Supplementary Material

Total synthesis of structures proposed for quinocitrinines A and B and their analogs. Microwave energy as efficient tool for generating heterocycles

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7  220nm

7  254nm
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Figure S44. QTOF-MS of compound 6b

**Generated Molecular Formulas**

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Figure S45. MALDI-TOF MS of compound 6b
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Figure S47. H-NMR of compound 6a in DMSO
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Figure S49. DEPT of compound 6a in DMSO
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*Generated Molecular Formulas*  

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Figure S52. HPLC of compound 6a

Figure S53. H-NMR of compound 6c in DMSO
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Figure S55. COSY of compound 6c in DMSO
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Figure S59. QTOF-MS of compound 6c

File Name: QTOFdataTraining\by3\VC1090\VC1090_DHB(THF)_RP\PEP\M95\A1-61

**Generated Molecular Formulas**

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Date: 21-Feb-2010

VICTORIA23A 15 (0.278) Cn (Cen, 4, 80.00, Ar); Sm (Mn, 2x1.00); Sb (1,40.00); Cm (1:290) TOF MSMS 283.
Figure S60. MALDI-TOF MS of compound 6c

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Figure S72. QTOF-MS of compound 6e
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![MALDI-TOF MS of compound 6e](image)

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Figure S80. QTOF-MS of compound 6f

Generated Molecular Formulas
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![MALDI-TOF MS of compound 6f](image)

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![HPLC of compound 6f](image)
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Figure S88. HPLC of compound 6g

4-methoxy-2-nitrobenzaldehyde

\[ \text{\chemimage{H\ring{}O\to\ring{}|O\to\ring{}}H} \]

$\text{^1HNMR:}$ (300 MHz, DMSO-d$_6$), $\delta_{\text{H}}$ (ppm): 3.94 (s,3H), 7.42 (dd,1H,$J=8.7$Hz, $J=2.4$Hz), 7.62(d,1H,$J=2.4$Hz), 7.96 (s,3H, $J=8.7$Hz), 10.04 (s,1H).
\( ^{13}\text{CNMR} \): (75 MHz, DMSO-\text{d}_6), \delta_C (ppm): 56.72, 109.8, 118.58, 122.05, 132.61, 151, 163.54, 188.22. (yield 11\%) \textbf{MS}: MW=181 g/mol, MH\(^+\)=182. \textbf{HPLC}: t_R = 2.974 min.

Figure S89. H-NMR of 4-methoxy-2-nitrobenzaldehyde in DMSO.
Figure S90. C-NMR of 4-methoxy-2-nitrobenzaldehyde in DMSO

Figure S91. DEPT of 4-methoxy-2-nitrobenzaldehyde in DMSO
Figure S92. HPLC of 4-methoxy-2-nitrobenzaldehyde

2-amino-4-methoxybenzaldehyde

\[
\begin{array}{c}
\text{O} \\
\text{NH}_2 \\
\text{O} \\
\end{array}
\]

\(^{1}\text{HNMR:}\) (300 MHz, DMSO-\(d_6\)), \(\delta (\text{ppm})\): 3.75 (s, 3H), 6.23 (m, 2H), 7.19 (bs, NH), 7.42 (d, 1H, \(J=9.3\text{Hz}\)), 9.63 (s, 1H).

\(^{13}\text{CNMR:}\) (75 MHz, DMSO-\(d_6\)), \(\delta (\text{ppm})\): 55.17, 97.66, 104.30, 112.92, 137.61, 153.02, 164.71, 191.62. (yield 83%). \textbf{MS:}\ MW=151.16 \text{g/mol}, MH\(^+\)=152. \textbf{HPLC:}\ \(t_R=2.51\text{ min}\).
Figure S93. H-NMR of 4-methoxy-2-nitrobenzaldehyde in DMSO

Figure S94. C-NMR of 4-methoxy-2-nitrobenzaldehyde in DMSO
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Figure S103. C-NMR of compound 6h in DMSO

Figure S104. DEPT of compound 6h in DMSO
Figure S105. QTOF-MS of compound 6h

![QTOF-MS of compound 6h](image)

Figure S106. QTOF-MS of compound 6h

![QTOF-MS of compound 6h](image)
Figure S107. HPLC of compound 6h

5a

$\text{\textsuperscript{1}H}N\text{MR:}$ (300 MHz, DMSO-d$_6$), $\delta_H$(ppm): 4.56 (s,2H), 7.68 (t,1H,J=6.9Hz), 7.89 (t,1H,J=6.9Hz), 8.10 (d,1H,J=8.7Hz), 8.21 (d,1H,J=8.7Hz), 8.76 (s,1H), 8.94(bs,N-H).

$\text{\textsuperscript{13}C}N\text{MR:}$ (75 MHz, DMSO-d$_6$), $\delta_C$(ppm): 46.68, 124.08, 126.62, 127.02, 128.50, 129.87, 131.37, 132.24, 149.12, 163.14, 167.81.(yield 89%) $\textbf{MS}$: MW=184 g/mol, MH$^+$ =185.

$\text{HPLC:}$ $t_R = 3.26$min.
Figure S108. H-NMR of compound 5a in DMSO

Figure S109. C-NMR of compound 5a in DMSO
Figure S110. HPLC of compound 5a

Figure S111. QTOF-MS of compound 5a
Figure S112. QTOF-MS of compound 5a

**5b** (major SS)

![Chemical Structure of 5a]

**$^1$HNMR:** (300 MHz, DMSO-d$_6$, $\delta$H(PPM): 0.49 (d,3H,J=6.6Hz), 0.98 (t,3H, J=7.5Hz), 1.33 (m,1H), 1.60 (m,1H), 2.24 (m,1H), 4.76 (d,1H,J=2.1Hz), 7.67 (m,1H), 7.87 (m,1H), 8.11 (d,1H,J=8.1Hz), 8.19 (d,1H,J=8.1Hz), 8.71 (s,1H), 9.01 (bs,1H).

**$^{13}$CNMR:** (75 MHz, DMSO-d$_6$, $\delta$C(PPM): 11.98, 12.64, 15.42, 26.35, 37.32, 60.82, 83.73, 124.45, 126.63, 128.69, 129.79, 131.28, 131.91, 149.19, 165.49, 167.80. (yield 50.8%) **MS:** MW=240 g/mol, MH$^+$ =241. **HPLC:** $t_R$ = 3.88min.

**5b** (minor RS)

![Chemical Structure of 5b]

**$^1$HNMR:** (300 MHz, DMSO-d$_6$, $\delta$H(PPM): 0.77 (t,3H,J=7.5Hz), 0.93 (d,3H,J=7.2Hz), 0.92 (m,1H), 1.17 (m,1H), 2.16 (m,1H), 4.69 (d,1H,J=2.7Hz), 7.67 (m,1H), 7.87 (m,1H), 8.11
(d,1H,J=8.1Hz), 8.19 (d,1H,J=8.1Hz), 8.70 (s,1H), 9.04 (bs,1H). $^{13}$CNMR: (75 MHz, DMSO-d$_6$, $\delta_{(ppm)}$: 11.79, 12.64, 15.42, 23.37, 37.55, 62.01, 83.73, 124.62, 127.09, 128.79, 129.79, 131.28, 131.84, 149.06, 165.09, 167.49. (yield 43.2%) MS: MW=240 g/mol, MH$^+$ =241. HPLC: $t_R$=3.88 min.

Figure S113. H-NMR of compound 5b in DMSO
Figure S114. C-NMR of compound 5b in DMSO

Figure S115. DEPT of compound 5b in DMSO
Figure S116. QTOF-MS of compound 5b

![QTOF-MS of compound 5b]"}

Figure S117. HPLC of compound 5b

![HPLC of compound 5b]"

5c

\[
\begin{align*}
\text{1H NMR:} & \quad (300 \text{ MHz, DMSO-d6, } \delta_{\text{H}}(\text{ppm}): \\
& 0.65 \text{ (d, } 3\text{H, } J=6.9\text{Hz), } 1.06 \text{ (d, } 3\text{H, } J=6.9\text{Hz), } 2.43 \\
& (\text{m, } 1\text{H), } 4.65 \text{ (d, } 1\text{H, } J=3.3\text{Hz), } 7.67 \text{ (m, } 1\text{H), } 7.87 \text{ (m, } 1\text{H), } 8.11 \text{ (d, } 1\text{H, } J=8.4\text{Hz), } 8.19
\end{align*}
\]
(d,1H,J=8.1Hz), 8.72 (s,1H), 9.04 (bs,1H). $^{13}$CNMR: (75 MHz, DMSO-d$_6$, δ$_	ext{C}$ ppm): 15.75, 19.21, 30.77, 62.48, 124.39, 126.65, 127.09, 128.76, 129.78, 131.26, 131.90, 149.12, 165.15, 167.68. (yield 63%) MS: MW=226 g/mol, MH$^+$=227. HPLC: $t_R$=3.67 min.

Figure S118. H-NMR of compound 5c in DMSO
Figure S119. C-NMR of compound 5c in DMSO

Figure S120. DEPT of compound 5c in DMSO
Figure S121. QTOF-MS of compound 5c

Figure S122. HPLC of compound 5c

**5d**

\[
\begin{align*}
\text{HNMR:} \quad & (300 \text{ MHz, DMSO-}d_6, \delta \text{ H(ppm)}: 3.25 \text{ (m,2H), 5.09 \ (t,1H,J=4.8Hz), 7.05} \\
& \text{ (m,5H),7.67 \ (m,1H), 7.92 \ (m,1H), 8.15 \ (d,1H,J=8.7Hz), 8.19 \ (m,1H,J=8.1Hz), 8.56 \ (s,1H),} \\
& 9.01 \ (\text{NH, bs}) . \quad 13\text{CNMR:} \quad & (75 \text{ MHz, DMSO-}d_6, \delta \text{ C (ppm)}: 38.07, 57.94, 124.21, 126.26, 
\end{align*}
\]
126.71, 127.00, 127.72, 128.69, 129.76, 131.32, 131.88, 135.81, 149.04, 164.88, 166.96.
(yield 88.7%) \textbf{MS}: MW=274 g/mol, MH^+=275.

\textbf{HPLC}: t_R = 3.97 min.

Figure S123. H-NMR of compound 5d in DMSO
Figure S124. C-NMR of compound 5d in DMSO

Figure S125. DEPT of compound 5d in DMSO
Figure S126. QTOF-MS of compound 5d

![QTOF-MS of compound 5d](image)

Figure S127. HPLC of compound 5d

![HPLC of compound 5d](image)

5e

![Chemical structure of 5e](image)

$^1$HNMR: (300 MHz, DMSO-$d_6$), $\delta$ [ppm]: 1.49 (d, 3H, J=6.6Hz), 4.78 (q, 1H, J=6.6Hz), 7.67 (m, 1H), 7.88 (m, 1H), 8.12 (d, 1H, J=8.1Hz), 8.19 (d, 1H, J=8.1Hz), 8.73 (s, 1H), 9.02 (bs, 1H).
$^{13}$CNMR: (75 MHz, DMSO-d$_6$, $\delta$ C (ppm): 19.25, 53.35, 123.46, 126.67, 127.15, 128.64, 129.79, 131.29, 132.33, 149.16, 166.72. (yield 54.7%) MS: MW=198 g/mol, MH$^+$ =199.

HPLC: $t_R = 3.29$ min.

Figure S128. H-NMR of compound 5e in DMSO
Figure S129. C-NMR of compound 5e in DMSO

![C-NMR of compound 5e in DMSO](image1)

Figure S130. QTOF-MS of compound 5e

![QTOF-MS of compound 5e](image2)

![LC-MS of 220nm](image3)

![LC-MS of 254nm](image4)
Figure S131. HPLC of compound 5e

5f

$^{1}$HNMR: (300 MHz, DMSO-d$_6$), $\delta_{H(\text{ppm})}$: 0.89 (d, 3H, J=6.6Hz), 1.01 (d, 3H, J=6.6Hz), 1.46 (m, 1H), 1.88 (m, 1H), 2.20 (m, 1H), 4.73 (dd, 1H, J=8.7Hz, J=3.9Hz), 7.67 (m, 1H), 7.87 (m, 1H), 8.12 (d, 1H, J=8.1Hz), 8.19 (d, 1H, J=8.1Hz), 8.72 (s, 1H), 9.16 (bs, 1H, NH). $^{13}$CNMR: (75 MHz, DMSO-d$_6$), $\delta_{C(\text{ppm})}$: 21.81, 23.47, 24.53, 39.55, 43.10, 55.90, 123.69, 126.65, 127.17, 128.69, 129.80, 130.29, 132.25, 149.16, 166.37, 167.19. (yield 95.8%) MS: MW=240 g/mol, MH$^+$=241. HPLC: $t_R = 3.91$ min.
Figure S132. H-NMR of compound 5f in DMSO

Figure S133. C-NMR of compound 5f in DMSO
Figure S134. DEPT of compound 5f in DMSO

VICA30 274 (5.079) Cn (Cen, Ar); Sm (Mn, 2x1.00); Sb (1,40.00); Cm (223:298:32.79)

[Mass Table]

Figure S135. QTOF-MS of compound 5f

5f 220nm

5f 254nm
Figure S136. HPLC of compound 5f

\[ \text{5g} \]

\begin{align*}
^{1}\text{HNMR:} & \quad (300 \text{ MHz, DMSO-}\text{d}_6)\ , \delta_{\text{H}(\text{ppm})}: \quad 3.00 \ (\text{dd,} 1\text{H}, J=6.6\text{Hz, } J=16.2\text{Hz}), \ 3.13 \ (\text{dd,} 1\text{H}, J=5.1\text{Hz, } J=16.2\text{Hz}), \ 5.04 \ (\text{d,} 2\text{H}, J=1.8\text{Hz}), \ 5.08 \ (\text{d,} 1\text{H}, J=5.7\text{Hz}), \ 7.26 \ (\text{m,} 5\text{H}), \\
& \quad 7.69 \ (\text{m,} 1\text{H}), \ 7.89 \ (\text{m,} 1\text{H}), \ 8.09 \ (\text{d,} 1\text{H}, J=8.4\text{Hz}), \ 8.20 \ (\text{dd,} 1\text{H}, J=1.5\text{Hz, } J=8.4\text{Hz}), \ 8.71 \ (\text{s,} 1\text{H}), \ 9.06 \ (\text{bs, } \text{NH}). \\
^{13}\text{CNMR:} & \quad (75 \text{ MHz, DMSO-}\text{d}_6)\ , \delta_{\text{C}(\text{ppm})}:37.35, \ 54.15, \ 65.73, \ 123.91, \\
& \quad 126.73, \ 127.21, \ 127.81, \ 127.90, \ 128.25, \ 128.59, \ 129.82, \ 131.31, \ 132.18, \ 135.73, \ 149.04, \\
& \quad 164.74, \ 167.19, \ 169.55. \ (\text{yield } 66\%) \ \text{MS:} \ MW=332 \ \text{g/mol, } \text{MH}^{+}=332. \ \text{HPLC:} \ t_R = 4.25 \ \text{min.}
\end{align*}
Figure S137. H-NMR of compound 5g in DMSO

Figure S138. C-NMR of compound 5g in DMSO
Figure S139. DEPT of compound 5g in DMSO

![Figure S139](image1)

Figure S140. HPLC of compound 5g

![Figure S140](image2)