Supporting Information

Synthesis of modified β-methoxyphenylalanines via diazonium chemistry and their incorporation in desoxycyclomarin analogues

Alexander Kiefer, Uli Kazmaier*

Institute for Organic Chemistry, Saarland University, 66123 Saarbrücken
(2R,3R)-N-Boc-3-hydroxy-1-O-(tert-butyl dimethylsilyl)-para-nitrophenylalaninol (2)
(2R,3R)-N-Boc-3-methoxy-1-O-(tert-butyldimethylsilyl)-para-nitrophenylalaninol (3a)
(2R,3R)-N-Boc-3-methoxy-1-O-(tert-butyldimethylsilyl)-\textit{para}-aminophenylalaninol (3b)
(2R,3R)-N-Boc-3-methoxy-1-O-(tert-butyldimethylsilyl)-para-bromophenylalaninol (3c)
(2R,3R)-N-Boc-3-methoxy-1-O-(tert-butyldimethylsilyl)-para-azidophenylalaninol (3d)
(2R,3R)-N-Boc-3-methoxy-1-O-(tert-butyldimethylsilyl)-phenylalaninol (3e)
(2R,3R)-N-Boc-3-methoxy-para-nitrophenylalaninol (4a)
(2R,3R)-N-Boc-3-methoxy-para-bromophenylalaninol (4c)
(2R,3R)-N-Boc-3-methoxy-para-azidophenylalaninol (4d)
**(2R,3R)-N-Boc-3-methoxy-phenylalaninol (4e)**

![Chemical Structures](image)

**Chemical Shifts (ppm)**

<table>
<thead>
<tr>
<th>Carbon Number</th>
<th>Chemical Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>118.34</td>
</tr>
<tr>
<td>2</td>
<td>128.466</td>
</tr>
<tr>
<td>3</td>
<td>127.997</td>
</tr>
<tr>
<td>4</td>
<td>126.976</td>
</tr>
<tr>
<td>5</td>
<td>83.351</td>
</tr>
<tr>
<td>6</td>
<td>79.543</td>
</tr>
<tr>
<td>7</td>
<td>77.317</td>
</tr>
<tr>
<td>8</td>
<td>76.682</td>
</tr>
<tr>
<td>9</td>
<td>63.819</td>
</tr>
<tr>
<td>10</td>
<td>57.095</td>
</tr>
<tr>
<td>11</td>
<td>28.245</td>
</tr>
</tbody>
</table>
(2S,3R)-N-Boc-3-methoxy-para-nitrophenylalanine (5a)
(2S,3R)-N-Boc-3-methoxy-para-azidophenylalanine (5d)
(2S,3R)-N-Boc-3-methoxy-para-azidophenylalanine (5d)
(2S,3R)-N-Boc-3-methoxyphenylalanine (5e)
$N$-Boc-$(2S,3R)$-(3-methoxy-$para$-nitrophenylalanyl)-(S)-valyl-(S)-N-methyl-leucine methyl ester (7a)
N-Boc-(2S,3R)-(3-methoxy-para-bromophenylalanyl)-(S)-valyl-(S)-N-methyl-leucine methyl ester (7c)
N-Boc-(2S,3R)-(3-methoxy-para-azidophenylalanyl)-(S)-valyl-(S)-N-methyl-leucine methyl ester (7d)
N-Boc-(S)-alanyl-(2S,3R)-(3-methoxy-para-nitrophenylalanyl)-(S)-valyl-(S)-N-methyl-leucine methyl ester (9a)
$N$-Boc-$(S)$-alanyl-$(2S,3R)$-$(3$-methoxy-para-bromphenylalanyl)$(S)$-valyl-$(S)$-$N$-methyl-leucine methyl ester (9c)
N-Boc-(S)-alanyl-(2S,3R)-(3-methoxy-para-azidophenylalanyl)-(S)-valyl-(S)-N-methyl-leucine methyl ester (9d)
N-Alloc-N-methyl-(2S,4R)-[5-(tert-butyldimethylsilyl)oxy-leucyl]-(S)-alanyl-(2S,3R)-(3-methoxy-para-nitrophenylalanyl)-(S)-valyl-(S)-N-methyl-leucine methyl ester (11a)
N-Alloc-N-methyl-(2S,4R)-[5-(tert-butyldimethylsilyl)oxy-leucyl]-(S)-alanyl-(2S,3R)-(3-methoxy-para-bromophenylalanyl)-(S)-valyl-(S)-N-methyl-leucine methyl ester (11c)
N-Alloc-N-methyl-(2S,4R)-[5-(tert-butyldimethylsilyl)oxy-leucyl]-(S)-alanyl-(2S,3R)-(3-methoxy-para-azidophenylalanyl)-(S)-valyl-(S)-N-methyl-leucine methyl ester (11d)
$N$-Alloc-(S)-[N'-tert-prenyl-tryptophanyl]-N-methyl-(2S,4R)-[5-(tertbutyldimethylsilyl)-oxy-leucyl]-(S)-alanyl-(2S,3R)-(3-methoxy-para-nitrophenylalanyl)-(S)-valyl-(S)-N-methyl-leucine methyl ester (13a)
N-Alloc-(S)-[N'- tert-prenyl-tryptophanyl]-N-methyl-(2S,4R)-[5-(tertbutyldimethylsilyl)-oxy-leucyl]-(S)-alanyl-(2S,3R)-(3-methoxy-para-bromophenylalanyl)-(S)-valyl-(S)-N-methyl-leucine methyl ester (13c)
N-Alloc-(S)-[N'-tert-prenyl-triptophany]-N-methyl-(2S,4R)-[5-(tertbutyldimethylsilyl)-oxy-leucyl]-(S)-alanyl-(2S,3R)-(3-methoxy-para-azidophenylalanyl)-(S)-valyl-(S)-N-methyl-leucine methyl ester (13d)
$N$-Alloc-(2S,3R)-(2-amino-3,5-dimethyl-hex-4-enoyl)-(S)-$N'$-tert-prenyl-trytophanyl-$N$-methyl-(2S,4R)-[5-(tert-butyldimethylsilyloxy-leucyl]-(S)-alanyl-(2S,3R)-(3-methoxy-para-nitrophenylalan)l-(S)-valyl-(S)-$N$-methyl-leucine methyl ester (15a)
N-Alloc-(2S,3R)-(2-amino-3,5-dimethyl-hex-4-enoyl)-(S)-N’tert-prenyl-trypophanyln-N-methyl-(2S,4R)-[5-(tert-butyldimethylsilyloxy-leucyl]-(S)-alanyl-(2S,3R)-(3-methoxy-para-bromophenylalanyl)-(S)-valyl-(S)-N-methyl-leucine methyl ester (15c)
N-Alloc-(2S,3R)-(2-amino-3,5-dimethyl-hex-4-enoyl)-(S)-N'-tert-prenyl-tryptophanyl-N-methyl-(2S,4R)-[5-(tert-butyldimethylsilyloxy)leucyl)-(S)-alanyl-(2S,3R)-(3-methoxy-para-azidophenylalanyl)-(S)-valyl-(S)-N-methyl-leucine methyl ester (15d)
cyclo-(2S,3R)-(2-Amino-3,5-dimethyl-hex-4-enoyl)-(S)-N’-tert-prenyl-tryptophanyl-N-methyl-(2S,4R)-[5-(tert-butyldimethylsilyl)oxy-leucyl]-(S)-alanyl-(2S,3R)-(3-methoxy-para-nitrophenylalanyl)-(S)-valyl-(S)-N-methyl-leucine (16a)
cyclo-(2S,3R)-(2-Amino-3,5-dimethyl-hex-4-enoyl)-(S)-N'-tert-prenyl-tryptophanyl-N-methyl-(2S,4R)-[5-(tert-butyldimethylsilyl)oxy-leucyl]-(S)-alanyl-(2S,3R)-(3-methoxy-para-aminophenylalanyl)-(S)-valyl-(S)-N-methyl-leucine (16b)
(2S,R)-12-Amino-3,5-dimethylhex-4-enoyl-(S)-valyl-leucyl-13-methoxy-para-
bromophenylalanyl-(S)-valyl-(S)-N-methyl-leucine (16c)

(cyclo-(2S,R)-12-Amino-3,5-dimethylhex-4-enoyl-(S)-valyl-leucyl-13-methoxy-para-
bromophenylalanyl)-(S)-valyl-(S)-N-methyl-leucine (16c)
cyclo-(2S,3R)-(2-Amino-3,5-dimethyl-hex-4-enoyl)-(S)-N'-tert-prenyl-tryptophanyl-N-methyl-(2S,4R)-[5-(tert-butylidimethylsilyloxy-leucyl]-(S)-alanyl-(2S,3R)-(3-methoxy-para-azidophenylalanyl)-(S)-valyl-(S)-N-methyl-leucine (16d)