Synthesis of (−)-Bulgecinine and 5-epi-Bulgecinine through Proline-Catalyzed Asymmetric α-Hydroxylation of an Aldehyde Derived from L-Glutamic acid

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Supporting Information

1. $^1$H and $^{13}$C spectra of all new compounds

2. HPLC Chromatograms for proline-catalyzed asymmetric reaction
Compound 4
Compound 5
Compound 6
Compound 7
Compound 8
Compound 10
Compound 11
Compound 12
Compound 13a
Compound 13b
Compound 1
Compound 2
HPLC chromatograms for asymmetric α-hydroxylation of aldehyde 3

Chiral HPLC: OD-H column, 6% isopropanol/hexane, flow rate 0.5 ml/min, UV detection at 254 nm.

Column chromatography (70:30 petroleum ether/EtOAc); clear oil (1.23 g, 86%): [α]D27: +3.71 (c 0.78, CHCl3); IR (Thin film): 3443, 3272, 2978, 2929, 2875, 1694, 1681 cm⁻¹; ¹H NMR (CDCl3, 400 MHz): δ = 7.27–7.23 (2H, m), 6.99–6.95 (3H, m), 4.27–4.09 (1H, m), 3.98–3.78 (5H, m), 2.29–1.88 (2H, m), 1.55, 1.48 (15H, s) ppm; ¹³C NMR (CDCl3, 100 MHz): δ = 152.7, 148.5, 131.1, 129.1, 122.9, 122.3, 114.9, 93.9, 93.4, 81.7, 81.4, 80.7, 80.5, 68.4, 67.8, 65.0, 64.6, 54.9, 54.2, 34.5, 34.0, 32.0, 31.7, 29.8, 28.5, 27.7, 24.5, 23.3, 14.2 ppm; HRMS (ESI-TOF) m/z : [M+H]+calcd for C₁₉H₃₁N₄O₅ 367.2233, found: 367.2237.

Note: The additional peaks in the NMR spectra are observed due to the presence of diastereomers.
Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

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Totals : 1.01484e5 1146.86505

*** End of Report ***
HPLC chromatograms for asymmetric α-hydroxylation of aldehyde 3

Chiral HPLC: OD-H column, 6% isopropanol/hexane, flow rate 0.5 ml/min, UV detection at 254 nm

Column chromatography (70:30 petroleum ether/EtOAc); clear oil (1.20 g, 84%): [α]$_D^{27}$: +6.66 (c 0.45, CHCl$_3$); IR (Thin film): 3452, 3276, 2978, 2933, 2876, 1697, 1601 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 400 MHz): δ = 7.26–7.22 (2H, m), 6.96–6.93 (3H, m), 4.09 (1H, bs), 3.97–3.76 (5H, m), 2.00–1.87 (2H, m), 1.54, 1.48 (15H, s) ppm; $^{13}$C NMR (CDCl$_3$, 100 MHz): δ = 152.7, 148.5, 129.1, 122.9, 122.3, 114.9, 93.7, 93.3, 82.6, 81.7, 80.7, 80.0, 68.4, 68.1, 65.3, 64.6, 55.9, 54.9, 34.4, 29.8, 28.5, 27.8, 26.9, 25.4, 24.5, 23.3 ppm; HRMS (ESI-TOF) m/z: [M+H]$^+$ calcd for C$_{19}$H$_{31}$N$_2$O$_5$ 367.2233, found: 367.2237.
### Area Percent Report

**Sorted By:** Signal

Multiplier: 1.0000

Integration: 1.0000

Multiplier & Dilution Factor with ISTDs

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**Totals:**

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