Supporting Information:

First stereoselective total synthesis of cryptomoscatone D2 and synthesis of (5R,7S)-kurzilactone and (+)-cryptofolione via an asymmetric acetate aldol approach

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Contents:

General

Comparison of the $^1$H and $^{13}$C NMR data of Isolated and Synthetic natural products

$^1$H and $^{13}$C spectrum of all new compounds
General techniques: All reactions requiring anhydrous conditions were conducted in flame dried glass apparatus under an atmosphere of nitrogen. THF and Et₂O were freshly distilled from sodium benzophenone ketyl prior to use. CH₂Cl₂ was freshly distilled on CaH₂, toluene and benzene were distilled on molten sodium metal. Anhydrous MeOH was obtained by distillation from magnesium alkoxide and stored under nitrogen over activated 4 Å° molecular sieves. Reactions were followed by TLC analysis using silica plates with fluorescent indicator (254 nm) and visualized with a UV lamp, phosphomolybdic acid or anisaldehyde or β-naphthol solution or alkaline KMnO₄ solution. All commercially available reagents were purchased and were typically used as supplied. Optical rotations were measured at ambient temperature (25 °C) on CHCl₃ solutions with polarimeter using 1 ml capacity cell with 100 mm path length. Infrared spectra were recorded using a thin film supported between NaCl plates or as a solid embedded in a KBr disc. ¹H and ¹³C NMR spectra were recorded in Fourier transform mode at the field strength specified either on a 200 MHz or 300 MHz or 500 MHz spectrometer. Spectra were obtained on CDCl₃ solutions in 5 mm diameter tubes; Chemical shifts in ppm are quoted relative to the residual signals of chloroform (δH 7.26 ppm or δC 77.0 ppm). Multiplicities in the ¹H NMR spectra are described as: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, td = triplet of double, q = quartet, p = pentet, m = multiplet, br = broad; coupling constants are reported in Hz. For low (MS) and high (HRMS) resolution mass spectra ion mass/charge (m/z) ratios are reported as values in atomic mass units.
<table>
<thead>
<tr>
<th></th>
<th>Isolated Cryptomoscatone D2</th>
<th>Synthetic Cryptomoscatone D2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>$\delta_H$ (J Hz) CDCl$_3$</td>
<td>$\delta_H$ (J Hz) CDCl$_3$</td>
</tr>
<tr>
<td>2</td>
<td>164.5</td>
<td>164.8</td>
</tr>
<tr>
<td>3</td>
<td>6.03 $ddd$ 1H (10, 2, 1)</td>
<td>5.98 $d$ 1H (10)</td>
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<tr>
<td>4</td>
<td>6.90 $ddd$ 1H (10, 5, 4)</td>
<td>6.83-6.89 $m$ 1H</td>
</tr>
<tr>
<td>5</td>
<td>2.39 $m$ 2H</td>
<td>2.29-2.35 $m$ 2H</td>
</tr>
<tr>
<td>6</td>
<td>4.66 $dddd$ 1H (11, 9, 5, 3)</td>
<td>4.60-4.66 $m$ 1H</td>
</tr>
<tr>
<td>1'</td>
<td>1.86 $m$ 2H</td>
<td>1.70-1.90 $m$ 4H (1' &amp; 3')</td>
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<tr>
<td>2'</td>
<td>4.38 $m$ 1H</td>
<td>4.33-4.40 $m$ 1H</td>
</tr>
<tr>
<td>3'</td>
<td>1.67 $t$ 2H (6)</td>
<td>43.2</td>
</tr>
<tr>
<td>4'</td>
<td>4.75 $dd$ 1H (10, 6)</td>
<td>4.71-4.79 $m$ 1H</td>
</tr>
<tr>
<td>5'</td>
<td>6.30 $dd$ 1H (16, 6)</td>
<td>6.27 $dd$ 1H (16, 6)</td>
</tr>
<tr>
<td>6'</td>
<td>6.64 $d$ 1H (16)</td>
<td>6.61 $d$ 1H (16)</td>
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<tr>
<td>HAr</td>
<td>7.30 $m$ 5H</td>
<td>7.19-7.38 $m$ 5H</td>
</tr>
<tr>
<td>1''</td>
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<td>136.6</td>
</tr>
<tr>
<td>2''/6''</td>
<td>126.5</td>
<td>126.5</td>
</tr>
<tr>
<td>3''/5''</td>
<td>128.6</td>
<td>128.5</td>
</tr>
<tr>
<td>4''</td>
<td>127.8</td>
<td>127.6</td>
</tr>
</tbody>
</table>

$^1$H (200 MHz), $^{13}$C (50 MHz) NMR data for naturally isolated cryptomoscatone D2. Ref 2

$^1$H (300 MHz), $^{13}$C (75 MHz) NMR data for synthetic cryptomoscatone D2. Chemical shifts in ppm (J in Hz)
$^1$H (400 MHz), $^{13}$C (62.5 MHz) NMR data for naturally isolated (5R,7S)-Kurzilactone$^{9,12a}$

$^1$H (300 MHz), $^{13}$C (75 MHz) NMR data for synthetic (5R,7S)-Kurzilactone. Chemical shifts in ppm ($J$ in Hz)
$^1$H (200 MHz), $^{13}$C (50 MHz) NMR data for naturally isolated (+)-Cryptofolione.\textsuperscript{Ref1, 11a}

$^1$H (500 MHz), $^{13}$C (75 MHz) NMR data for synthetic (+)-Cryptofolione.

Chemical shifts in ppm ($J$ in Hz)
$^1$H NMR SPECTRUM (300 MHz) OF COMPOUND 16 IN CDCl$_3$

$^{13}$C NMR SPECTRUM (75 MHz) OF COMPOUND 16 IN CDCl$_3$
$^1$H NMR SPECTRUM (300 MHz) OF COMPOUND 9 IN CDCl$_3$

$^13$C NMR SPECTRUM (75 MHz) OF COMPOUND 9 IN CDCl$_3$
**H NMR SPECTRUM (300 MHz) OF COMPOUND 23 IN CDCl₃**

- δ 1.64, 4.58, 7.84, 7.23, 7.58, 7.86, 8.05, 11.39

**C NMR SPECTRUM (75 MHz) OF COMPOUND 23 IN CDCl₃**

- δ 29.71, 29.86, 18.62, 18.03, 4.38, 4.31