

# Expedient Construction of the Vibsanin E Core Without the Use of Protecting Groups

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## Experimental

<sup>1</sup>H and <sup>13</sup>C n.m.r spectra were recorded on Bruker AV400 (400.13MHz; 100.62MHz), AV300 (300.13MHz; 75.47MHz) and DRX500 (500.13MHz; 125.76MHz) instruments in deuteriochloroform (CDCl<sub>3</sub>). Coupling constants are given in Hz and chemical shifts are expressed as δ values in ppm. High and low resolution EI mass spectral data were obtained on a KRATOS MS 25 RFA. Microanalyses were performed by the University of Queensland Microanalytical Service.

### 3-Methyl-3-(4-methylpent-3-enyl)cyclohexanone 8

<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ 0.91 (s, 3H), 1.22-1.27 (m, 2H), 1.48-1.67 (m, 2 H), 1.56 (bs, 3H), 1.62 (bd, J 1.2 Hz, 3H), 1.78-1.94 (m, 4H), 2.06-2.19 (m, 2H), 2.24 (bt, J 6.6, 2H), 5.02-5.07 (m, 1H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) δ 17.4, 21.93, 21.96, 24.7, 25.5, 35.7, 38.4, 40.8, 41.5, 53.5, 124.2, 131.3, 212.0. Mass spectrum m/z (EI) 194 (M<sup>+</sup>, 7%), 151 (8), 111 (100), 97 (5), 83 (6), 69 (23), 55 (18). *Anal.* Calcd. for C<sub>13</sub>H<sub>22</sub>O: C, 80.35; H, 11.41. Found: C, 80.25; H, 11.64.

### 5-Methyl-5-(4-methylpent-3-enyl)-2-cyclohexenone 9

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 1.00 (s, 3H), 1.30-1.38 (m, 2H), 1.56 (bs, 3H), 1.64 (bd, J 1.1 Hz, 3H), 1.85-1.98 (m, 2H), 2.13-2.17 (m, 1H), 2.21-2.25 (m, 1H), 2.27-2.33 (m, 2H), 5.01-5.06 (m, 1H), 5.99 (dt, J 2.0, 10.1 Hz, 1H), 6.81-6.85 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 17.5, 22.3, 24.7, 25.6, 36.5, 38.1, 41.4, 50.1, 124.0, 129.0, 131.7, 148.2, 199.8. Mass spectrum m/z (EI) 192 (M<sup>+</sup>, 12%), 149 (10), 124 (25), 109 (100), 95 (5), 81 (13), 69 (18), 55 (10). *Anal.* Calcd. for C<sub>13</sub>H<sub>20</sub>O: M<sup>+</sup> 192.1514. Found: M<sup>+</sup> 192.1507.

### 2-Hydroxymethyl-5-methyl-5-(4-methylpent-3-enyl)-2-cyclohexenone 10

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 0.91 (s, 3H), 1.22-1.29 (m, 2H), 1.48 (s, 3H), 1.56 (s, 3H), 1.79-1.90 (m, 2H), 2.10-2.30 (m, 4H), 2.94 (bs, OH), 4.14-4.15(m, 2H), 4.94-4.98 (m, 1H), 6.70-6.73 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 17.6, 22.4, 24.7, 25.6, 36.7, 38.0, 41.3, 50.3, 60.6, 124.1, 131.7, 137.5, 144.2, 200.4. Mass spectrum m/z (EI) 222 (M<sup>+</sup>, 9%), 204 (14), 189 (10), 164 (8), 161

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(15), 139 (22), 121 (86), 109 (53), 97 (22), 83 (18), 69 (49), 55 (39), 41 (100). *Anal.* Calcd. for C<sub>14</sub>H<sub>22</sub>O<sub>2</sub>: C, 75.63; H, 9.97. Found: C, 75.65; H, 10.27.

**1,7,7-Trimethyl-6-oxa-tricyclo[6.2.2.0<sup>4,9</sup>]dodecan-3-one 11**

M.p. 61-61°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 0.94 (s, 3H), 1.04 (s, 3H), 1.20-1.32 (m, 3H), 1.24 (s, 3H), 1.49-1.59 (m, 3H), 1.76-1.80 (m, 1H), 1.93-1.95 (m, 1H), 2.07 (d, J 16.5 Hz, 1H), 2.29 (dd, J 16.5, 3 Hz, 1H), 2.66-2.70 (m, 1H), 3.52 (dd, J 3.6, 11.9 Hz, 1H), 4.46 (d, J 11.9 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 20.8, 22.8, 27.8, 31.0, 31.9, 33.9, 38.9, 41.46, 42.3, 46.4, 53.3, 58.6, 73.7, 210.4. Near IR (Nujol) υ (cm<sup>-1</sup>) 1709, 1702, 1695. Mass spectrum m/z (EI) 222 (M<sup>+</sup>, 14%), 207 (18), 164 (10), 146 (3), 136 (4), 129 (6), 121 (6), 109 (8), 106 (10), 94 (100), 79 (14). *Anal.* Calcd. for C<sub>14</sub>H<sub>22</sub>O<sub>2</sub>: M<sup>+</sup> 222.1614. Found: M<sup>+</sup> 222.1619.

**2-Ethoxycarbonyl-1,7,7-trimethyl-6-oxa-tricyclo[6.2.2.0<sup>4,9</sup>]dodecan-3-one 15**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 0.99 (s, 3H), 1.07 (s, 3H), 1.07-1.24 (m, 2H), 1.25 (s, 3H), 1.27 (t, J 7.1, 3H), 1.29-1.47 (m, 1H), 1.54-1.68 (m, 2H), 1.85 (dt, J 13.3, 3.2, 1H), 2.03-2.07 (m, 1H), 2.35-2.45 (m, 1H), 2.67-2.75 (m, 1H), 3.06 (s, 1H), 3.58 (dd, J 12.0, 3.6, 1H), 4.12-4.29 (m, 2H), 4.44 (d, J 12.0, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 14.2, 20.6, 22.5, 27.5, 29.1, 31.8, 34.6, 37.5, 42.3, 43.2, 46.2, 58.1, 60.6, 66.2, 73.5, 168.8, 204.5. Mass spectrum m/z (EI) 294 (M<sup>+</sup>, 14%), 279 (18), 276 (3), 266 (4), 249 (9), 236 (9), 233 (7), 221 (2), 205 (2), 190 (11), 181 (3), 175 (3), 162 (8), 143 (26), 134 (11), 115 (9), 109 (12), 94 (100), 79 (19). *Anal.* Calcd. for C<sub>17</sub>H<sub>26</sub>O<sub>4</sub>: M<sup>+</sup> 294.1831. Found: M<sup>+</sup> 294.1831.

**2-Ethoxycarbonyl-1,8,8-trimethyl-7-oxa-tricyclo[7.2.2.0<sup>5,10</sup>]dodecan-3-one 20**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ 1.04 (s, 3H), 1.09 (s, 3H), 1.10-1.21 (m, 1H), 1.22-1.28 (m, 1H), 1.25 (t, J 7.1, 3H), 1.27 (s, 3H), 1.31-1.47 (m, 1H), 1.52-1.62 (m, 1H), 1.73 (dd, J 14.5, 5.4, 1H), 1.95 (dt, J 14.5, 2.5, 1H), 2.16-2.25 (m, 2H), 2.54-2.62 (m, 1H), 2.63 (s, 1H), 2.64 (AB, 1H), 3.05-3.18 (m, 1H), 3.62 (dd, J 11.8, 3.6, 1H), 4.13 (q, J 7.1, 2H), 4.31 (dd, J 10.7, 1.1, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 14.2, 21.9, 23.8, 27.4, 31.2, 33.0, 33.7, 34.2, 42.8, 44.3, 46.4, 51.3, 51.6, 60.4, 61.7, 73.6, 174.0, 210.1. Mass spectrum m/z (EI) 308 (M<sup>+</sup>, 4%), 293 (14), 290 (4), 275 (1), 269 (1), 263 (5), 250 (68), 245 (1), 214 (1), 204 (19), 196 (6), 177 (10), 156 (90), 135 (10), 128 (18), 110 (23), 101 (94), 94 (100). *Anal.* Calcd. for C<sub>18</sub>H<sub>28</sub>O<sub>4</sub>: M<sup>+</sup> 308.1988. Found: M<sup>+</sup> 308.1989.