Supporting Information

Concise Three-Component Synthesis of Defucogilvocarcin M

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Spectroscopic and analytical data for the compounds in schemes 3 and scheme 4.

Scheme 3.

Reagents and conditions: (a) $\text{Me}_3\text{SiC}\equiv\text{CH}$, cat. $(\text{Ph}_3\text{P})_2\text{PdCl}_2$, Et_3N , DMF, 90 °C (68%); (b) K_2CO_3 , MeOH (96%); (c) $\text{Et}_4\text{N}^+(\text{HBr}_2)^-$, CH_2Cl_2 (95%); (d) LiAlH_4 , THF, $-78 \rightarrow 0$ °C (90%); (e) MnO_2 , CHCl_3 (89%); (f) 1,3-propanediol, cat. TsOH, benzene, reflux (85%).

Mp. 80–83 °C (hexane)

Rf 0.55 (hexane/EtOAc = 80/20)

^1H NMR (CDCl_3 , δ)

7.24 (s, 1H), 6.82 (s, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 2.37 (s, 3H), 0.27 (s, 9H)

^{13}C NMR (CDCl_3 , δ)

167.4, 161.1, 139.6, 134.8, 122.5, 114.7, 109.3, 103.5, 98.7, 56.2, 52.0, 21.8, 0.04

IR (KBr)

2961, 2158, 1711, 1608, 1439, 1328, 1203, 1074, 995, 845 cm^{-1}

Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_3\text{Si}$: C, 65.18; H, 7.29. Found: C, 65.11; H, 7.48.

Mp. 93–95 °C (hexane)

Rf 0.30 (hexane/EtOAc = 70/30)

^1H NMR (CDCl_3 , δ)

7.31 (s, 1H), 6.88 (s, 1H), 3.91 (s, 6H), 3.58 (s, 1H), 2.39 (s, 3H)

^{13}C NMR (CDCl_3 , δ)

166.7, 161.5, 140.0, 134.3, 122.7, 114.7, 108.5, 85.8, 77.6, 56.2, 52.1, 21.8

IR (KBr)

3257, 2954, 1724, 1602, 1464, 1438, 1322, 1291, 1242, 1206, 1189, 1069, 855, 841, 787, 700 cm^{-1}

Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{O}_3$: C, 70.57; H, 5.92. Found: C, 70.53; H, 6.05.

Mp. 75–77 °C (hexane)

Rf 0.70 (hexane/EtOAc = 70/30)

^1H NMR (CDCl_3 , δ)

7.20 (s, 1H), 6.88 (s, 1H), 5.86 (d, 1H, $J = 1.6$ Hz), 5.65 (d, 1H, $J = 1.6$ Hz), 3.88 (s, 6H), 2.39 (s, 3H)

^{13}C NMR (CDCl_3 , δ)

167.5, 156.7, 140.3, 131.3, 126.5, 123.8, 121.9, 121.2, 115.2, 56.2, 52.2, 21.6

IR (KBr)

1723, 1641, 1602, 1461, 1325, 1208, 1073, 903, 883, 600 cm^{-1}

Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{BrO}_3$: C, 50.55; H, 4.60. Found: C, 50.75; H, 4.74.

ii

Mp. 43–46 $^{\circ}\text{C}$ (hexane/ $\text{Et}_2\text{O} = 10/3$)

Rf 0.30 (hexane/ $\text{EtOAc} = 70/30$)

^1H NMR (CDCl_3 , δ)

6.92 (s, 1H), 6.68 (s, 1H), 5.97 (d, 1H, $J = 1.5$ Hz), 5.73 (d, 1H, $J = 1.5$ Hz), 4.70 (d, 2H, $J = 6.3$ Hz), 3.86 (s, 3H), 2.37 (s, 3H), 1.85 (t, 1H, $J = 6.3$ Hz)

^{13}C NMR (CDCl_3 , δ)

156.4, 140.6, 139.3, 125.3, 123.5, 122.8, 120.5, 111.2, 62.5, 56.0, 21.8

IR (KBr)

3374, 2937, 1607, 1463, 1309, 1155, 1041, 902, 838, 597 cm^{-1}

Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{BrO}_2$: C, 51.38; H, 5.09. Found: C, 51.64; H, 5.38.

iii

Mp. 40–42 $^{\circ}\text{C}$, dec. (hexane)

Rf 0.70 (hexane/ $\text{EtOAc} = 70/30$)

^1H NMR (CDCl_3 , δ)

10.30 (s, 1H), 7.34 (s, 1H), 6.97 (s, 1H), 6.13 (d, 1H, $J = 1.7$ Hz), 5.84 (d, 1H, $J = 1.7$ Hz), 3.92 (s, 3H), 2.42 (s, 3H)

^{13}C NMR (CDCl_3 , δ)

191.6, 156.6, 1408, 133.5, 130.0, 125.0, 120.7, 119.3, 117.2, 56.2, 21.7

IR (film)

1694, 1601, 1464, 1311, 1204, 1153, 1080, 924, 849, 786, 597 cm^{-1}

Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{BrO}_2$: C, 51.79; H, 4.35. Found: C, 51.80; H, 4.58.

Mp. 106-108 $^{\circ}\text{C}$ (hexane/EtOAc = 2/1)

Rf 0.55 (hexane/ CH_2Cl_2 /Et₂O = 70/15/15)

^1H NMR (CDCl_3 , δ)

7.13 (s, 1H), 6.70 (s, 1H), 6.00 (d, 1H, $J = 1.0$ Hz), 5.78 (d, 1H, $J = 1.0$ Hz), 5.64 (s, 1H), 4.23–4.09 (m, 2H), 3.98–3.89 (m, 2H), 3.86 (s, 3H), 2.36 (s, 3H), 2.24 (dtt, 1H, $J_1 = 13.2$, $J_2 = 5.1$, $J_3 = 12.7$ Hz), 1.28 (dtt, 1H, $J_1 = 13.2$, $J_2 = 1.2$, $J_3 = \sim 0$ Hz)

^{13}C NMR (CDCl_3 , δ)

156.1, 140.7, 136.8, 125.2, 123.4, 122.9, 118.6, 112.4, 99.3, 67.4, 56.0, 25.7, 21.8

IR (KBr)

1607, 1463, 1309, 1155, 1041, 902, 838, 597 cm^{-1}

Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{BrO}_3$: C, 53.69; H, 5.47. Found: C, 53.90; H, 5.57.

Scheme 4.

A pair of the rotational isomers (1.6:1) is included.

Mp. $144\text{--}147^\circ\text{C}$

Rf 0.17 (hexane/acetone = 85/15)

^1H NMR (CDCl_3 , δ) [*signals by the minor component of the rotational isomers]

7.44–7.26 (m, 7H), *7.15 (dd, 1H, $J_1 = 7.6$, $J_2 = 8.3$ Hz), *7.10 (s, 1H), 6.95 (d, 1H, $J = 7.3$ Hz), 6.85 (d, 1H, $J = 8.3$ Hz), *6.75 (d, 1H, $J = 8.3$ Hz), 6.72 (s, 1H), *6.70 (s, 1H), *6.49 (d, 1H, $J = 7.6$ Hz), 5.97 (s, 1H), *5.70 (d, 1H, $J = 1.5$ Hz), *5.59 (s, 1H), 5.50 (d, 1H, $J = 1.5$ Hz), *5.40 (d, 1H, $J = 1.5$ Hz), 5.31 (d, 1H, $J = 1.5$ Hz), 5.20 (d, 1H, $J = 12.2$ Hz), *5.16 (d, 1H, $J = 12.5$ Hz), 5.15 (d, 1H, $J = 12.2$ Hz), *5.11 (d, 1H, $J = 12.5$ Hz), 4.63 (s, 1H), 4.23 (dd, 1H, $J_1 = 4.9$, $J_2 = 11.2$ Hz), 4.12 (dd, 1H, $J_1 = 4.9$, $J_2 = 11.2$ Hz), *4.06 (dd, 1H, $J_1 = 4.9$, $J_2 = 11.2$ Hz), 3.99–3.73 (m, 2H), *3.87 (s, 3H), 3.78 (s, 3H), *3.68 (s, 3H), *3.63 (s, 3H), 3.62 (s, 3H), 3.24 (s, 3H), 2.38 (s, 3H), *2.35 (s, 3H), 2.24 (dt, 1H, $J_1 = 13.2$, $J_2 = 4.9$, $J_3 = 12.7$ Hz), *2.17 (dt, 1H, $J_1 = 13.2$, $J_2 = 4.9$, $J_3 = 12.6$ Hz), 1.38 (br-d, 1H, $J = 13.2$ Hz), *1.34 (br-d, 1H, $J = 13.2$ Hz)

^{13}C NMR (CDCl_3 , δ)

156.3, 156.0, 153.0, 152.5, 150.7, 150.3, 142.8, 142.5, 138.7, 138.6, 138.6, 137.9, 136.9, 136.8, 132.3, 132.3, 132.2, 132.1, 128.5, 127.8, 127.1, 126.2, 125.8, 122.9, 122.3, 120.0, 118.9, 115.0, 114.9, 112.9, 112.7, 112.4, 111.3, 110.1, 109.0, 99.8, 89.5, 88.7, 70.4, 70.2, 67.4, 67.3, 67.1, 67.0, 56.2, 55.6, 53.3, 53.2, 52.0, 51.3, 26.0, 25.8, 21.6

IR (KBr)

3431, 2940, 2838, 1606, 1482, 1377, 1274, 1240, 1082, 1020, 913, 842, 748 cm^{-1}

Anal. Calcd for $\text{C}_{31}\text{H}_{34}\text{O}_7$: C, 71.80; H, 6.61. Found: C, 71.71; H, 6.73.

Mp. 69–73 °C

Rf 0.55 (hexane/ CH_2Cl_2 / Et_2O = 40/30/30)

^1H NMR (CDCl_3 , δ)

7.99 (d, 1H, $J = 7.9$ Hz), 7.64 (d, 2H, $J = 7.3$ Hz), 7.42 (dd, 2H, $J_1 = J_2 = 7.3$ Hz), 7.40

(dd, 1H, $J_1 = 7.3$, $J_2 = 7.9$ Hz), 7.33 (t, 1H, $J = 7.3$ Hz), 7.30 (s, 1H), 7.01 (d, 1H, $J = 7.3$ Hz), 6.86 (s, 1H), 6.65 (s, 1H), 5.88 (s, 1H), 5.25 (s, 2H), 5.19 (s, 1H), 4.17 (dd, 1H, $J_1 = 5.1$, $J_2 = 11.5$ Hz), 4.10 (dd, 1H, $J_1 = 5.1$, $J_2 = 11.5$ Hz), 3.87 (s, 3H), 3.72 (s, 3H), 3.73 (ddd, 1H, $J_1 = 2.2$, $J_2 = 11.5$, $J_3 = 12.5$ Hz), 3.62 (ddd, 1H, $J_1 = 2.2$, $J_2 = 11.5$, $J_3 = 12.5$ Hz), 2.46 (s, 3H), 2.18 (dt, 1H, $J_1 = 13.2$, $J_2 = 5.1$, $J_3 = 12.5$ Hz), 1.27 (br-d, 1H, $J = 13.2$ Hz)

^{13}C NMR (CDCl_3 , δ)

156.8, 155.8, 150.0, 143.2, 140.1, 138.6, 137.7, 128.8, 128.6, 128.3, 127.5, 127.0, 125.8, 121.7, 119.1, 118.7, 116.7, 113.0, 110.3, 109.3, 99.9, 71.5, 67.4, 67.3, 56.9, 56.0, 25.5, 21.8

IR (neat)

3358, 2957, 1599, 1460, 1375, 1309, 1079, 753 cm^{-1}

Anal. Calcd for $\text{C}_{30}\text{H}_{30}\text{O}_6$: C, 74.06; H, 6.22. Found: C, 73.91; H, 6.31.

Mp. 194–195 °C (hexane/EtOAc = 7/4)

Rf 0.46 (hexane/EtOAc = 60/40)

^1H NMR (CDCl_3 , δ)

7.62 (d, 2H, $J = 7.1$ Hz), 7.45–7.39 (m, 4H), 7.33 (t, 1H, $J = 7.3$ Hz), 7.25 (s, 1H), 7.02–7.95 (m, 1H), 6.80 (s, 1H), 6.79 (s, 1H), 5.25 (s, 2H), 5.12 (s, 1H), 4.14 (dd, 1H, $J_1 = 4.9$, $J_2 = 11.5$ Hz), 4.04 (dd, 1H, $J_1 = 4.9$, $J_2 = 11.5$ Hz), 3.91 (s, 3H), 3.75 (ddd, 1H, $J_1 = 2.2$, $J_2 = 11.5$, $J_3 = 12.7$ Hz), 3.71 (s, 3H), 3.64 (ddd, 1H, $J_1 = 2.2$, $J_2 = 11.5$, $J_3 = 12.7$ Hz), 2.42 (s, 3H), 2.17 (dt, 1H, $J_1 = 13.4$, $J_2 = 4.9$, $J_3 = 12.7$ Hz), 2.03 (s, 3H), 1.27 (br-d, 1H, $J = 13.4$ Hz)

^{13}C NMR (CDCl_3 , δ)

169.1, 156.43, 156.37, 154.2, 139.7, 138.2, 138.0, 137.5, 130.3, 128.3, 127.5, 127.1,

126.9 , 125.9, 122.1, 118.7, 118.1, 114.8, 112.2, 109.1, 109.0, 99.9, 71.4, 67.2, 56.2, 56.0, 25.7, 21.8, 20.4

IR (KBr)

2959, 2845, 1760, 1578, 1395, 1271, 1198, 1082, 1021, 758 cm^{-1}

Anal. Calcd for $\text{C}_{32}\text{H}_{32}\text{O}_7$: C, 72.71; H, 6.10. Found: C, 72.65; H, 6.24.

v

Mp 193–195 °C (hexane/EtOAc = 1/3)

Rf 0.61 (hexane/ CH_2Cl_2 /Et₂O = 40/30/30)

^1H NMR (CDCl_3 , δ)

9.71 (s, 1H), 7.61 (d, 2H, $J = 7.3$ Hz), 7.47 (s, 1H), 7.47–7.39 (m, 4H), 7.33 (t, 1H, $J = 7.3$ Hz), 7.05 (s, 1H), 7.04–6.96 (m, 1H), 6.76 (s, 1H), 5.24 (s, 2H), 3.92 (s, 3H), 3.80 (s, 3H), 2.47 (s, 3H), 2.01 (s, 3H)

^{13}C NMR (CDCl_3 , δ)

192.6, 168.9, 157.1, 156.4, 154.7, 139.7, 138.3, 137.4, 134.7, 130.3, 128.4, 127.6, 127.5, 126.9, 123.7, 119.0, 118.5, 117.2, 114.5, 109.6, 108.5, 71.5, 56.4, 56.2, 21.7, 20.3

IR (KBr)

1749, 1690, 1579, 1392, 1311, 1219, 1080, 750 cm^{-1}

Anal. Calcd for $\text{C}_{29}\text{H}_{26}\text{O}_6$: C, 74.03; H, 5.57. Found: C, 73.91; H, 5.77.

Mp. 223–226 °C (EtOAc/CHCl₃ = 1/5)

R_f 0.68 (hexane/EtOAc = 50/50)

¹H NMR (CDCl₃, δ)

8.31 (s, 1H), 8.20 (d, 1H, J = 8.1 Hz), 7.88 (s, 1H), 7.61 (d, 2H, J = 7.6 Hz), 7.48 (dd, 1H, J₁ = 7.8, J₂ = 8.1 Hz), 7.43 (dd, 2H, J₁ = 7.3, J₂ = 7.6 Hz), 7.34 (t, 1H, J = 7.3 Hz), 7.07 (s, 1H), 7.02 (d, 1H, J = 7.8 Hz), 5.20 (s, 2H), 4.03 (s, 3H), 3.97 (s, 3H), 2.45 (s, 3H)

¹³C NMR (CDCl₃, δ)

161.5, 157.1, 155.6, 152.8, 140.3, 139.7, 137.4, 128.4, 127.6, 127.1, 126.9, 126.7, 123.1, 122.7, 121.9, 118.0, 117.8, 115.2, 113.7, 110.0, 104.1, 71.3, 56.4, 56.1, 21.6

IR (KBr)

1716, 1592, 1398, 1336, 1297, 1122, 1062, 852, 746 cm⁻¹

Anal. Calcd for C₂₇H₂₂O₅: C, 76.04; H, 5.20. Found: C, 75.99; H, 5.29.

defucogilvocarcin M (**1a**)

Mp. 289–291 °C (EtOAc/CHCl₃ = 1/7.5~1/2.2)

R_f 0.51 (hexane/EtOAc = 50/50)

¹H NMR (CDCl₃, δ)

9.34 (s, 1H), 8.23 (s, 1H), 8.05 (dd, 1H, J₁ = 0.7, J₂ = 7.6 Hz), 7.89 (s, 1H), 7.48 (dd, 1H, J₁ = 7.6, J₂ = 7.6 Hz), 7.07 (s, 1H), 6.99 (dd, 1H, J₁ = 0.7, J₂ = 7.6 Hz), 4.12 (s, 3H), 4.07

(s, 3H), 2.48 (s, 3H)

^{13}C NMR (CDCl_3 , δ)

161.2, 157.0, 154.2, 151.8, 141.3, 139.9, 128.4, 126.2, 123.0, 122.8, 121.8, 118.1, 114.6,
113.4, 112.9, 112.4, 101.8, 56.2, 56.0, 21.6

IR (KBr)

3370, 1716, 1614, 1438, 1386, 1245, 1175, 1124, 1060, 846, 781 cm^{-1}

Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{O}_5$: C, 71.42; H, 4.80. Found: C, 71.45; H, 4.97.