Chirality Extension of an Oxazine Building Block En Route to Total Syntheses of (+)-Hyacinthacine A$_2$ and Sphingofungin B

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Supporting information

S2 $^1$H NMR of syn-5a
S3 $^{13}$C NMR of syn-5a
S4 $^1$H NMR of anti-5a
S5 $^{13}$C NMR of anti-5a
S6 NOESY of trans-6
S7 NOESY of cis-6
S8 $^1$H NMR of syn-5b
S9 $^{13}$C NMR of syn-5b
S10 $^1$H NMR of anti-5b
S11 $^{13}$C NMR of anti-5b
S12 $^1$H NMR of syn-5c
S13 $^{13}$C NMR of syn-5c
S14 $^1$H NMR of anti-5c
S15 $^{13}$C NMR of anti-5c
S16 $^1$H NMR of syn-5d
S17 $^{13}$C NMR of syn-5d
S18 $^1$H NMR of anti-5d
S19 $^{13}$C NMR of anti-5d
S20 $^1$H NMR of syn-5e
S21 $^{13}$C NMR of syn-5e
S22 $^1$H NMR of anti-5e
S23 $^{13}$C NMR of anti-5e
S24 $^1$H NMR of syn-5f
S25 $^{13}$C NMR of syn-5f
S26 $^1$H NMR of anti-5f
S27 $^{13}$C NMR of anti-5f
S28 $^1$H NMR of precursor of 8
S29 $^{13}$C NMR of precursor of 8
S30 $^1$H NMR of 8
S31 $^{13}$C NMR of 8
S32 $^1$H NMR of 7
S33 $^{13}$C NMR of 7
S34 $^1$H NMR of 9
S35 $^{13}$C NMR of 9
S36 $^1$H NMR of 1
S37 $^{13}$C NMR of 1
S38 Comparison of reported NMR data with those of 1
S39 $^1$H NMR of 13
S40 $^{13}$C NMR of 13
S41 $^1$H NMR of 14
S42 $^{13}$C NMR of 14
S43 $^1$H NMR of 15
S44 $^{13}$C NMR of 15
S45 $^1$H NMR of 16
S46 $^{13}$C NMR of 16
S47 $^1$H NMR of 17
S48 $^{13}$C NMR of 17
S49 $^1$H NMR of 2
S50 $^{13}$C NMR of 2
S51 Comparison of reported NMR data with those of 2
syn-5a (700 MHz, CDCl₃)
syn-5a (175 MHz, CDCl₃)
anti-5a (500 MHz, CDCl₃)
anti-5a (125 MHz, CDCl₃)
trans-6 (NOESY)
cis-6 (NOESY)

Acetal methyl

$\text{cis-6 (NOESY)}$

[Chemical structure diagram]

Acetal methyl

F1 Chemical Shift (ppm)

F2 Chemical Shift (ppm)
**syn-5b (700 MHz, CDCl₃)**

![NMR Spectrum of syn-5b](image)

**NMR Data:**
- **8.5 to 8.0 ppm:** 2.00, 3.73
- **7.5 to 7.0 ppm:** 1.01, 1.03, 1.08, 1.09, 0.97
- **6.5 to 6.0 ppm:** 0.87, 0.90
- **5.5 to 5.0 ppm:** 1.0, 1.1
- **4.5 to 4.0 ppm:** 1.5, 2.0, 3.0, 3.5
- **2.5 to 2.0 ppm:** 2.0, 2.5, 3.0
- **1.5 to 1.0 ppm:** 4.0, 4.5
- **0.5 to 0.0 ppm:** 6.4, 14.7
syn-5b (175 MHz, CDCl₃)
anti-5b (700 MHz, CDCl$_3$)
anti-5b (175 MHz, CDCl₃)
syn-5c (700 MHz, CDCl₃)
**syn-5c (175 MHz, CDCl₃)**

![NMR spectrum of syn-5c](image)

Diagram showing the NMR spectrum with peaks at various ppm values.
anti-5c (700 MHz, CDCl₃)
anti-5c (175 MHz, CDCl₃)
syn-5d (700 MHz, CDCl$_3$)
syn-5d (175 MHz, CDCl₃)
anti-5d (700 MHz, CDCl₃)
anti-5d (175 MHz, CDCl₃)
syn-5e (700 MHz, CDCl₃)
syn-5e (175 MHz, CDCl₃)
anti-5e (700 MHz, CDCl₃)
anti-5e (175 MHz, CDCl$_3$)
syn-5f (700 MHz, CDCl₃)
**syn-5f (175 MHz, CDCl₃)**

![Proton NMR spectrum of syn-5f](image)

**Chemical Structure**

- TBS: tert-butyldimethylsilyl group
- OH: hydroxyl group
- Ph: phenyl group

**NMR Data**

- 1H: 6.93, 7.23, 7.32, 7.42, 7.47, 7.74, 7.79
- 13C: 51.27, 53.28, 58.85, 65.87, 66.13, 69.78, 70.67, 70.87, 72.80

**ppm Scale**

- Range: 0 to 165
anti-5f (700 MHz, CDCl₃)
anti-5f (175 MHz, CDCl₃)
Precursor of 8 (700 MHz, CDCl₃)
Precursor of 8 (175 MHz, CDCl₃)
$8 (700 \text{ MHz, CDCl}_3)$
8 (175 MHz, CDCl₃)
7 (700 MHz, CDCl₃)
7 (175 MHz, CDCl$_3$)
9 (700 MHz, CDCl₃)
9 (175 MHz, CDCl₃)
1 (700 MHz, D$_2$O)
1 (175 MHz, D$_2$O)
Table 1. Comparison of reported $^1$H NMR data with those of 1.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Asano et al. $^4$ (natural product)</th>
<th>Fox et al. $^5$a (pH 7.6)</th>
<th>Fox et al. $^5$a (pH 9.0)</th>
<th>Izquierdo et al. $^5$i</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_2$O</td>
<td>3.81 (t, $J = 8.8$ Hz, 1H)</td>
<td>3.87–3.76 (m, 3H)</td>
<td>3.79–3.71 (m, 3H)</td>
<td>3.88–3.80 (m, 3H)</td>
<td></td>
</tr>
<tr>
<td>H-2</td>
<td>3.80 (dd, $J = 11.8$, 3.9 Hz, 1H)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
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<tr>
<td>H-1</td>
<td>3.76 (dd, $J = 8.8$, 7.1 Hz, 1H)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
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<tr>
<td>H-8</td>
<td>3.67 (dd, $J = 11.8$, 6.5 Hz, 1H)</td>
<td>3.70 (dd, $J = 12.0$, 6.3 Hz, 1H)</td>
<td>3.63 (dd, $J = 12.1$, 6.0 Hz, 1H)</td>
<td>3.75–3.71 (m, 1H)</td>
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<tr>
<td>H-7a</td>
<td>3.32 (m, 1H)</td>
<td>3.37–3.30 (m, 1H)</td>
<td>3.37 (m, 1H)</td>
<td>3.40–3.36 (m, 1H)</td>
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<tr>
<td>H-5</td>
<td>2.96 (ddd, $J = 11.0$, 7.3, 5.9 Hz, 1H)</td>
<td>3.08–2.99 (m, 1H)</td>
<td>3.04 (broad dt, $J = 11.7$, 6.5 Hz, 1H)</td>
<td>3.10–3.05 (m, 1H)</td>
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<tr>
<td>H-5</td>
<td>2.81 (dt, $J = 11.0$, 5.6 Hz)</td>
<td>2.95–2.82 (m, 2H)</td>
<td>2.93–2.85 (m, 2H)</td>
<td>2.96–2.88 (m, 2H)</td>
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<tr>
<td>H-3</td>
<td>2.77 (ddd, $J = 8.8$, 6.5, 3.9 Hz, 1H)</td>
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<tr>
<td>H-7</td>
<td>1.97 (m, 1H)</td>
<td>2.07–1.91 (m, 2H)</td>
<td>1.96–1.72 (m, 4H)</td>
<td>2.06–2.00 (m, 1H)</td>
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<tr>
<td>H-6</td>
<td>1.90 (m, 1H)</td>
<td>-</td>
<td>-</td>
<td>2.00–1.95 (m, 1H)</td>
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<tr>
<td>H-6</td>
<td>1.82 (m, 1H)</td>
<td>-</td>
<td>1.91–1.77 (m, 2H)</td>
<td>-</td>
<td>1.93–1.85 (m, 2H)</td>
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<tr>
<td>H-7</td>
<td>1.77 (m, 1H)</td>
<td>-</td>
<td>-</td>
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</tr>
</tbody>
</table>

Table 2. Comparison of reported $^{13}$C NMR data with those of 1.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Asano et al. $^4$ (natural product)</th>
<th>Fox et al. $^5$a (pH 7.6)</th>
<th>Fox et al. $^5$a (pH 9.0)</th>
<th>Izquierdo et al. $^5$i</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>D$_2$O</td>
<td>82.9</td>
<td>82.5</td>
<td>81.09</td>
<td>79.4</td>
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<tr>
<td>C-1</td>
<td>79.8</td>
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<td>C-2</td>
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<tr>
<td>C-7a</td>
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<tr>
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<td>C-6</td>
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<td>27.3</td>
<td>27.3</td>
<td>26.32</td>
<td>24.4</td>
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13 (175 MHz, CDCl₃)
14 (500 MHz, CDCl₃)
$^{14}$ (125 MHz, CDCl$_3$)
15 (700 MHz, CDCl₃)
15 (175 MHz, CDCl₃)
16 (700 MHz, CDCl$_3$)
16 (175 MHz, CDCl₃)

[Diagram of chemical structure with spectral data]
17 (700 MHz, CDCl$_3$)
17 (175 MHz, CDCl$_3$)
2 (700 MHz, CD$_3$OD)
2 (175 MHz, CD₃OD)
### Table 3. Comparison of reported $^1$H NMR data with those of 2.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Kobayashi et al.$^9$</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CD$_3$OD</td>
<td>CD$_3$OD</td>
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<tr>
<td>0.89 (t, $J = 6.4$ Hz, 3H)</td>
<td>0.91 (t, $J = 7.0$ Hz, 3H)</td>
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<tr>
<td>1.18–1.60 (m, 20H)</td>
<td>1.32–1.46 (m, 20H)</td>
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<tr>
<td>1.98–2.06 (m, 2H)</td>
<td>2.08–2.10 (m, 2H)</td>
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</tr>
<tr>
<td>3.49 (brs, 1H)</td>
<td>3.52 (brs, 1H)</td>
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<tr>
<td>3.60 (d, $J = 6.9$ Hz, 1H)</td>
<td>3.64 (dd, $J = 6.5$, 1.7 Hz, 1H)</td>
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<tr>
<td>3.77 (d, $J = 3.6$ Hz, 1H)</td>
<td>3.78 (d, $J = 4.9$ Hz, 1H)</td>
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<tr>
<td>4.06–4.10 (m, 2H)</td>
<td>4.17–4.19 (m, 2H)</td>
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<tr>
<td>5.47 (dd, $J = 15.2$, 7.3 Hz, 1H)</td>
<td>5.51 (dd, $J = 15.4$, 7.4 Hz, 1H)</td>
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<tr>
<td>5.77 (dt, $J = 15.2$, 6.6 Hz, 1H)</td>
<td>5.80 (dt, $J = 14.6$, 6.4 Hz, 1H)</td>
<td></td>
</tr>
</tbody>
</table>

### Table 4. Comparison of reported $^{13}$C NMR data with those of 2.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Kobayashi et al.$^9$</th>
<th>This work</th>
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<tr>
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<td>CD$_3$OD</td>
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