Supporting Information

Asymmetric Total Synthesis of Naturally Occurring Spiroyclic Tetranorsesquiterpenoid Lanceolactone A

Ranjan Kumar Acharyya and Samik Nanda*

Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur, 721302, India

Content | Page no
--- | ---
1. NMR data comparison for natural and synthetic lanceolactone A | S2
2. NMR data for al compounds | S3-S21
3. Crystal data for compound 2 | S22
Table SI-1: NMR comparison table of natural and synthetic Lanceolactone A

<table>
<thead>
<tr>
<th>Position</th>
<th>Reported $^1$H $\delta$ (ppm); $J$ (Hz)</th>
<th>Observed $^1$H $\delta$ (ppm); $J$ (Hz)</th>
<th>$\Delta\delta$ (ppm)</th>
<th>Reported $^{13}$C $\delta$ (ppm)</th>
<th>Observed $^{13}$C $\delta$ (ppm)</th>
<th>$\Delta\delta$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>170.0</td>
<td>169.9</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5.86, q, (1.4)</td>
<td>5.87, q, (1.6)</td>
<td>0.01</td>
<td>119.4</td>
<td>119.4</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>163.9</td>
<td>163.8</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td>115.2</td>
<td>115.1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.08, m; 2.21, m</td>
<td>2.09, m; 2.22, m</td>
<td>34.3</td>
<td>34.3</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2.18, m; 2.25, m</td>
<td>2.18, m; 2.24, m</td>
<td>36.1</td>
<td>36.0</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>87.5</td>
<td>87.4</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>5.92, dd, (10.7, 1.1)</td>
<td>5.93, dd, (10.8, 1.2)</td>
<td>0.01</td>
<td>142.2</td>
<td>142.2</td>
<td>0.0</td>
</tr>
<tr>
<td>9</td>
<td>5.06, dd, (10.7, 1.1) 5.27, dd, (17.3, 1.2)</td>
<td>5.09, dd, (10.8, 1.2) 5.27, dd, (17.3, 1.2)</td>
<td>112.2</td>
<td>112.2</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1.52, s</td>
<td>1.54, s</td>
<td>0.02</td>
<td>27.7</td>
<td>27.7</td>
<td>0.0</td>
</tr>
<tr>
<td>11</td>
<td>2.05, d, (1.4)</td>
<td>2.07, d, (1.6)</td>
<td>0.02</td>
<td>12.6</td>
<td>12.5</td>
<td>0.1</td>
</tr>
</tbody>
</table>
$^1$H NMR of compound 6 (400 MHz, CDCl$_3$)

13C NMR of compound 6 (101 MHz, CDCl$_3$)
DEPT-135- NMR of compound 6 (101 MHz, CDCl₃)

\[ \text{Diagram of compound 6} \]

\[ \text{NMR spectrum of compound 6} \]

\[ \text{Chemical shifts: 18.09, 51.01, 64.17 ppm} \]

\[ \text{1H NMR of compound 7 (400 MHz, CDCl₃)} \]

\[ \text{Diagram of compound 7} \]

\[ \text{NMR spectrum of compound 7} \]

\[ \text{Chemical shifts: 9.33, 2.72, 0.93, 1.00, 2.04, 5.96, 3.89 ppm} \]

\[ \text{Additional peaks at: 1.05, 1.06, 1.06, 1.06, 1.07, 1.07, 1.09, 1.09, 1.10, 1.11, 1.12, 1.40, 2.60, 2.61, 2.72, 2.74, 3.66, 3.69, 3.69, 3.72 ppm} \]

\[ \text{Additional peaks at: 7.38, 7.39, 7.39, 7.40, 7.41, 7.41, 7.43, 7.43, 7.43, 7.44, 7.44, 7.45, 7.45, 7.46, 7.46, 7.47, 7.47, 7.48, 7.70, 7.70, 7.72 ppm} \]
$^{13}$C NMR of compound 7 (101 MHz, CDCl$_3$)

DEPT-135- NMR of compound 7 (101 MHz, CDCl$_3$)
**$^1$H NMR of compound 8 (400 MHz, CDCl$_3$)**

TBDPSO $\text{OH}$ TMS

**$^{13}$C NMR of compound 8 (101 MHz, CDCl$_3$)**

TBDPSO $\text{OH}$ TMS
DEPT-135- NMR of compound 8 (101 MHz, CDCl₃)

\[
\text{TBDPSO} \quad \text{OH} \quad \text{TMS}
\]

1H NMR of compound 4 (400 MHz, CDCl₃)

\[
\text{TBDPSO} \quad \text{OH}
\]
$^{13}$C NMR of compound 4 (101 MHz, CDCl$_3$)

DEPT-135- NMR of compound 4 (101 MHz, CDCl$_3$)
$^{1}H$ NMR of compound 5 (400 MHz, CDCl$_3$)

$^{13}C$ NMR of compound 5 (101 MHz, CDCl$_3$)
DEPT-135- NMR of compound 5 (101 MHz, CDCl₃)

\[ \begin{align*}
\text{CO}_2\text{H}
\end{align*} \]

1H NMR of compound 3 (400 MHz, CDCl₃)

\[ \begin{align*}
\text{TBDPSO}_2\text{OH}
\end{align*} \]
$^{13}$C NMR of compound 3 (101 MHz, CDCl$_3$)

DEPT-135- NMR of compound 3 (101 MHz, CDCl$_3$)
NOESY Spectrum of compound 3 (600 MHz, CDCl₃)

1H NMR of compound 9 (400 MHz, CDCl₃)
\textbf{\(^{13}\text{C} \text{ NMR of compound 9 (126 MHz, CDCl}_3\)}}

\begin{center}
\includegraphics[width=\textwidth]{c_nmr.png}
\end{center}

\textbf{DEPT-135- NMR of compound 9 (126 MHz, CDCl\textsubscript{3})}
H NMR of compound 10 (400 MHz, CDCl$_3$)

1$^3$C NMR of compound 10 (126 MHz, CDCl$_3$)
DEPT-135- NMR of compound 10 (126 MHz, CDCl$_3$)

$^1$H NMR of compound 2 (400 MHz, CDCl$_3$)
$^{13}$C NMR of compound 2 (126 MHz, CDCl$_3$)

DEPT-135- NMR of compound 2 (126 MHz, CDCl$_3$)
$^1$H NMR of compound 11 (400 MHz, CDCl$_3$)

$^{13}$C NMR of compound 11 (151 MHz, CDCl$_3$)
DEPT-135- NMR of compound 11 (151 MHz, CDCl$_3$)

$^1$H NMR of compound 1; Lanceolactone A (600 MHz, CDCl$_3$)
$^{13}$C NMR of compound 1; Lanceolactone A (151 MHz, CDCl$_3$)

DEPT-135- NMR of compound 1; Lanceolactone A (151 MHz, CDCl$_3$)
HSQC spectrum of compound 1; Lanceolactone A (600 MHz, CDCl₃)

COSY Spectrum of compound 1; Lanceolactone A (600 MHz, CDCl₃)
HMBC Spectrum of compound 1; Lanceolactone A (600 MHz, CDCl₃)

NOESY Spectrum of compound 1; Lanceolactone A (600 MHz, CDCl₃)
Crystal data and structure refinement for compound 2

X-ray crystal data of compound 2 (the following crystal has been deposited at the Cambridge Crystallographic Data Centre and has the deposition number CCDC NO: 1834617

CCDC NO: 1834617
ORTEP presentation (drawn at 50% probability)
Bond precision: C-C = 0.0050 Å  Wavelength=0.71073

Cell: 
  a=11.660(14)  b=12.070(9)  c=18.027(13)
  alpha=90  beta=100.58(7)  gamma=90

Temperature: 290 K

<table>
<thead>
<tr>
<th>Calculated</th>
<th>Reported</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>2494(4)</td>
</tr>
<tr>
<td>Space group</td>
<td>P 21/c</td>
</tr>
<tr>
<td>Hall group</td>
<td>-P 2ybc</td>
</tr>
<tr>
<td>Moiety formula</td>
<td>C26 H32 O4 Si</td>
</tr>
<tr>
<td>Sum formula</td>
<td>C26 H32 O4 Si</td>
</tr>
<tr>
<td>Mr</td>
<td>436.61</td>
</tr>
<tr>
<td>Dx, g cm⁻³</td>
<td>1.163</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Mu (mm⁻¹)</td>
<td>0.122</td>
</tr>
<tr>
<td>F000</td>
<td>936.0</td>
</tr>
<tr>
<td>F000’</td>
<td>936.73</td>
</tr>
<tr>
<td>h,k,lmax</td>
<td>13,14,21</td>
</tr>
<tr>
<td>Nref</td>
<td>4325</td>
</tr>
<tr>
<td>Tmin,Tmax</td>
<td>0.978,0.984</td>
</tr>
<tr>
<td>Tmin’</td>
<td>0.978</td>
</tr>
</tbody>
</table>

Correction method= Not given

Data completeness= 0.991  Theta(max)= 24.860

R(reflections)= 0.0499(2513)  wR2(reflections)= 0.1623(4284)

S = 0.894  Npar= 285