Supplementary data

First Enantioselective Total Synthesis of Altersolanol A

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S1. General methods for chemical synthesis procedures

Unless specified, the reactions were carried out by standard Schlenk-technique under dry Ar/N₂ and magnetic stirring. All reagents were used as purchased from commercial suppliers without further purification. Glassware was oven-dried at 120 °C overnight. Solvents were dried and purified by conventional methods prior to use. THF and dichloromethane were used directly from a MB SPS-800 (M Braun). Solvents for chromatography (petroleum ether, ethyl acetate, dichloromethane and methanol) were distilled prior to use. Column chromatography was performed on silica gel 60, 0.040-0.063 nm (230-400 mesh). Thin layer chromatography (TLC) was performed on silica gel POLY-GRAM® SIL G/U254 plates (Macherey-Nagel) and was visualized by UV light (254/366 nm UV-lamp) and cerium-molybdate-solution [10 g Ce(SO₄)₂·4 H₂O, 25 g phosphomolybdic acid, 60 mL conc. H₂SO₄, 940 mL H₂O]. Preparative TLC was performed on precoated TLC plates SIL G-100 UV₂₅₄ (20 cm x 20 cm) (Macherey-Nagel). NMR spectra were recorded on a Bruker Advance DRX/600 spectrometer. ¹H-NMR analysis were admitted at 600 MHz and ¹³C-NMR analysis were measured proton decoupled at 151 MHz. Chemical shifts are reported in ppm relative to residual solvent signals (CDCl₃: 7.26 ppm for ¹H-NMR and 77.16 ppm for ¹³C-NMR, DMSO-d₆: 2.50 ppm for ¹H-NMR and 39.52 ppm for ¹³C-NMR, MeOD-d₄: 3.31 ppm for ¹H-NMR and 49.0 ppm for ¹³C-NMR). The multiplicity in NMR spectra is given in the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. The enantiomeric excess of the products were determined by HPLC (DIONEX GmbH, Chiralcel ODH, Chiralpak IA, Chiralpak IB, Chiralpak IC columns, flow 0.5 mL min⁻¹, 25°C). High resolution mass spectra were recorded on FT-IR-MS using electrospray ionization (ESI⁺) at the Heinrich Heine University Dusseldorf (Applied Biosystems/ MDS SCIEXQ Model Trap 4000).

GC-MS analysis was performed on a HP 6890 gas chromatograph (Hewlett Packard Inc) equipped with a HP 6890 series injector and a split injection system, fitted with a HP- ms column (30 m x 0.25 mm, 0.25 µm) and coupled with a mass selective detector 5973 mass spectrometer. Infrared data were recorded on a Perkin-Elmer SpectrumOne instrument and Perkin-Elmer SpectrumTwo instrument as neat samples. Melting points were measured on a Büchi Melting Point B-540 instrument. Optical rotations were recorded on an A. Krüss Optronic P8000 polarimeter.
S2. Compound characterization

S2.1 Synthesis procedure of the catalyst (S)- and (R)-L2

![Scheme 1: Synthetic route of 3,3'-Ph2-BINOL (S)- and (R)-L2.](image)

(R)-2,2'-Dimethoxy-1,1'-binaphthalene (21)

In a 500 mL flask a solution of (R)-BINOL (20) (9.00 g, 31.4 mmol), Mel (9.78 mL, 157 mmol) and K2CO3 (14.8 g, 107 mmol) in acetone (290 mL) was refluxed under nitrogen atmosphere for 20 h. After full conversion the reaction mixture was cooled to ambient temperature and volatile compounds were removed in vacuo. The resulting white solid was partitioned between water and dichloromethane (200 mL). The layers were then separated, and the aqueous layer was further extracted with dichloromethane (3 x 100 mL). The combined organic extracts were washed with brine (1 x 100 mL) and dried over anhydrous MgSO4, filtered and concentrated under reduced pressure. The crude solid was used without any further purification. The product 21 was isolated as a white crystalline solid (9.10 g, 100%). The spectroscopic data are in agreement with previously reported literature values.1
Rt = 0.5 (PE/EE, 80:20); mp 232 °C (in PE); \([\alpha]_{D}^{20} = +50.7\) (c = 1.00, CHCl3). δH (600 MHz, CDCl3) 3.77 (s, 6H, OCH3) 7.11 (d, J 8.4 Hz, 2H, arom. H), 7.19-7.25 (m, 2H, arom. H), 7.30-7.34 (m, 2H, arom. H), 7.47 (d, J 9.0 Hz, 2H, arom. H), 7.87 (d, J 8.2 Hz, 2H, arom. H), 7.98 (d, J 9.0 Hz, 2H, arom. H). δC (151 MHz, CDCl3) 57.1 (OCH3), 114.1 (arom. CH), 119.8 (arom. CH), 123.7 (arom. CH), 125.4 (arom. CH), 126.4 (arom. CH), 128.1 (arom. CH), 129.4 (arom. CH), 129.5 (arom. CH), 134.2 (arom. CH), 155.1 (arom. CH) ppm; \(\nu_{\text{max}}/\text{cm}^{-1}\) 3075, 3048, 2958, 2931, 2838, 1615, 1590, 1505, 1461, 1322, 1263, 1249, 1148, 1132, 1090, 1063, 1019, 896, 809, 781, 746, 679, 595, 519; GC-MS (EI, 70eV): m/z (%) = 314 (100) [M+], 268 (64), 239 (26), 120 (31).

(R)-3,3’-Dibromo-2,2’-dimethoxy-1,1’-binaphthalene (22)

In a 1 L Schlenk-flask TMEDA (10.9 mL, 72.5 mmol) was dissolved in ether (540 mL) and n-BuLi (c = 1.6 M in hexane, 37.8 mL, 94.6 mmol) was added at room temperature. The solution was stirred for 15 min and (R)-2,2’-Dimethoxy-1,1’-binaphthalene (21) (9.91 g, 31.5 mmol) was then added in one portion and stirred overnight. The resulting brownish suspension was cooled to -78 °C and bromine (19.4 mL, 378 mmol) was added over a period of 15 min. The reaction mixture was warmed to room temperature and stirred for additional 4 h. A saturated Na2SO3 solution (500 mL) was added cautiously and the reaction was stirred for another 4 h. The reaction was diluted with ether (200 mL) then water (200 mL) and the organic layer was washed with brine (100 mL), dried over MgSO4 and concentrated under reduced pressure. The product 22 was purified via column chromatography (PE:EE = 90:10) and could be isolated as a light-yellow solid (8.94 g, 60%). The spectroscopic data are in agreement with previously reported literature values.2

Rt = 0.6 (PE/EE, 90:10); mp 173 °C (in PE); \([\alpha]_{D}^{25} +11.4\) (c 1.01 in CHCl3). δH (600 MHz, CDCl3) 3.51 (s, 6H, OCH3) 7.08 (d, J 8.6 Hz, 2H, arom. H), 7.26-7.29 (m, 2H, arom. H), 7.41-7.44 (m, 2H, arom. H), 7.82 (d, J 8.2 Hz, 2H, arom. H), 8.27 (s, 2H, arom. H) ppm; δC (151 MHz, CDCl3) 61.2
(OCH$_3$)$_3$, 117.7 (arom. CH), 125.9 (arom. CH), 126.0 (arom. CH), 126.7 (arom. CH), 127.0 (arom. CH), 127.3 (arom. CH), 131.6 (arom. CH), 133.2 (arom. CH), 133.3 (arom. CH), 152.7 (arom. CH) ppm; $\nu_{\text{max}}$/cm$^{-1}$ 2939, 1570, 1493, 1456, 1388, 1352, 1233, 1138, 1045, 1021, 976, 900, 878, 850, 806, 751, 675, 605, 584, 516, 466; GC-MS (EI, 70eV): m/z (%) = 472 (100) [M$^+$], 426 (21), 361 (23), 239 (27), 156 (36), 118 (48), 112 (35).

(R)-2,2'-Dimethoxy-3,3'-diphenyl-1,1'-binaphthalene (23)

In a 250 mL Schlenk-flask (R)-3,3'-Dibromo-2,2'-dimethoxy-1,1'-binaphthalene (22) was dissolved in 1,2-dimethoxyethane (94 mL) and Pd(PPh$_3$)$_4$ (1.44 g, 1.24 mmol) was added in one portion thereafter. After the reaction mixture was stirred for 30 min phenylboronic acid (5.56 g, 45.5 mmol) and aqueous NaHCO$_3$ (10.4 g in 122 ml water) were added. The resulting suspension was then refluxed for 18 h. The conversion was measured via $^1$H-NMR. The reaction mixture formed a colourless solution with a brownish residue and was cooled to room temperature. Once cool ethyl acetate (100 mL) was added and layers were partitioned. The organic layer was washed with brine (50 mL), dried with MgSO$_4$, filtered and concentrated under reduced pressure. The crude product was then transferred to a silica column (PE:EE = 97:3) and product 23 could be isolated as a colourless solid (9.42 g, 97%). The spectroscopic data are in agreement with previously reported literature values.$^3$

R$_f$ = 0.4 (PE/EE, 97:3); mp 99 °C (in PE); [$\alpha$]$^D_{20}$ -0.3 (c 1.00 in CHCl$_3$); $\delta$H (600 MHz, CDCl$_3$) 3.19 (s, 6H, OCH$_3$), 7.23-7.28 (m, 6H, arom. H), 7.37-7.43 (m, 4H, arom. H), 7.44-7.47 (m, 4H, arom. H), 7.76-7.79 (m, 4H, arom. H), 7.92 (d, $J$ 8.2 Hz, 2H, arom. H), 7.98 (s, 2H, arom. H) ppm; $\delta$C (151 MHz, CDCl$_3$) 60.7 (OCH$_3$), 125.1 (arom. CH), 126.0 (arom. CH), 126.1 (arom. CH), 126.4 (arom. CH), 127.4 (arom. CH), 128.2 (arom. CH), 128.5 (arom. CH), 129.5 (arom. CH), 130.7
(arom. CH), 131.0 (arom. CH), 133.8 (arom. CH), 135.2 (arom. CH), 139.1 (arom. CH), 154.3 (arom. CH) ppm; \( \nu_{\text{max}}/\text{cm}^{-1} \): 3056, 2931, 1492, 1459, 1443, 1403, 1350, 1248, 1216, 1143, 1016, 890, 749, 697, 620, 541, 508; GC-MS (EI, 70eV): \( m/z \) (%) = 466 (100) [M\(^+\)], 420 (27).

(R)-3,3'-Diphenyl-[1,1'-binaphthalene]-2,2'-diol ((R)-L2)

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\text{In a 500 mL Schlenk-flask 23 (9.42 g, 20.2 mmol) was dissolved in CH}_2\text{Cl}_2 (280 mL) and BBr}_3 (1M solution in \text{CH}_2\text{Cl}_2, 72.7 mL, 72.7 mmol) at \text{-78 °C was added. The reaction mixture was warmed to room temperature, stirred for 16h and quenched with water (170 mL) with external ice bath cooling. The organic phase was separated and the aqueous layer was extracted with CH}_2\text{Cl}_2 (3 x 100 mL). The combined organic layers were washed with brine (100 mL), dried with MgSO}_4, filtered and concentrated }_{\text{in vacuo}}. \text{ The crude product was purified by column chromatography (PE:EE = 90:10) and product (R)-L2 could be isolated as a colourless solid (8.08 g, 91%, 99.5:0.5 er). The spectroscopic data are in agreement with previously reported literature values.}^3

R\(_f\) = 0.3 (PE/EE, 90:10). mp 196 °C (in PE); [\( \alpha \)]\(_D\)\(^{24}\) +73.1 (c 1.00 in CHCl\(_3\), 99:1 er), \( \delta \)H (600 MHz, CDCl\(_3\)) 5.35 (s, 2H, 2-OH), 7.24 (d, \( J \) 8.6 Hz, 2H, arom. H), 7.31-7.35 (m, 4H, arom. H), 7.38-7.43 (m, 4H, arom. H), 7.48-7.52 (m, 4H, arom. H), 7.74 (d, \( J \) 7.5 Hz, 2H, arom. H), 7.93 (d, \( J \) 8.0 Hz, 2H, arom. H), 8.03 (s, 2H, arom. H) ppm; \( \delta \)C (151 MHz, CDCl\(_3\)) 112.6 (arom. CH), 124.1 (arom. CH), 124.5 (arom. CH), 127.5 (arom. CH), 127.9 (arom. CH), 128.6 (arom. CH), 128.6 (arom. CH), 129.6 (arom. CH), 129.8 (arom. CH), 130.9 (arom. CH), 131.5 (arom. CH), 133.1 (arom. CH), 137.7 (arom. CH), 150.3 (arom. CH) ppm; \( \nu_{\text{max}}/\text{cm}^{-1} \): 3484, 3392, 3056, 1624, 1495, 1426, 1382, 1367, 1318, 1235, 1128, 1077, 894, 786, 766, 748, 702, 684, 617, 552, 492; GC-MS (EI, 70eV): \( m/z \) (%) = 472 (100) [M\(^+\)], 426 (21), 361 (23), 239 (27), 156 (36), 118 (48), 112 (35). HRMS (ESI, positive-ion): calc.: 439.1698 (C\(_{32}\)H\(_{23}\)O\(_2\)) [(M+H\(^+\)]\(^\dagger\)), found: 439.1688; HPLC column:
Chiralpak IC (250 mm· 46 mm, Fa. Daicel); solvent: heptane/2-propanol = 90:10; flowrate: 0.5 mL/min, detection: 249 nm; \( t_R \) [(R)-2] 16.3 min; \( t_R \) [(S)-2] 10.5 min.

### S2.2 Synthesis of dienophile 5d

![Scheme 2: Synthesis of dienophile 5d.](image)

**Methyl (Z/E)-3-methoxybut-2-enoate (26)**

In a 250 mL Schlenk-flask methyl acetoacetate (24) (55.6 mL, 517 mmol), trimethyl orthoformate (25) (56.6 mL, 517 mmol) and a catalytic amount (18 drops) of conc. \( \text{H}_2\text{SO}_4 \) were added and the reaction mixture was stirred for 18 h at room temperature. GC-MS was used for reaction monitoring and after full conversion, 12 drops of quinoline were added and stirred for 30 min. Afterwards the crude liquid was purified by vacuum distillation and product 26 was isolated as a colourless liquid (61.6 g, 92%). The spectroscopic data are in agreement with previously reported literature values.4

bp 87-90 °C (69 mbar); \( \delta \)H (600 MHz, CDCl\(_3\)) 2.28 (s, 3H, 4-H), 3.62 (s, 3H, 3-OCH\(_3\)), 3.67 (s, 3H, 1-OCH\(_3\)), 5.01 (s, 1H, 2-H) ppm; \( \delta \)C (151 MHz, CDCl\(_3\)) 19.0 (C-1), 50.9 (1-OCH\(_3\)), 55.5 (3-OCH\(_3\)), 90.6 (C-2), 168.4 (C-1), 173.4 (C-3) ppm; \( \nu_{\text{max}}/\text{cm}^{-1} \) 2950, 2844, 1711, 1623, 1436, 1393, 1349, 1276, 1228, 1193, 1136, 1049, 927, 815, 741; GC-MS (EI, 70 eV): \( t_R \) = 8.3 min, m/z (%) 130 (26) [(M+H\(^+\)], 99 (100) [(M-CH\(_3\))]\(^+\)], 69 (13), 59 (29) [(M-C\(_4\)H\(_7\)O)]\(^+\)].
((1,3-Dimethoxybuta-1,3-dien-1-yl)oxy)trimethylsilane 27

In a 50 mL Schlenk-tube diisopropylamine (3.24 mL, 23.0 mmol) was dissolved in THF (13 mL), cooled to -78 °C and n-BuLi (c = 2.5 M in hexane, 9.20 mL, 23.1 mmol) was added. After 15 min methyl (Z/E)-3-methoxybut-2-enoate (26) (2.50 g, 19.2 mmol) was added and stirred for an additional hour. Afterwards at -78 °C, TMSCl (3.00 mL, 23.5 mmol) was added and the reaction mixture was warmed to room temperature and stirred for 1 h. Then THF was evaporated under reduced pressure and the residue was resolved in n-pentane (50 ml), extracted with a water:NaHCO₃-solution (1:1,1 x 50 mL) and the organic layer was dried with MgSO₄, filtered and the solvent was evaporated. The product 27 was obtained as a yellow oil (3.73 g, 95%) and was used without further purification. The product can be stored at -20 °C without decomposition. The spectroscopic data are in agreement with previously reported literature values.⁴

δH (600 MHz, CDCl₃) 0.25 (s, 9H, OSi(CH₃)₃), 3.56 (s, 3H, OCH₃), 3.57 (s, 3H, OCH₃), 3.98 (dd, 2J₄Ha,4Hb 1.8 Hz, 4J₄Hb,2 1.5 Hz, 1H, 4-Hb), 4.31 (d, 4J₂₂,4Hb 1.5 Hz, 1H, 2-H), 4.35 (d, 2J₄Ha,4Hb 1.3 Hz, 1H, 4-Ha) ppm; δC (151 MHz, CDCl₃) 0.5 (Si(CH₃)₃), 54.3 (OCH₃), 55.2 (OCH₃), 75.7 (C-2), 78.8 (C-4), 158.9 (C-1), 158.9 (C-1) ppm, νmax/cm⁻¹ 2996, 2960, 2903, 2841, 1656, 1630, 1442, 1389, 1351, 1266, 1252, 1200, 1167, 1095, 965, 841, 778, 759, 698, 634, 575, 464; GC-MS (EI, 70 eV): tR = 7.7 min, m/z (%) = 187 (89) [(M-CH₃)+], 171 (86) [(M-OCH₃)+], 98 (72) [C₅H₆O₂⁺], 89 (75) [OTMS⁺], 73 (100), 67 (52).

2-Chloro-8-hydroxy-6-methoxynaphthalene-1,4-dione 5d

In a Schlenk-tube 2,6-dichloro-1,4-benzoquinone (28) (796 mg, 4.50 mmol) was dissolved in THF (41 mL) and cooled to -30 °C. A solution of diene 27 (1.00 g, 4.95 mmol) in THF (10 mL)
was added over a period of 30 min and stirred for 1 h. The reaction solution was then warmed to room temperature and stirred overnight. The reaction mixture was transferred to a 500 mL round bottom flask and 100 g of silica was added. The THF was evaporated under reduced pressure and a yellow residue was let stand overnight. The reaction mixture was transferred to a 500 mL round bottom flask and 100 g of silica was added. The THF was evaporated under reduced pressure and a yellow residue was let stand overnight. The silica was then washed with acetone, concentrated and the residue was purified by column chromatography (CH₂Cl₂:n-pentane = 50:50). The product 5d was obtained as an orange solid (507 mg, 47%). The spectroscopic data are in agreement with previously reported literature values.⁵

R_f = 0.3 (CH₂Cl₂:n-pentane = 50:50); mp 177 °C (in CH₂Cl₂); δH (600 MHz, CDCl₃) 3.92 (s, 3H, OCH₃), 6.66 (d, 4J₇,₅ 2.5 Hz, 1H, 7-H), 7.13 (s, 1H, 3-H), 7.18 (d, 4J₅,₇ 2.5 Hz, 1H, 3-H), 11.91 (s, 1H, 8-OH) ppm; δC (151 MHz, CDCl₃) 56.4 (OCH₃), 106.3 (C-7), 109.5 (C-8a), 109.1 (C-5), 133.5 (C-2), 136.3 (C-3), 146.8 (C-4a), 165.2 (C-8), 168.9 (C-6), 181.0 (C-4), 181.9 (C-1) ppm; ν_max/cm⁻¹ 3051, 1659, 1629, 1574, 1593, 1504, 1430, 1390, 1309, 1286, 1257, 1239, 1202, 1181, 1136, 1081, 1003, 891, 860, 847, 808, 761, 689. HRMS (ESI, positive-ion): calc.: 236.9960 (C₁₁H₆O₄Cl) [(M+H)⁺], found: 236.9961.

S2.3 Synthesis of diene 6d

(E)-1-(tert-Butyldimethylsilyl)oxy-3-methyl-buta-1,3-butadiene 6d

In a 100 mL Schlenk-flask 3-methylbut-2-enal (5.00 ml, 51.8 mmol) and TBSCI (11.7 g, 77.8 mmol) were dissolved in acetonitrile (50 mL) and NaI (12.4 g, 82.9 mmol) and Et₃N (11.6 mL, 82.9 mmol) were added. The reaction was stirred at room temperature under a nitrogen atmosphere and ¹H-NMR was used to monitor the reaction (18 h). The reaction mixture was extracted with n-pentane (3 x 100 mL), the combined organic layers were washed with saturated NaCO₃ (2 x 50 mL), dried over MgSO₄ and filtered. The filtrates volume was then evaporated. The residue was distilled under reduced pressure and product 6d was isolated as a clear colourless oil (8.25 g, 80 %). The spectroscopic data are in agreement with previously reported literature values.⁶
bp 83 °C (15 mbar); δH (600 MHz, CDCl₃) 0.16 (s, 6H, Si(CH₃)₂), 0.93 (s, 9H, SiC(CH₃)₃), 1.80 (s, 3H, 3-CH₃), 4.67 (m, 1H, 4-H₃), 4.74 (m, 1H, 4-H₉), 5.82 (d, 3J₂,1 12.4 Hz, 1H, 2-H), 6.53 (d, 3J₁₂, 12.4 Hz, 1H, 1-H) ppm; δC (151 MHz, CDCl₃) -5.1 (Si(CH₃)₂), 18.5 (SiC), 19.2 (3-CH₃), 25.8 ((SiC(CH₃)₃), 111.9 (C-4), 116.3 (C-2), 140.0 (C-3), 142.4 (C-1) ppm; νmax/cm⁻¹ 2955, 2930, 2887, 2859, 1644, 1606, 1472, 1463, 1390, 1362, 1168, 1071, 1006, 922, 870, 828, 779, 670.

GC-MS (EI, 70 eV): tR = 6.4 min, m/z (%) = 198 (26) [M⁺], 141 (M-C₄H₉) (100), 127 (22), 113 (17), 101 (34), 75 (52), 59 (24).

S2.4 Further Epoxidation experiments

To improve the diastereomeric ratio in the epoxidation procedure, we first tested the classical Sharpless reaction.⁷ Under the reported reaction conditions (1S,2S)-14 led to decomposition and no products could be observed.

Next, we used the vanadium-catalysed epoxidation reaction (VO(acac)₂/tBuOOH-system), which is known as a selective cis-epoxidation reagent for pseudo-axial allylic alcohols (Scheme 3).⁸

![Scheme 3: Epoxidation of (1S,2S)-14 via VO(acac)₂/tBuOOH-system.](image)

In a 20 mL Schlenk-flask allyl alcohol (1S,2S)-14 (40.0 mg, 96.0 μmol, 1.00 equiv.) was dissolved in CH₂Cl₂ (2 mL) and vanadyl acetylacetone (5.01 mg, 19.2 μmol, 0.20 equiv.) and tBuOOH (5.5 M in dodecane, 17.5 μL, 10.7 μmol, 1.00 equiv.) was added and the reaction mixture was stirred at room temperature for 44 h. After full conversion 10-(w/w)-% NaHSO₃ (20 mL) and sat. NaHCO₃ was added and the layers were separated. The aqueous layer was extracted with CH₂Cl₂ (2 x 20 mL) and the combined organic layer were dried over MgSO₄, filtered and the crude product was purified via column chromatography (PE:EE = 80:20) and the product was isolated as yellow solid (18.2 mg, 42.1 μmol, 44%).

The analytical data were in agreement with (1aR,2R,3S,9bS)-16 reported in the article. The yield is the same as reported with the mCPBA procedure that there is no advantage for the
vanadium-catalysed reaction procedure. Also, tBuOOH is that reactive that an attack of the benzoquinone double bond takes place and epoxide 29 can be observed without known absolute configuration of the epoxide.
S3. Notes and References

S4. NMR spectra of compounds

Figure 1: $^1$H and $^{13}$C-NMR-Spectra of 21 in CDCl$_3$ (600 MHz/151 MHz).
Figure 2: $^1$H and $^{13}$C-NMR-Spectra of 22 in CDCl$_3$ (600 MHz/151 MHz).
Figure 3: $^1$H and $^{13}$C-NMR-Spectra of 23 in CDCl$_3$ (600 MHz/151 MHz).
Figure 4: $^1$H and $^{13}$C-NMR-Spectra of (R)-L2 in CDCl$_3$ (600 MHz/151 MHz).
Figure 5: $^1$H and $^{13}$C-NMR-Spectra of 26 in CDCl$_3$ (600 MHz/151 MHz).
Figure 6: $^1$H and $^{13}$C-NMR-Spectra of 27 in CDCl$_3$ (600 MHz/151 MHz).
Figure 7: $^1$H and $^{13}$C-NMR-Spectra of 5d in CDCl$_3$ (600 MHz/151 MHz).
Figure 8: $^1$H and $^{13}$C-NMR-Spectra of 6d in CDCl$_3$ (600 MHz/151 MHz).
Figure 9: $^1$H and $^{13}$C-NMR-Spectra of (1R,4aR,9aR)-10 in CDCl$_3$ (600 MHz/151 MHz).
Figure 10: $^1$H and $^{13}$C-NMR-Spectra of (15,25)-14 in CDCl$_3$ (600 MHz/151 MHz).
Figure 11: $^1$H and $^{13}$C-NMR-Spectra of $(1\alpha S,2R,3\beta S,9\beta R)-15$ in CDCl$_3$ (600 MHz/151 MHz).
Figure 12: $^1$H and $^{13}$C-NMR-Spectra of (1aR,2R,3S,9bS)-16 in CDCl$_3$ (600 MHz/151 MHz).
Figure 13: $^1$H and $^{13}$C-NMR-Spectra of (15,2R,3R,45)-17 in DMSO (600 MHz/151 MHz).
Figure 14: $^1$H and $^{13}$C-NMR-Spectra of (1R,2S,3R,4S)-1 (altersolanol A) in MeOD (600 MHz/151 MHz).
Figure 15: HPLC chromatograms of racemic 10 (above) and (1R,4aR,9aR)-10 (Table 1, entry 6 and 8) (below).
Figure 16: HPLC chromatograms of racemic 14 (above) and (1S,2S)-14 (below).

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<td>787,820</td>
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<th>Ret.Time</th>
<th>Peak Name</th>
<th>Height</th>
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<th>Rel.Area</th>
<th>Amount</th>
<th>Type</th>
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Figure 17: HPLC chromatograms of racemic 15 (above) and (1αS,2R,3S,9bR)-15 (below).

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<tr>
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<td>7,228</td>
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<td>BM</td>
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<tr>
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<table>
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<th>Height</th>
<th>Area</th>
<th>Rel.Area</th>
<th>Amount</th>
<th>Type</th>
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</thead>
<tbody>
<tr>
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<td>57,545</td>
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<tr>
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<td>1304,921</td>
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Figure 18: HPLC chromatograms of racemic 16 (above) and (1\textit{a}R,\textit{a}R,3\textit{b}S,9\textit{b}S)-15 (below).
Figure 19: HPLC chromatograms of racemic 17 (above) and (1S,2R,3R,4S)-17 (below).
Figure 20: HPLC chromatograms of racemic altersolanol A (1) (above) and altersolanol A (1R,2S,3R,4S)-1 (below).
Figure 21: HPLC chromatograms of racemic altersolanol A (1) (above), synthesised altersolanol A (1R,2S,3R,4S)-1 (middle) and the authentic sample of natural product by Prof. Proksch (below).
S6. Reversed-phase HPLC chromatograms

Figure 22: Achiral reversed-phase HPLC chromatogram of racemic 17 and (1S,2R,3R,4S)-17.
Figure 23: Achiral reversed-phase HPLC chromatogram of racemic altersolanol A 1 and (1S,2R,3R,4S)-1.