2$ (0.28 g, 2.0 mmol) in CH_2Cl_2 and pentane (1:1, 15 mL) was added dropwise over 2 h and the resulting mixture stirred at that temperature for 3 h. The reaction was quenched with aq. sat. NaHCO_3 and the product extracted with EtOAc.

⁵ A. Fürstner, I. Konetzki, *Tetrahedron Lett.* **1998**, *39*, 5721-5724.

The combined extracts were dried over Na₂SO₄ and evaporated, and the residue purified by flash chromatography (hexane/EtOAc, 10 : 1) to furnish glycoside **26** as a colorless oil (0.88 g, 76%). $[\alpha]_D^{20} = -11$ (c = 0.14, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ = 7.35-7.15 (m, 15H), 5.77 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.00-4.87 (m, 3H), 4.81-4.74 (m, 2H), 4.68-4.52 (m, 4H), 4.35 (d, *J* = 8.0 Hz, 1H), 3.78-3.60 (m, 5H), 3.50-3.40 (m, 1H), 2.10-1.97 (m, 2H), 1.94 (s, 3H), 1.60-1.35 (m, 4H), 1.06 ppm (d, *J* = 6.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 169.4, 138.9, 138.2, 138.0, 128.40, 128.38, 128.32, 128.0, 127.8 (2C), 127.7, 127.6 (2C), 127.5, 114.4, 99.5, 83.1, 78.1, 75.22, 75.20, 75.0, 74.9, 73.6, 73.4, 69.0, 36.4, 33.6, 24.6, 20.9, 19.8 ppm; IR (film): $\tilde{\nu}$ = 3064, 3031, 2865, 1749, 1497, 1454, 1373, 1231, 1057, 909, 736, 698 cm⁻¹; MS (EI): *m/z* (%): 497 (2), 475 (< 1), 383 (9), 277 (7), 181 (5), 127 (3), 91 (100), 55 (9); HRMS (ESI⁺): calcd for C₃₆H₄₄O₇+Na⁺: 611.2979 [M+Na]⁺; found: 611.2979.

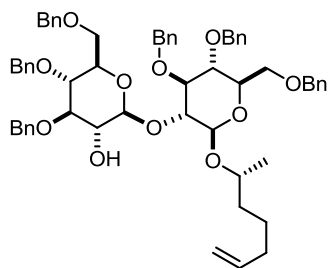
Monosaccharide 27. NaOMe (26 mg, 0.49 mmol) was added to a solution of compound **26** (0.26 g, 0.44 mmol) in MeOH (10 mL). After stirring for 40 h, the reaction



was quenched with aq. sat. NaHCO₃ and the product extracted with EtOAc. The combined organic layers were dried over Na₂SO₄ and evaporated, and the residue purified by flash chromatography (hexane/EtOAc, 5:1) to give product **27** as a colorless oil (0.21 g, 89%). $[\alpha]_D^{20} = -12$ (c = 0.15, CH₂Cl₂);

¹H NMR (400 MHz, CDCl₃): δ = 7.40-7.16 (m, 15H), 5.78 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.02-4.89 (m, 2H), 4.93 (d, *J* = 11.3 Hz, 1H), 4.82 (d, *J* = 10.8 Hz, 1H), 4.81 (d, *J* = 11.3 Hz, 1H), 4.60 (d, *J* = 12.2 Hz, 1H), 4.55 (d, *J* = 13.0 Hz, 1H), 4.54 (d, *J* = 12.2 Hz, 1H), 4.27 (d, *J* = 7.6 Hz, 1H), 3.90-3.88 (m, 1H), 3.74-3.62 (m, 2H), 3.62-3.53 (m, 2H), 3.53-3.40 (m, 2H), 2.26 (brs, 1H), 2.13-1.97 (m, 2H), 1.70-1.39 (m, 4H), 1.15 ppm (d, *J* = 6.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 138.8, 138.7, 138.3, 138.2, 128.39, 128.36, 128.32, 128.0, 127.9, 127.7, 127.64, 127.61, 127.5, 114.5, 100.6, 84.7, 77.6, 75.2, 75.0, 74.9, 74.7, 74.6, 73.5, 69.1, 36.6, 33.6, 24.7, 19.8 ppm; IR (film): $\tilde{\nu}$ = 3453, 3064, 3030, 2908, 2863, 1639, 1496, 1453, 1357, 1208, 1110, 1058, 1027, 909, 734, 696 cm⁻¹; MS (EI): *m/z* (%): 455 (4), 341 (5), 253 (3), 235 (5), 163 (5), 91 (100), 55 (8), 41 (1); HRMS (ESI⁺): calcd for C₃₄H₄₂O₆+Na⁺: 569.2874 [M+Na]⁺; found: 569.2876.

Disaccharide 29. A solution of BF₃·OEt₂ (50 mg, 0.35 mmol) in a mixture of CH₂Cl₂ and pentane (1 : 1, 6 mL) was added dropwise over 2.5 h to a solution

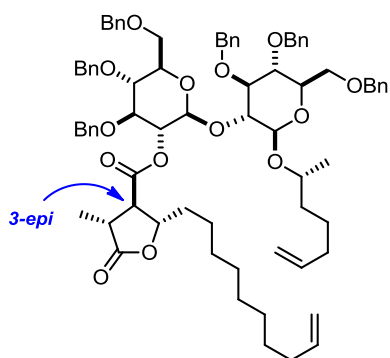


of imidate **25** (0.21 g, 0.33 mmol)⁵ and compound **27** (0.16 g, 0.30 mmol) in a mixture of CH₂Cl₂ and pentane (1:1, 6 mL) at -20 °C. The resulting mixture was stirred at this temperature for 2.5 h before the reaction was quenched with aq. sat. NaHCO₃ and the product extracted with EtOAc. The combined organic layers were dried over Na₂SO₄ and evaporated, and the residue purified by

flash chromatography (hexane/EtOAc, 5:1), providing disaccharide **28** which contained some minor impurities.

This crude material was dissolved in MeOH (5 mL) and NaOMe (0.018 g, 0.33 mmol) was added. After stirring for 40 h, the reaction was quenched with aq. sat. NaHCO₃, the product extracted with CH₂Cl₂, and the combined extracts were dried over Na₂SO₄ and evaporated. Purification of the residue by flash chromatography (hexane/EtOAc, 5:1) afforded disaccharide **29** as a white solid (0.25 g, 83% over both steps). Mp: 93-94 °C; $[\alpha]_D^{20} = -9$ (c = 0.13, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ = 7.42-7.15 (m, 30H), 5.80 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.05-4.91 (m, 3H), 4.90-4.80 (m, 4H), 4.72-4.44 (m, 9H), 3.90-3.80 (m, 1H), 3.80-3.40 (m, 13H), 2.13-1.98 (m, 2H), 1.60-1.38 (m, 4H), 1.16 ppm (d, *J* = 6.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 138.9 (2C), 138.3, 138.19, 138.17, 137.8, 137.3, 128.6, 128.5, 128.32, 128.31, 128.28, 128.23, 128.18, 128.13, 128.09, 127.9 (2C), 127.82, 127.80, 127.60, 127.58, 127.53, 127.48, 127.43, 114.4, 104.2, 100.6, 84.0, 83.9, 81.0, 78.7, 77.1, 77.0, 76.7, 76.4, 75.6, 75.1, 75.0, 74.84, 74.81 (2C), 73.5, 73.4, 69.1, 68.7, 36.5, 33.7, 24.5 ppm; IR (film): $\tilde{\nu} = 3420, 3064, 3031, 2900, 1497, 1453, 1356, 1212, 1068, 1027, 908, 749, 696$ cm⁻¹; HRMS (ESI⁺): calcd for C₆₁H₇₀O₁₁+Na⁺: 1001.4810 [M+Na]⁺; found: 1001.4815.

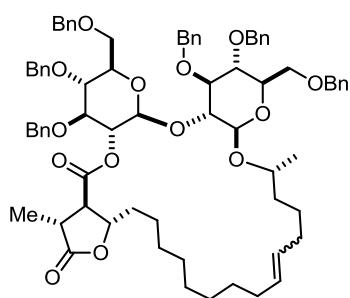
Compound 3-*epi*-30. DMAP (13 mg, 0.11 mmol) was added to a solution of acid **23** (28 mg,



0.10 mmol) in CH₂Cl₂ (1.5 mL) and the resulting solution stirred for 5 min before *N,N'*-diisopropylcarbodiimide (DIC, 14 mg, 0.11 mmol) was introduced. After stirring for 10 min, disaccharide **29** (58 mg, 59 μmol) was added and the resulting mixture stirred at ambient temperature for 24 h. The reaction was quenched with H₂O, the product extracted with a mixture of EtOAc and hexane, the combined organic layers were dried over Na₂SO₄ and evaporated, and the residue was purified by flash chromatography

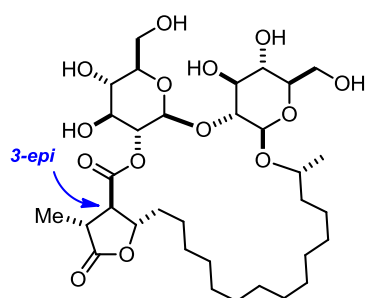
(hexane/EtOAc, 8:1) to give 3-*epi*-**30** (71 mg, 97%) as a colorless oil. A minor diastereomer (derived from cyanohydrin **15** of only 89% ee) was not separable at this stage by flash chromatography. $[\alpha]_D^{20} = -15$ (c = 0.14, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): δ = 7.37-7.00 (m, 30H), 5.77 (ddt, *J* = 16.8, 10.3, 6.6 Hz, 1H), 5.76 (ddt, *J* = 16.8, 10.4, 6.5 Hz, 1H), 5.08 (dd, *J* = 9.4, 8.1 Hz, 1H), 5.02-4.68 (m, 10H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.59-4.49 (m, 6H), 4.44 (d, *J* = 7.3 Hz, 1H), 4.33-4.24 (m, 1H), 3.90-3.42 (m, 11H), 3.40-3.33 (m, 1H), 2.27 (dd, *J* = 11.2, 9.2 Hz, 1H), 2.18 (dq, *J* = 11.2, 6.6 Hz, 1H), 2.08-1.93 (m, 4H), 1.75-1.63 (m, 1H), 1.60-1.10 (m, 17H), 1.12 (d, *J* = 6.2 Hz, 3H), 1.01 ppm (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 176.9, 168.8, 139.1, 138.8, 138.3, 138.2, 137.91, 137.86, 137.8, 137.6, 128.5, 128.4, 128.3 (4C), 127.9 (3C), 127.8 (2C), 127.7, 127.6, 127.57 (3C), 127.5, 127.1, 114.5, 114.1, 99.8, 99.3, 84.8, 82.9, 80.3, 78.8, 78.2, 77.9, 75.8, 75.3, 75.0, 74.83, 74.79, 74.6, 74.5, 74.4, 73.6, 73.5, 68.9, 68.4, 53.5, 38.4, 36.6, 35.3, 33.8, 33.6, 29.5, 29.4 (2C), 29.1, 28.9, 25.7, 24.7, 19.5, 14.7 ppm; IR (film): $\tilde{\nu} = 3063, 3030, 2926, 2856, 1779, 1749, 1640, 1497, 1454, 1360, 1064, 1027, 910, 735, 967$ cm⁻¹; HRMS (ESI⁺): calcd for C₇₇H₉₄O₁₄+Na⁺: 1265.6536 [M+Na]⁺; found: 1265.6537.

3-*epi*-Gobienine A (3-*epi*-1). Complex **31** (2.7 mg, 2.9 μmol)⁶ was added to a solution of 3-*epi*-**30** (36 mg, 29 μmol) in CH_2Cl_2 (20 mL) and the resulting mixture stirred at 40 °C for 14 h. After reaching room temperature, the solvent was evaporated and the residue purified by flash chromatography (hexane/EtOAc = 5:1 + 0.1% Et_3N) to afford cycloalkene **3-*epi*-32** as an *E/Z*-mixture (32 mg, 91%).



After reaching room temperature, the solvent was evaporated and the residue purified by flash chromatography (hexane/EtOAc = 5:1 + 0.1% Et_3N) to afford cycloalkene **3-*epi*-32** as an *E/Z*-mixture (32 mg, 91%). $[\alpha]_D^{20} = -22$ ($c = 0.09$, CH_2Cl_2); IR (film): $\tilde{\nu} = 2926, 2855, 1779, 1752, 1497, 1454, 1360, 1249, 1067, 1028, 735, 697 \text{ cm}^{-1}$;

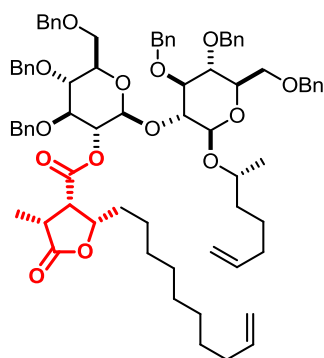
HRMS (ESI^+): calcd for $\text{C}_{75}\text{H}_{90}\text{O}_{14}+\text{Na}^+$: 1237.6223 $[\text{M}+\text{Na}]^+$; found: 1237.6217. This product mixture was used in the next step without further characterization.



A mixture comprising cycloalkene **3-*epi*-32** (7.1 mg, 5.8 μmol) and Pd/C (10% w/w, 3.0 mg) in MeOH (1 mL), EtOAc (1 mL) and HCO_2H (0.05 mL) was stirred under H_2 atmosphere (1 atm, balloon) for 18 h at ambient temperature. The catalyst was then filtered off through a pad of Celite, the filtrate was evaporated and the residue purified by flash chromatography ($\text{CH}_2\text{Cl}_2/\text{MeOH}$, 5:1) to afford **3-*epi*-1** as a white solid (3.6 mg, 91%).

$[\alpha]_D^{20} = -28$ ($c = 0.06$, MeOH); IR (film): $\tilde{\nu} = 3358, 2924, 2854, 1747, 1665, 1570, 1457, 1406, 1378, 1257, 1187, 1068, 1031, 896, 721 \text{ cm}^{-1}$; HRMS (ESI^+): calcd for $\text{C}_{33}\text{H}_{56}\text{O}_{14}+\text{Na}^+$: 699.3562 $[\text{M}+\text{Na}]^+$; found: 699.3559. For the NMR data, see Table S4.

Compound 30. For the success of the reaction, it was important to use freshly distilled CH_2Cl_2 containing < 1 ppm of water (Karl Fischer titration).



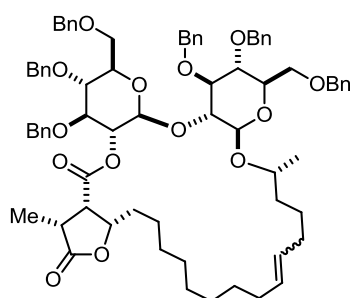
Acid **23** (33.0 mg, 117 μmol) was transferred into a Schlenk flask using dry toluene. The solvent was evaporated in vacuo before a solution of DMF in CH_2Cl_2 (2 μM , 2.8 mL) was added. Oxalyl chloride (38 μL , 0.47 mmol) was introduced and the solution stirred for 3 h before the solvent and the excess reagent were evaporated in vacuo.

In a separate flask, disaccharide **29** (76 mg, 77 μmol) was dissolved in dry toluene and the solvent removed in vacuo to co-evaporate traces of water. The dried material was dissolved in CH_2Cl_2 (0.3 mL) and the resulting solution added to the solid acid chloride (rinsing the flask with CH_2Cl_2 , 3 x 0.2 mL). The mixture was cooled to 0 °C before triethylamine (65 μL , 0.47 mmol) was added, and stirring was continued for 2 h at this temperature. For work up, sat. aq. NaHCO_3 was introduced, the mixture extracted with ethyl acetate (5x), the combined organic layers were dried over Na_2SO_4 and the solvents evaporated. The residue was purified by flash chromatography (silica of 15-40 μm ,

⁶ A. Fürstner, O. Guth, A. Düffels, G. Seidel, M. Liebl, B. Gabor, R. Mynott, *Chem. Eur. J.* **2001**, *7*, 4811-4820.

hexanes/ethyl acetate 90/10 → 80/20) to give ester **3-epi-30** (21 mg, 21%) as a clear oil, several mixed fractions, and a fraction of pure diene **30**. The mixed fractions were combined and re-subjected to flash chromatography on silica (silica of 15-40 μm, hexanes/acetone 95/5 → 90/10) to afford a second crop of product **30** as a clear oil (64 mg, 66%, combined yield). The product contained a diastereomeric impurity, which originates from cyanohydrin **15** used as the starting material that had only been 89% optically pure; this by-product was removed after the RCM step (see below). $[\alpha]_D^{20} = -34$ ($c = 1.0$, CH_2Cl_2); $^1\text{H NMR}$ (600 MHz, CDCl_3): $\delta = 7.39 - 7.17$ (m, 28H), 7.12 - 7.06 (m, 2H), 5.80 (ddt, $J = 16.9, 10.2, 6.7$ Hz, 1H), 5.74 (ddt, $J = 17.0, 10.2, 6.8$ Hz, 1H), 5.10 (dd, $J = 9.4, 7.6$ Hz, 1H), 4.98 (dq, $J = 17.2, 1.8$ Hz, 1H), 4.96 (d, $J = 7.7$ Hz, 1H), 4.94 (dq, $J = 17.1, 1.7$ Hz, 1H), 4.92 (ddt, $J = 10.2, 2.2, 1.2$ Hz, 1H), 4.89 (d, $J = 12.0$ Hz, 1H), 4.89 (d, $J = 10.4$ Hz, 1H), 4.90 - 4.87 (m, 1H), 4.79 (d, $J = 10.6$ Hz, 1H), 4.76 (d, $J = 10.8$ Hz, 1H), 4.71 - 4.66 (m, 2H), 4.65 - 4.53 (m, 6H), 4.30 (d, $J = 7.5$ Hz, 1H), 4.30 (ddd, $J = 9.4, 5.2, 4.2$ Hz, 1H), 3.87 (t, $J = 9.3$ Hz, 1H), 3.85 (dd, $J = 8.8, 7.6$ Hz, 1H), 3.79 - 3.66 (m, 5H), 3.65 - 3.56 (m, 3H), 3.40 - 3.33 (m, 2H), 3.20 (dd, $J = 7.5, 5.1$ Hz, 1H), 2.84 (qi, $J = 7.2$ Hz, 1H), 2.07 - 1.90 (m, 4H), 1.71 (dddd, $J = 14.3, 9.6, 9.1, 5.5$ Hz, 1H), 1.59 - 1.02 (m, 15H), 1.27 (d, $J = 7.1$ Hz, 3H), 1.15 (d, $J = 6.2$ Hz, 3H), 1.00 - 0.80 ppm (m, 2H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) $\delta = 176.9, 168.4, 139.2, 139.0, 138.2(4), 138.1(9), 138.1(2), 138.0(5), 137.9, 137.6, 128.6, 128.4(2), 128.3(9), 128.3(2), 128.3(0), 128.2, 128.0, 127.9(1), 127.8(8), 127.8(2), 127.6, 127.5(2), 127.4(9), 127.2, 126.3, 114.3, 114.1, 99.9, 98.6, 86.0, 81.8, 79.1, 78.4, 78.0, 76.2, 75.8, 75.4, 75.2, 74.8(9), 74.8(7), 74.8, 73.7, 73.6, 73.5, 73.2, 68.8, 68.1, 50.5, 39.3, 36.5, 33.8, 33.6, 30.6, 29.5, 29.2, 29.0, 28.9, 28.7, 26.1, 24.7, 20.0, 10.8$ ppm; IR (film): $\tilde{\nu} = 2926, 2856, 1780, 1746, 1639, 1497, 1454, 1360, 1181, 1149, 1069, 1027, 909, 734, 697$ cm^{-1} ; MS (ESI⁺): m/z : 1265 [M+Na]⁺, 644.3 [M+2Na]²⁺; HRMS (ESI⁺): calcd for $\text{C}_{77}\text{H}_{94}\text{O}_{14}+\text{Na}^+$: 1265.6536 [M+Na]⁺; found: 1265.6541.

Compound 32. Complex **31** (2.8 mg, 3.0 μmol) was added to a solution of diene **30** (37 mg,

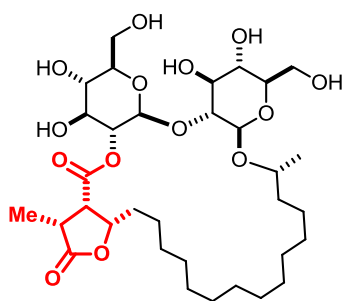


30 μmol) in CH_2Cl_2 (21 mL) and the resulting mixture was stirred at reflux temperature for 16 h. After reaching ambient temperature, the solvent was evaporated and the residue purified by flash chromatography (silica of 15-40 μm, hexanes/ethyl acetate 90/10 → 85/15) to yield product **32** as a clear oil (30 mg, 83%, *E/Z* mixture). It is of note that the minor diastereomers originating from the imperfect enantiomeric purity of the

cyanohydrin **15** (89% *ee*) were removed at this point (2 mg, 5%). $[\alpha]_D^{20} = -26$ ($c = 1.0$, CH_2Cl_2); $^1\text{H NMR}$ (600 MHz, CDCl_3): $\delta = 7.45 - 7.08$ (m, 30H), 5.44 - 5.22 (m, 2H), 5.13 - 4.84 (m, 5H), 4.84 - 4.76 (m, 1H), 4.71 - 4.54 (m, 8H), 4.53 - 4.38 (m, 1H), 4.38 - 4.27 (m, 1H), 4.01 - 3.51 (m, 10H), 3.45 - 3.37 (m, 1H), 3.35 - 3.12 (m, 2H), 2.78 - 2.64 (m, 1H), 2.27 - 1.79 (m, 6H), 1.79 - 1.69 (m, 1H), 1.65 - 1.21 (m, 15H), 1.23 - 1.13 (m, 3H), 1.09 ppm (d, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): $\delta = 177.2, 177.1, 168.1, 168.0, 138.6(5), 138.6(2)$ *br*, 138.3(0) *br*, 138.2(8), 138.2(2), 138.1(8), 138.1(3) *br*, 138.0(5) *br*, 137.9(9) *br*,

137.8(9), 137.6(5), 137.6(2), 131.0 *br*, 130.6, 130.1, 129.9, 128.4, 128.3(4), 128.3(2), 128.2(9), 128.2(5), 128.1, 128.0, 127.9, 127.8(8), 127.7(9), 127.7(5), 127.7(1), 127.7(0), 127.6(2), 127.5(8), 127.5, 127.4(9), 127.4(7) *br*, 127.4(4) *br*, 127.0(6) *br*, 127.0(3) *br*, 126.4, 126.3, 100.6 *br*, 99.8 *br*, 98.0, 97.7, 85.5 *br*, 85.2 *br*, 81.4, 79.9, 79.7, 78.6, 78.5, 78.4, 78.3, 75.3, 75.2, 74.9(8), 74.9(5), 74.9(3), 74.8(6), 74.8(4), 74.4, 74.3, 74.2, 74.0, 73.5, 73.4, 73.3, 72.7, 72.6 *br*, 68.9, 68.8, 67.8 *br*, 67.6 *br*, 51.3, 51.1 *br*, 39.1, 39.0, 35.9, 35.5 *br*, 32.4, 32.0, 30.6, 29.5 *br*, 29.4, 29.0(7), 29.0(2) *br*, 28.9, 28.5, 27.9, 27.6, 26.8, 26.3, 26.1 *br*, 24.2 *br*, 24.0 *br*, 20.4 *br*, 19.7 *br*, 10.5, 10.3 ppm; IR (film): $\tilde{\nu}$ = 2924, 2855, 1782, 1744, 1497, 1454, 1360, 1183, 1069, 1027, 735, 697 cm^{-1} ; HRMS (ESI⁺): calcd for C₇₅H₉₀O₁₄+Na⁺: 1237.6223 [M+Na]⁺; found: 1237.6229.

Nominal Gobienine A (1). Palladium on charcoal (10% *w/w*, 6.7 mg, 6.3 μmol) was added to



a solution of olefin **32** (15.2 mg, 12.5 μmol) in a mixture of methanol (2.1 mL), ethyl acetate (2.1 mL) and formic acid (105 μL). The suspension was stirred for 27 h under an atmosphere of H₂ (1 atm, balloon) before the catalyst was filtered off through a pad of Celite which was carefully rinsed with methanol. The combined filtrates were evaporated and the residue purified by flash chromatography (CH₂Cl₂/methanol,

90/10) to afford nominal gobienine A **1** (7.9 mg, 93%) as a white powder. $[\alpha]_D^{20} = -37$ ($c = 0.66$, CH₂Cl₂); IR (film): $\tilde{\nu}$ = 3443, 2923, 2854, 1770, 1739, 1378, 1338, 1224, 1194, 1079, 1033, 1005, 992 cm^{-1} ; HRMS (ESI⁺): calcd for C₃₃H₅₆O₁₄+Na⁺: 699.3562 [M+Na]⁺; found: 699.3558. For the NMR data, see Table S3.

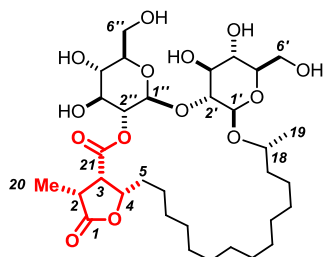


Table S3. ^1H NMR and ^{13}C NMR data of nominal gobienine A (**1**) in $\text{C}_5\text{D}_5\text{N}/\text{CD}_3\text{OD}$ (1:1, v/v);

Numbering scheme as shown in the Insert

The shifts of ^1H NMR signals, for which no multiplicity is given, were extracted from 2D spectra

^{13}C	^{13}C NMR (150 MHz) ^[a]	^1H	^1H NMR (600 MHz) ^[b]
1	179.7	-	-
2	40.4	2	3.04 qi (7.0)
3	52.1 broad	3	3.49 dd (6.9, 5.1)
4	81.2	4	4.47 dt (5.2, 7.0)
5	31.6	5a	1.95 m
		5b	
6	26.9	6a	1.45
		6b	1.41
7	30.0	7a	1.26
		7b	
8	29.5 (broad), 29.4, 29.1 (broad), 28.9, 28.6(5), 28.6(2) (broad), 28.5(5) (broad), 28.2(9) (broad) not individually assigned	8a/b	1.24 – 1.18
9		9a/b	
10		10a/b	
11		11a/b	
12		12a/b	
13		13a/b	
14		14a/b	
15		15a/b	
16	25.1	16a	1.38
		16b	1.32
17	37.7 broad	17a	1.57 m
		17b	1.32
18	76 very broad	18	3.90
19	20 broad	19	1.14 d (6.2)
20	11.0	20	1.42 d (7.1)
21	170.0	-	-
1'	101.5 broad	1'	4.54 d (7.0)
2'	80 very broad	2'	3.79
3'	78.2 broad	3'	3.81 t (9.1)
4'	71.7	4'	3.64 dd (9.5, 8.8)
5'	78.5	5'	3.44
6'	62.7	6'a	4.09 dd (11.9, 2.3)
		6'b	3.91 dd (12.0, 5.5)
1''	100.9 broad	1''	5.33
2''	77.1 broad	2''	5.07 dd (9.4, 8.2)
3''	77.0 broad	3''	3.67 t (9.2)
4''	72.2 broad	4''	3.72 t (9.1)
5''	78.7	5''	3.44
6''	62.6	6''a	4.06 dd (11.9, 2.3)
		6''b	3.88 dd (12.0, 5.2)

[a] δ_{C} (ppm); [b] δ_{H} (ppm), multiplicity, coupling constant J (Hz).

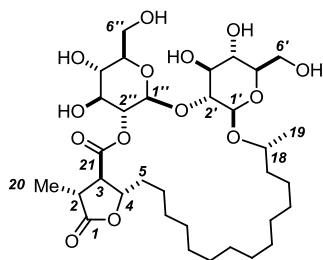


Table S4. ^1H NMR and ^{13}C NMR data of 3-*epi*-1 in $\text{C}_5\text{D}_5\text{N}/\text{CD}_3\text{OD}$ (1:1, v/v).

Numbering scheme as shown in the Insert.

The shifts of ^1H NMR signals, for which no multiplicity is given, were extracted from 2D spectra

^{13}C	^{13}C NMR (150 MHz) ^[a]	^1H	^1H NMR (600 MHz) ^[b]
1	178.6	-	-
2	40.4	2	3.16 dq (11.4, 7.1)
3	54.9	3	2.87 dd (11.4, 9.4)
4	80.0	4	4.94 dt (3.4, 9.1)
5	36.2	5a	1.96
		5b	1.64 m
6	26.6	6a	1.42 m
		6b	
7	29.8	7a	1.26
		7b	
8	29.7, 29.5, 28.7(8), 28.7(6), 28.7(4), 28.7(3), 28.4, 28.0 not individually assigned	8a/b	1.26 – 1.18
9			
10			
11			
12			
13			
14			
15			
16	25.1	16a	1.34
		16b	
17	38.0	17a	1.50
		17b	1.34
18	74.5	18	3.91
19	20.1	19	1.12 d (6.2)
20	15.2	20	1.25 d (7.1)
21	171.2	-	-
1'	101.3	1'	4.53 d (7.6)
2'	82.9	2'	3.55
3'	77.5	3'	3.71 t (9.0)
4'	72.3	4'	3.55
5'	78.2	5'	3.45 ddd (9.7, 6.2, 2.3)
6'	63.3	6'a	4.12 dd (11.6, 2.3)
		6'b	3.85 dd (11.7, 6.3)
1''	102.0	1''	5.17 d (8.1)
2''	77.4	2''	5.21 dd (9.1, 8.3)
3''	76.4	3''	3.82 t (9.0)
4''	71.4	4''	3.88 t (9.3)
5''	78.7	5''	3.53
6''	62.1	6''a	4.09 dd (11.9, 2.3)
		6''b	4.01 dd (11.9, 4.1)

[a] δ_{C} (ppm); [b] δ_{H} (ppm), multiplicity, coupling constant J (Hz).

