Supporting Information

Asymmetric Total Synthesis of (+)-Fumimycin via 1,2-Addition to Ketimines

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General

$^1$H NMR spectra were recorded on a 400 MHz or a 500 MHz spectrometer as solutions. Chemical shifts are expressed in parts per million (ppm, $\delta$) downfield from tetramethylsilane (TMS) and are referenced to CHCl$_3$ (7.26 ppm), acetone-D$_5$ (2.05 ppm) DMSO-D$_5$ (2.50 ppm) and methanol-D$_3$ (3.31 ppm) as internal standards. All coupling constants are absolute values and $J$ values are expressed in Hertz (Hz). The description of signals include: s = singlet, br. s = broad singlet, d = doublet, t = triplet, q = quartet, sept. = septet, m = multiplet, mc = centred multiplet, dd = doublet of doublets, ddd = doublet of dd, dt = doublet of triplets, dm = doublet of multiplets etc. The spectra were analyzed according to first order. $^{13}$C NMR spectra were recorded on a 100 MHz or a 125 MHz spectrometer as solutions. Chemical shifts are expressed in parts per million (ppm, $\delta$) downfield from tetramethylsilane (TMS) and are referenced to CDCl$_3$ (77.0 ppm), acetone-D$_6$ (sept., 30.8 ppm), DMSO-D$_6$ (sept. 29.4 ppm) and methanol-D$_3$ (sept., 49.1 ppm) as internal standards. MS EI (electron ionization mass spectrometry, 70 eV) or FAB (fast atom bombardment): The molecular fragments are quoted as the relation between mass and charge ($m/z$), the intensities as a percentaged value relative to the intensity of the base signal (100%). The abbreviation [M$^+$] refers to the molecule-ion. IR spectra were recorded as thin films on KBr or using ATR (attenuated total reflection). The deposit of the absorption band was given in wave numbers $\nu$ in cm$^{-1}$. Routine monitoring of reactions was performed using Silica gel coated aluminium plates (silica gel 60), which were analyzed under UV-light at 254 nm and/or dipped into a solution of molybdatophosphate (5% phosphor molybdic acid in ethanol, dipping solution) and/or KMnO$_4$ solution and heated with a heat gun. Solvent mixtures are understood as volume/volume. Solid materials were powdered. Tetrahydrofuran was distilled from sodium/potassium under argon prior to use. Dichloromethane was distilled from calcium hydride, toluene was distilled from sodium. All reactions involving moisture sensitive reactants were conducted under an argon atmosphere using oven dried glassware. All other solvents, reagents and chemicals were used as purchased unless stated otherwise.

The CD-spectra were recorded on a Jasco J815-150S at 20 °C as solutions in CH$_3$CN.
Overview of the total synthesis of (±)-fumimycin

\[ \text{HO-MeO-OH} \quad \text{MeO} \quad \text{OTBS} \quad \text{CO}_2\text{Et} \]

Scheme S1: The total synthesis of (±)-fumimycin (rac-1).

1. a) allylbromide, K$_2$CO$_3$, acetone, reflux, 85%; b) H$_2$O$_2$, B(OH)$_3$, H$_2$SO$_4$, THF, 30 °C, 81%; c) CICOCO$_2$Et, TiCl$_4$, CH$_2$Cl$_2$, –15 °C, 82%; d) TBSCl, \( \overline{\overline{i}} \)Pr$_2$NEt, CH$_2$Cl$_2$, rt; e) H$_2$NOH•HCl, pyridine, EtOH, reflux, 91% over two steps; f) ClPPh$_2$, NE$_3$, THF, –50 °C, 74%; g) MeMgBr, toluene, –78 °C, 65%; h) DMF, 120 °C; i) DMF, reflux, 55% over two steps; j) RhCl$_3$•H$_2$O, EtOH, 45 °C, 96% (E:Z 10:1); k) BI$_3$, CH$_2$Cl$_2$, –20 °C, 90%; l) TIPSOTf, 2,6-lutidine, CH$_2$Cl$_2$, –15 °C → rt, 83%; m) HCl, MeOH, 55 °C; n) CICOCHCHCO$_2$tBu, pyridine, CH$_2$Cl$_2$, 0 °C → rt, 24% over two steps; o) TBAF, AcOH, THF, rt, 93%; p) TFA, CH$_2$Cl$_2$, 0 °C → rt, quant.

Overview of the total synthesis of (+)-fumimycin

Scheme S2: Asymmetric 1,2-addition to ketimine 6 and subsequent steps to (+)-fumimycin.

* Measured by HPLC. ** Fumimycin proved to be too polar for the use of measurement of the enantiomeric excess by HPLC. Since racemisation of the quaternary stereocentre under mild deprotection conditions can be excluded, fumimycin should also possess an enantiomeric excess of 90%.
Experimental procedures:

(R)-2-[6-(tert-Butyl-dimethyl-silanyloxy)-benzo[1,3]dioxol-5-yl]-2-diphenylphosphinoyl amino-propionic acid ethyl ester

A solution of quinine (176 mg, 0.542 mmol, 5.00 eq.) in THF at 0 °C was treated with MeLi (1.6 M in Et₂O, 0.34 ml, 0.54 mmol, 5.0 equiv.) and cooled to –70 °C. After 30 min MeMgBr (3 M in Et₂O, 47 μl, 0.14 mmol, 1.3 equiv.) was added. After further 30 min, a solution of ketimine 4 (60.0 mg, 0.109 mmol) in THF (0.36 ml) was added slowly. After 22 h NH₄Cl-solution (40 ml) and EtOAc (15 ml) were added. The phases were separated; the organic phase was washed with NH₄Cl-solution (40 ml), dried over Na₂SO₄, filtered through silica gel and evaporated under reduced pressure. The crude product (65% ee) was purified by flash chromatography (cHex:EtOAc 1:2 → 1:4), yielding 5 (35.3 mg, 57%, 65% ee) as orange oil.

$\text{t}_{r}$: 15.78 min (minor enantiomer), 18.23 min (major enantiomer), (IA-column, nHeptane:iPrOH 80:20, 10 °C, 0.5 ml/min).

$[\alpha]_D^{20}$: –27.7, $c = 0.26$ in MeOH (with 57% ee); corresponds to $[\alpha]_D^{20} = –48.6$ (with 100% ee).

NMR, IR, and MS data according to the racemic compound reported in the literature (P. J. Gross, S. Bräse, Chem. Eur. J. DOI: 10.1002/chem.201001036)
(R)-2-[5-Allyloxy-2-(tert-butyldimethylsilanyloxy)-4-methoxyphenyl]-2-diphenylphosphinoyl amino propionic acid ethyl ester

![Chemical Structure](2)

A solution of quinine (7.62 g, 23.5 mmol, 5.00 eq.) in THF at 0 °C was treated with MeLi (1.6 M in Et₂O, 15 ml, 23 mmol, 5.0 equiv.) and cooled to −70 °C. After 60 min MeMgBr (3 M in Et₂O, 2.0 ml, 6.1 mmol, 1.3 equiv.) was added. After further 30 min, a solution of ketimine 3 (2.79 g, 4.70 mmol) in THF (10 ml) was added within 20 min via syringe pump. After 16 h NH₄Cl-solution (200 ml) was added, the resulting mixture was extracted with EtOAc (4 × 150 ml). The combined organic phases were washed with NH₄Cl-solution (200 ml), dried over Na₂SO₄, filtered through silica gel and evaporated under reduced pressure. The crude product was purified by flash chromatography (cHex:EtOAc 1:2 → 1:3), yielding 2 (1.89 g, 66%, 59% ee) as brown oil.

*t*₁: 12.56 min (minor enantiomer), 14.97 min (major enantiomer), (nHeptane:iPrOH 80:20, 10 °C, 0.5 ml/min).


(R)-7-Diphenylphosphinoylamino-7-methyl-[1,3]dioxolo[4,5-f]benzofuran-6(7H)-one

![Chemical Structure](8)

A solution of silylether 4 (251 mg, 0.454 mmol, 53% ee) in DMF (3.0 ml) was heated to reflux. After 5 h, the solvent was removed under reduced pressure. Flash chromatography (cHex:EtOAc 1:2 → 1:3) yielded 8 (102 mg, 55%, 53% ee) as white solid.

*t*₁: 35.41 min (major enantiomer), 40.64 min (minor enantiomer); (nHeptane:iPrOH 99:1, 10 °C, 0.7 ml/min).

\[^{[\alpha]}_D\] = +2.7, c = 0.59 in MeOH (with 53% ee); corresponds to \[^{[\alpha]}_D\] = +5.2 (with 100% ee).

*R*₁ (cHex:EtOAc 1:2): 0.18.
\( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)): \( \delta = 1.68 \) (s, 3H), 3.81 (d, \( J_{\text{NH,P}} = 6.5 \) Hz, 1H), 5.84 (s, \( J = 1.1 \) Hz, 1H), 5.88 (s, \( J = 1.1 \) Hz, 1H), 6.32 (s, 1H), 6.93 (s, 1H), 7.26–7.30 (m, 2H), 7.34–7.54 (m, 4H), 7.56–7.64 (m, 2H), 7.84–7.92 (m, 2H) ppm.

\( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)): \( \delta = 27.5 \) (–, d, \( J_P = 5.2 \) Hz,), 58.8 (C\text{quad.}, \( J_P = 2.0 \) Hz), 93.9 (–), 101.5 (+), 106.3 (–), 119.1 (C\text{quad.}, d, \( J_P = 2.4 \) Hz), 128.3 (–, d, \( J_P = 13.0 \) Hz), 128.5 (–, d, \( J_P = 13.0 \) Hz), 131.5 (–, \( J_P = 10.1 \) Hz), 131.6 (–, d, \( J_P = 2.8 \) Hz), 131.8 (C\text{quad.}, d, \( J_P = 127.8 \) Hz), 131.9 (–, \( J_P = 9.6 \) Hz), 132.0 (–, d, \( J_P = 2.7 \) Hz), 132.8 (C\text{quad.}, d, \( J_P = 129.9 \) Hz), 144.0, 147.0, 148.5 (3 × C\text{quad.}), 178.5 (C\text{quad.}, d, \( J_P = 4.4 \) Hz) ppm.

**IR** (ATR): \( \nu = 2931 \) (w), 1810 (m), 1729 (w), 1615 (w), 1510 (w), 1461 (m), 1438 (m), 1275 (m), 1177 (m), 1122 (s), 1018 (m), 925 (m) cm\(^{-1}\).

**MS** (EI), m/z (%): 407 (66) [M\(^+\)], 379 (97) [C\(_{21}\)H\(_{18}\)NO\(_4\)P\(^+\)], 288 (44), 201 (100).

**HRMS** (EI) for C\(_{22}\)H\(_{18}\)NO\(_5\)P: calcd. 407.0923, found 407.0925.

\((R)-(E)-3-[5,6-Dihydroxy-3-methyl-2-oxo-4-((E)-propenyl)-2,3-dihydro-benzofuran-3-ylcarbamoyl]-acrylacid (fumimycin)*\)

\[ \alpha_D^{20} = +109, \ c = 0.26 \text{ in MeOH (with 90% ee),} \ [c = 0.00262 \ g/ml, l = 1 \text{ dm,} \ \alpha_{\text{measured}} = +0.286^\circ]; \ \text{corresponds to} \ [\alpha_D^{20} = +121 \text{ (with 100% ee)}.}^*\]

Experimental procedure, NMR, IR, and MS data according to the racemic compound reported in the literature (P. J. Gross, S. Bräse, *Chem. Eur. J.* accepted.).

* The optical rotation for natural fumimycin is reported by Kim *et al.* with \( [\alpha_D] = -11.9, \ (c = 0.26, \text{MeOH}). \) It is unknown, why the value of the synthesized fumimycin is factor ten higher than the literature value. One possible explanation is that natural fumimycin is not a single enantiomer, but an enantiomerically enriched mixture with about 10% ee.
CD-Spectral Data

Figure S1: Simulated CD-curves for fumimycin:

![CD-curves for fumimycin](image)

Figure S2: Measured CD-curve for (+)-fumimycin (20 °C, CH$_3$CN):

![CD-curve for (+)-fumimycin](image)
Figure S3: Simulated CD-curves for tricyclus 8:

Figure S4: Measured CD-curve for 8(20 °C, CH₃CN):

Computational Details:

Structures were optimized using polarized triple-ζ basis sets (def2-TZVP, Ref. ¹) starting from initial conformer geometries pre-screened by UFF². All structures were confirmed to be minima by force-constant calculations. Vertical excitation energies, rotatory strengths, and specific rotations were computed using time-dependent density functional theory (TDDFT)³ and diffuse-augmented basis sets of split valence quality (SVPD, Ref. ⁴). 35 singlet excitations were computed, corresponding to a maximum excitation energy of 191 nm. Explorative calculations employing larger TZVPD basis sets showed no significant changes in the computed CD spectra. The physically sound and well-tested⁵ one-parameter hybrid

⁴ D. Rappoport, F. Furche, submitted.
functional PBE0\(^6\) was used throughout along with fine quadrature grids (size m4\(^7\)). Solvation effects were included by the continuum salvation model COSMO\(^8\); the fast solvent response in the TDDFT calculations was neglected. To facilitate comparison to experiment, Gaussian line broadening with a uniform root mean square linewidth of 0.16 eV was applied to the computed line spectra. All calculations were performed using TURBOMOLE 6.2\(^9\).

The computed CD spectra of fumimycin show four characteristic bands A-D (Figure S1). An assignment of these bands in terms of electronic excitations is provided in Table S1. The A band is very weak and not distinguishable in the experimental spectrum. The B, C, and D bands are stronger and can be assigned. The \(+\leftrightarrow-\) intensity pattern computed for the (\(R\)) enantiomer is clearly present in the experimental spectrum of (+)-fumimycin and constitutes the basis of our assignment of the absolute configuration. The relative band intensities and the band positions are also in good agreement with experiment. Absolute intensities are predicted higher than the measured ones, this may be due to the neglect of vibronic and thermal effects which can greatly reduce intensities\(^{10}\).

To further corroborate our assignment of the absolute configuration of fumimycin, we computed the specific rotation in methanol solution. The computed \([\alpha]\)\(^{20}\) value of +258 °/[dm(g/cc)] for the (\(R\)) enantiomer is positive, which confirms the assignment based on the CD data. The absolute value is larger than the experimental result of +121 °/[dm(g/cc)], consistent with the overestimation of the computed CD intensities.

Finally, we attempted to simulate the CD spectrum of the tricycles 8. This task is much more challenging, because the diphenylphosphine oxide group of 8 is considerably more flexible than the fumaric acid group of fumimycin. The computed spectrum of (\(R\))-8 (Figure S3) correctly predicts the sign changes of the measured curve of (+)-8. The relative intensities agree less well, but the overall agreement is good enough to assign the absolute configuration of (+)-8 to be (\(R\)), which further supports our assignment for fumimycin.

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<table>
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<tr>
<th>Band</th>
<th>State(s)</th>
<th>ΔE</th>
<th>R</th>
<th>Assignment</th>
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<tr>
<td>A</td>
<td>3 $^1A$</td>
<td>353</td>
<td>3.5</td>
<td>$\pi$(ar) $\rightarrow$ $\pi^*$ (fum)</td>
</tr>
<tr>
<td>B</td>
<td>4 $^1A$</td>
<td>296</td>
<td>-8.6</td>
<td>$\pi$(ar) $\rightarrow$ $\pi$ (ar)</td>
</tr>
<tr>
<td>C</td>
<td>8 $^1A$</td>
<td>259</td>
<td>127.8</td>
<td>n(amide)+n(lactone CO) $\rightarrow$ $\pi^*$ (fum)</td>
</tr>
<tr>
<td>D</td>
<td>13 $^1A$</td>
<td>223</td>
<td>44.2</td>
<td>$\pi$(fum) $\rightarrow$ $\pi^<em>$ (fum), n(amide)+n(lactone CO) $\rightarrow$ $\pi^</em>$ (lactone-CO), n(lactone-CO) $\rightarrow$ $\pi^*$ (fum)</td>
</tr>
<tr>
<td></td>
<td>14 $^1A$</td>
<td>220</td>
<td>-94.0</td>
<td>$\pi$(fum) $\rightarrow$ $\pi^<em>$ (fum), n(amide)+n(lactone CO) $\rightarrow$ $\pi^</em>$ (ar), n(lactone) $\rightarrow$ $\pi^*$ (fum)</td>
</tr>
<tr>
<td></td>
<td>15 $^1A$</td>
<td>215</td>
<td>22.1</td>
<td>n(lactone-CO) $\rightarrow$ $\pi^*$ (fum)</td>
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<tr>
<td></td>
<td>17 $^1A$</td>
<td>207</td>
<td>-31.0</td>
<td>n(amide)+n(lactone CO) $\rightarrow$ $\pi^<em>$ (ar), n(amide)+n(lactone CO) $\rightarrow$ $\pi^</em>$ (lactone-CO)</td>
</tr>
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</table>

Table S1: Assignment of the main features in the CD spectrum of (R)-fumimycin. ΔE denotes computed excitation energies in nm, and R denotes the corresponding rotatory strengths in $10^{-40}$ erg cm$^3$. ar denotes the aromatic $\pi$ system including the conjugated propenyl group, fum the $\pi$ electron system of the fumaric acid side chain, and n(amide) and n(lactone-CO) stand for the lone pairs of the amide and lactone-CO groups, respectively.
HPLC-Data

**Figure S5:** HPLC-diagram of lactone 6 before recrystallisation (59% ee)

**Figure S6:** HPLC-diagram of lactone 6 after recrystallisation (90% ee)

**Figure S7:** HPLC-diagram of bisprotected fumimycin S-4 (90% ee)
Crystallographic Data:

The single-crystal X-ray diffraction studies were carried out on a Nonius Kappa-CCD diffractometer at 123(2) K using Mo Kα radiation (λ = 0.71073 Å). Direct Methods (SHELXS-97) (a) were used for structure solution, and full-matrix least-squares refinement on $F^2$ (SHELXL-97) (a). H atoms were localized by difference Fourier synthesis and refined using a riding model. H(N) were refined free. 8 crystallized in two polymorphs.

4: yellow crystals, C$_{29}$H$_{34}$NO$_6$PSi, $M = 551.63$, crystal size 0.40 x 0.30 x 0.10 mm, orthorhombic, space group P2$_1$2$_1$2$_1$ (No.19): $a = 10.199(1)$ Å, $b = 16.574(2)$ Å, $c = 17.054(2)$ Å, $V = 2882.8(6)$ Å$^3$, $Z = 4$, $\rho$(calcd) = 1.271 Mg m$^-3$, $F$(000) = 1168, $\mu = 0.179$ mm$^-1$, 41766 reflections (2θ max = 55°), 6611 unique [R int = 0.030], 343 parameters, R1 (I > 2σ(I)) = 0.027, wR2 (all data) = 0.071, GooF = 1.07, largest diff. peak and hole 0.297 and –0.235 e Å$^-3$. The absolute structure was determined by refinement of Flack's x-parameter, x = 0.00(6). (b) 9: orange crystals, C$_{23}$H$_{20}$NO$_6$P, $M = 437.37$, crystal size 0.50 x 0.25 x 0.25 mm, triclinic, space group P-1 (No.2): $a = 8.475(1)$ Å, $b = 11.476(1)$ Å, $c = 11.734(1)$ Å, $\alpha = 103.66(1)^\circ$, $\beta = 107.51(1)^\circ$, $\gamma = 94.34(1)^\circ$, $V = 1044.23(18)$ Å$^3$, $Z = 2$, $\rho$(calcd) = 1.391 Mg m$^-3$, $F$(000) = 456, $\mu = 0.173$ mm$^-1$, 10736 reflections (2θ max = 55°), 4749 unique [R int = 0.030], 283 parameters, 1 restraint, R1 (I > 2σ(I)) = 0.035, wR2 (all data) = 0.096, GooF = 1.05, largest diff. peak and hole 0.402 and –0.403 e Å$^-3$.

8: colourless crystals, C$_{22}$H$_{18}$NO$_5$P, $M = 407.34$, crystal size 0.40 x 0.25 x 0.15 mm, triclinic, space group P-1 (No.2): $a = 5.894(1)$ Å, $b = 10.203(2)$ Å, $c = 16.399(3)$ Å, $\alpha = 97.76(2)^\circ$, $\beta = 96.88(2)^\circ$, $\gamma = 99.17(2)^\circ$, $V = 954.53(3)$ Å$^3$, $Z = 2$, $\rho$(calcd) = 1.417 Mg m$^-3$, $F$(000) = 424, $\mu = 0.179$ mm$^-1$, 18403 reflections (2θ max = 55°), 4384 unique [R int = 0.050], 259 parameters, 82 restraints, R1 (I > 2σ(I)) = 0.064, wR2 (all data) = 0.177, GooF = 1.03, largest diff. peak and hole 0.665 and –0.573 e Å$^-3$. One phenyl group is disordered.

8-iPrÓH: colourless crystals, C$_{22}$H$_{18}$N O$_3$P – 1/4 iPr, $M = 422.37$, crystal size 0.25 x 0.15 x 0.10 mm, triclinic, space group P-1 (No.2): $a = 10.237(1)$ Å, $b = 16.524(1)$ Å, $c = 23.793(2)$ Å, $\alpha = 96.01(1)^\circ$, $\beta = 100.12(1)^\circ$, $\gamma = 97.69(1)^\circ$, $V = 3892.46(6)$ Å$^3$, $Z = 8$, $\rho$(calcd) = 1.441 Mg m$^-3$, $F$(000) = 1764, $\mu = 0.180$ mm$^-1$, 66291 reflections (2θ max = 55°), 17770 unique [R int = 0.067], 1100 parameters, 43 restraints, R1 (I > 2σ(I)) = 0.061, wR2 (all data) = 0.152, GooF = 1.02, largest diff. peak and hole 0.496 and –0.504 e Å$^-3$.
9: colourless crystals, C$_{24}$H$_{2}$N$_{2}$O$_{5}$P, $M = 435.40$, crystal size 0.24 x 0.16 x 0.08 mm, triclinic, space group P-1 (No.2): $a = 10.509(1)$ Å, $b = 13.334(1)$ Å, $c = 16.224(1)$ Å, $\alpha = 83.82(1)^\circ$, $\beta = 79.60(1)^\circ$, $\gamma = 75.14(1)^\circ$, $V = 2156.8(3)$ Å$^3$, $Z = 4$, $\rho$(calcd) = 1.341 Mg m$^{-3}$, $F(000) = 912$, $\mu = 0.164$ mm$^{-1}$, 29641 reflections ($2\theta_{\text{max}} = 55^\circ$), 9843 unique [R$_{\text{int}} = 0.071$], 568 parameters, 16 restraints, R1 ($I > 2\sigma(I)$) = 0.073, wR2 (all data) = 0.210, GooF = 1.02, largest diff. peak and hole 0.732 and −0.661 e Å$^{-3}$. One allyl group is disordered.

Crystallographic data (excluding structure factors) for the structure reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 786071 (4), CCDC 786072 (7), CCDC 786073 (8), CCDC 786074 (8-iPrOH) and CCDC 786075 (9). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge DB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

Figure S8: Molecular structure of 4 (displacement parameters are drawn at 50% of probability level).

Figure S9: Molecular structure of 7 (displacement parameters are drawn at 50% of probability level).
Figure S10: Molecular structure of 8 (displacement parameters are drawn at 50% of probability level).

Figure S11: Asymmetric unit 8-iPrOH (the four independent molecules and the solvent iPr are shown).
Figure S12: Asymmetric unit of 9 (displacement parameters are drawn at 50% of probability level).