A Chiral Auxiliary-Based Synthesis of the C5-C17 trans-Decalin Framework of Anthracimycin

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Supporting Information

S2 General Information
S3 $^1$H and $^{13}$C NMR Spectra
S21 NOESY Spectra for 17 + 18
S22 X-ray structure for 22
General Information

All reactions were carried out in flame- or oven-dried glassware under a dry nitrogen atmosphere unless otherwise stated. CH₂Cl₂, (CH₃)₂CO, DMF, THF CH₃CN and Et₂O were obtained from a solvent purifier from LC Technology Systems. Triethylamine was distilled from calcium hydride. All other reagents were used as received unless otherwise noted. Yields refer to chromatographically and spectroscopically (¹H NMR) homogenous materials, unless otherwise stated. Reactions performed at low temperature were either cooled with an acetone/dry ice bath to reach -78 °C, or acetone/brine/dry ice bath to reach -30 °C, or a water ice bath to reach 0 °C. Flash chromatography was carried out using 0.063-0.1 mm silica gel with the required solvent system. TLC was carried out using 0.2 mm Kieselgel F254 (Merck) silica plates and compounds were visualised using UV irradiation at 365 nM and/or staining with vanillin in methanolic sulphuric acid or potassium permanganate and potassium carbonate in aqueous sodium hydroxide. Melting points were measured with a Kofler hot-stage apparatus and are uncorrected. NMR spectra were recorded as indicated on the Bruker DRX-400 spectrometer operating at 400 MHz for ¹H nuclei, 100 MHz for ¹³C nuclei and 282 MHz for ¹⁹F nuclei. All chemical shifts are reported in ppm relative to tetramethylsilane (δ = 0 for ¹H NMR) and CDCl₃ (δ = 77.0 for ¹³C NMR). ¹H NMR data is reported as chemical shift, relative integral, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; m, multiplet), coupling constant (J, Hz), and assignment. Assignments were made with the aid of COSY, NOESY and HSQC experiments where required. High resolution mass spectra were recorded using a VG-70SE spectrometer at a nominal accelerating voltage of 70 eV or on a Bruker micrOTOF-Q II mass spectrometer.
Alcohol S2

PMBO\textsuperscript{+}CH\textsubscript{2}OH

S2

PMBO\textsuperscript{+}CH\textsubscript{2}OH

S2
Sulfide S3

\[
\text{PMBO} \quad \text{S} \quad \text{N} \quad \text{N}
\]

\[
\text{S3}
\]

\[
\text{PMBO} \quad \text{S} \quad \text{N} \quad \text{N}
\]

\[
\text{S3}
\]
Sulfone 8

![Chemical Structure](image)

![Chemical Structure](image)
Alcohol S4

TBSO
OH
S4

TBSO
OH
S4
Aldehyde 11
Iodide 12

![Chemical Structure of Iodide 12](image)

[S9]
Aldehyde 9

\[
\text{O} = \text{C} = \text{C} - \text{TBSO}
\]

\[\text{9}\]

\[
\text{O} = \text{C} = \text{C} - \text{TBSO}
\]

\[\text{9}\]

\[\eta (\text{ppm})\]

\[\delta (\text{ppm})\]
Alcohol 21
Ester 14
Enone 16
Adducts 17 and 18
Imide 20

[Chemical structure image]

S19
Adducts 17-18

[Diagram of chemical structures and NOESY correlation]
**Crystallization.** Single crystals of Adduct 22 were obtained by slow recrystallization of a solution of the compound in ethyl acetate.

![ORTEP diagram](image)

**Figure S1.** ORTEP diagram drawn with 50% ellipsoid probability of the crystal structure of Adduct 22.

**Table S1.** Crystal data and structure refinement details for N-Ts bicyclic ketone 20.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Empirical formula</td>
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<td>Formula weight</td>
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<tr>
<td>Temperature (K)</td>
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<td>Wavelength (Å)</td>
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<td>Space group</td>
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<tr>
<td>a (Å)</td>
<td>9.1302(3)</td>
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<tr>
<td>b (Å)</td>
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<tr>
<td>c (Å)</td>
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<tr>
<td>α (°)</td>
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<td>β (°)</td>
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<td>γ (°)</td>
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<td>V (Å³)</td>
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<td>Z</td>
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<td>D_c (Mg/m³)</td>
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<tr>
<td>F(000)</td>
<td>283</td>
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<tr>
<td>μ (mm⁻¹)</td>
<td>0.670</td>
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<tr>
<td>θ_max (°)</td>
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<tr>
<td>Total reflections</td>
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<tr>
<td>Unique reflections</td>
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<tr>
<td>Reflections [I &gt; 2σ(I)]</td>
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<td>Parameters</td>
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<tr>
<td>R(int)</td>
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<td>Goodness-of-fit</td>
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<tr>
<td>R [F² &gt; 2σ(F²)]</td>
<td>0.0448</td>
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<tr>
<td>wR (F², all data)</td>
<td>0.1169</td>
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