Supporting Information for

The Asymmetric Synthesis of the Tropane Alkaloid (+)-Pseudococaine via Ring-Closing Iodoamination

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1. Experimental

1.1. General Experimental

All reactions involving organometallic or other moisture sensitive reagents were carried out under a nitrogen or argon atmosphere using standard vacuum line techniques and glassware that was flame dried and cooled under nitrogen before use. Solvents were dried according to the procedure outlined by Grubbs and co-workers.\(^1\) Water was purified by an Elix® UV–10 system. All other solvents were used as supplied (analytical or HPLC grade) without prior purification. Organic layers were dried over MgSO\(_4\). Thin layer chromatography was performed on aluminium plates coated with 60 F\(_{254}\) silica. Plates were visualised using UV light (254 nm), iodine, 1% aq KMnO\(_4\), or 10% ethanolic phosphomolybdic acid. Flash column chromatography was performed on Kieselgel 60 silica.

Melting points are uncorrected. Optical rotations were recorded in a water-jacketed 10 cm cell. Specific rotations are reported in 10\(^{-1}\) deg cm\(^2\) g\(^{-1}\) and concentrations in g/100 mL. IR spectra were recorded on an ATR module. Selected characteristic peaks are reported in cm\(^{-1}\). NMR spectra were recorded in the deuterated solvent stated. Spectra were recorded at rt. The field was locked by external referencing to the relevant deuteron resonance.

1.2. Experimental Data

tert-Butyl (R,R)-3-[N-methyl-N-(α-methyl-p-methoxybenzyl)amino]hept-6-enoate 8

BuLi (2.18 M in hexanes, 4.31 mL, 9.39 mmol) was added dropwise via syringe to a stirred solution of (R)-N-methyl-N-(α-methyl-p-methoxybenzyl)amine\(^2\) (1.63 g, 8.94 mmol) in THF (10 mL) at −78 °C. After stirring for 30 min a solution of 6\(^3\) (1.63 g, 9.84 mmol, >99:1 dr) in THF (10 mL) at −78 °C was added dropwise via cannula. The reaction mixture was left to stir for a further 2 h, before addition of satd aq NH\(_4\)Cl (5 mL). The resultant mixture was allowed to warm to rt over 2 h then concentrated in vacuo. The residue was then partitioned between CH\(_2\)Cl\(_2\) (30 mL) and 10% aq citric acid (30 mL). The aqueous layer was extracted with CH\(_2\)Cl\(_2\) (2 × 30 mL) and the combined organic extracts were washed sequentially with satd aq NaHCO\(_3\) (50 mL), H\(_2\)O (50 mL) and brine (50 mL), then dried and concentrated in vacuo to give 8 in >99:1 dr. Purification via flash column chromatography (eluent 30–40 °C petrol/Et\(_2\)O, 50:1) gave 8 as a yellow oil (2.29 g, 74%, >99:1 dr); \([α]_D^{20} = 3.2 (c 1.3 \text{ in CHCl}_3); ν_{max} (\text{film}) 2975, 2932 (\text{C–H}), 1725 (\text{C=O}), 1640 (\text{C=C}); δ_H (400 MHz, CDCl\(_3\)) 1.26–1.36 (1H, m, C(4)H\(_A\)) overlapping 1.32 (3H, d, J 6.7, C(α)Me), 1.42 (9H, s, CMe\(_3\)), 1.51–1.58 (1H, m, C(4)H\(_B\)), 1.88–1.98 (1H, m, C(5)H\(_A\)), 2.05–2.13 (1H, m, C(5)H\(_B\)) overlapping 2.08 (1H, dd, J 13.7, 8.3, C(2)H\(_A\)) and 2.12 (3H, s, NMe), 2.38 (1H, dd, J 13.7, 5.6, C(2)H\(_B\)), 3.12–3.19 (1H, m, C(3)H), 3.56 (1H, q, J 6.7, C(α)H), 3.79 (3H, s, OMe), 4.89–4.99 (2H, m, C(7)H\(_2\)), 5.70–5.80 (1H, m, C(6)H), 6.83 (2H, d, J 8.7, Ar), 7.23 (2H, d, J 8.7, Ar); δ_C (100 MHz, CDCl\(_3\)) 21.8 (C(α)Me), 28.1 (CMe\(_3\)), 30.4, 30.8 (C(4), C(5)), 31.8 (NMe), 36.5 (C(2)), 55.2 (OMe), 55.5 (C(3)), 61.2 (C(α)), 79.9 (CMe\(_3\)), 113.5 (Ar), 114.2 (C(7)), 128.4, 138.0 (Ar), 138.8 (C(6)), 158.4 (Ar), 172.4 (C(1)); \(m/z\) (ESI\(^+\)) 348 ([M+H]\(^+\), 100%); HRMS (ESI\(^+\)) C\(_{21}\)H\(_{34}\)NO\(_3\)\(^+\) ([M+H]\(^+\)) requires 348.2533; found 348.2529.


\(^3\)Davies, S. G.; Fletcher, A. M.; Roberts, P. M.; Smith, A. D. Tetrahedron 2009, 65, 10192.
**tert-Butyl (2S,3R,aR,1’S)-2-(1’-hydroxyprop-2’-en-1’-yl)-3-[N-methyl-N-(α-methyl-p-methoxybenzyl)amino]hept-6-enoate 9 and tert-butyl (2S,3R,aR,1’R)-2-(1’-hydroxyprop-2’-en-1’-yl)-3-[N-methyl-N-(α-methyl-p-methoxybenzyl)amino]hept-6-enoate 10**

BuLi (1.87 M in hexanes, 0.69 mL, 1.15 mmol) was added dropwise via syringe to a stirred solution of (R)-N-methyl-N-(α-methyl-p-methoxybenzyl)amine \(^4\) (200 mg, 1.20 mmol) in THF (1 mL) at −78 °C. After stirring for 30 min a solution of 6 \(^5\) (200 mg, 1.10 mmol, >99:1 dr) in THF (1.2 mL) at −78 °C was added dropwise via cannula. The reaction mixture was left to stir for a further 2 h, before addition of acrolein (0.15 mL, 2.19 mmol). The resultant mixture was allowed to warm to rt over 2 h then concentrated in vacuo. The residue was then partitioned between CH₂Cl₂ (10 mL) and 10% aq citric acid (10 mL). The aqueous layer was extracted with CH₂Cl₂ (2 × 10 mL) and the combined organic extracts were washed sequentially with satd aq NaHCO₃ (30 mL), H₂O (30 mL) and brine (30 mL), then dried and concentrated in vacuo to give a 77:13:6:4 mixture of 9:10:11:12. Purification via flash column chromatography gave 9 as a pale yellow solid (261 mg, 59%, >99:1 dr); mp 79–83 °C; [α] \(^{25}_D\) +7.6 (c 1.9 in CHCl₃); \(\nu_{max}\) (KBr) 3482 (O–H), 2976, 2933 (C–H), 1700 (C=O), 1640 (C=C); \(\delta_H\) (400 MHz, CDCl₃) 1.36 (3H, d, J 6.7, C(α)Me), 1.46 (9H, s, CMe₃), 1.56–1.71 (2H, m, C(4)H₂), 2.08 (3H, s, NMe), 2.11–2.25 (2H, m, C(5)H₂), 2.60 (1H, dd, J 9.6, 2.5, C(2)H), 3.61–3.67 (1H, m, C(3)H) overlapping 3.64 (1H, q, J 6.7, C(α)H), 3.79 (3H, s, OMe), 4.27 (1H, br s, C(1)’H), 4.38 (1H, br s, OH), 4.94–4.98 (1H, m, C(7)H₃), 5.00–5.05 (1H, m, C(7)’H₃), 5.16 (1H, dt, J 10.6, 1.5, C(3’)H₃), 5.37 (1H, dt, J 17.2, 1.5, C(3’)’H₃), 5.73–5.83 (1H, m, C(6)H), 5.86–5.94 (1H, m, C(2)’H), 6.81 (2H, d, J 8.7, Ar), 7.19 (2H, d, J 8.7, Ar); \(\delta_C\) (100 MHz, CDCl₃) 21.9 (C(α)Me), 27.2 (C(4)), 28.3 (CMe₃), 32.1 (C(5)), 32.7 (NMe), 54.6 (C(2)), 55.2 (O Me), 57.2, 62.7 (C(3), C(α)), 71.1 (C(1)’), 81.3 (CMe₃), 113.4 (Ar), 114.6 (C(7), C(3)’), 128.5, 137.8 (Ar), 138.6, 139.1 (C(6), C(2)’), 158.5 (Ar), 173.3 (C(1)); m/z (ESI⁺) 829 ([M+Na]⁺, 100%), 426 ([M+Na]⁺, 20%), 404 ([M+H]⁺, 40%); HRMS (ESI⁺) C₂₃H₃₈NO₄⁺ ([M+H]⁺) requires 404.2795; found 404.2786. Further elution gave 10 as a pale yellow oil (31 mg, 7%, >99:1 dr); [α] \(^{20}_D\) +29.8 (c 1.5 in CHCl₃); \(\nu_{max}\) (film) 3400 (O–H), 2856, 2931, 2975 (C–H), 1723 (C=O), 1640 (C=C); \(\delta_H\) (400 MHz, CDCl₃) 1.36–1.42 (1H, m, C(4)H₃) overlapping 1.38 (3H, d, J 6.8, C(α)Me), 1.46 (9H, s, CMe₃), 1.75–1.84 (1H, m, C(4)’H₃), 1.91–2.00 (1H, m, C(5)H₃), 2.07–2.16 (1H, m, C(5)H₃), 2.19 (3H, s, NMe), 2.65 (1H, app t, J 5.3, C(2)H), 3.42–3.46 (1H, m, C(3)H), 3.80 (3H, s, OMe), 3.81 (1H, q, J 6.8, C(α)H), 4.66–4.69 (1H, m, C(1)’H), 4.95–4.99 (1H, m, C(7)H₂).


\(^5\) Davies, S. G.; Fletcher, A. M.; Roberts, P. M.; Smith, A. D. *Tetrahedron* 2009, 65, 10192.
5.23 (1H, dt, J 10.4, 1.5, C(3′)H\textsubscript{A}), 5.48 (1H, dt, J 16.9, 1.5, C(3′)H\textsubscript{B}), 5.64–5.75 (1H, m, C(6)H), 5.95 (1H, ddd, J 16.9, 10.4, 4.8, C(2′)H), 6.85 (2H, d, J 8.6, Ar), 7.19 (2H, d, J 8.6, Ar); \(\delta\)\textsubscript{C} (100 MHz, CDCl\textsubscript{3}) 20.0 (C(\alpha)Me), 25.2 (C(4)), 28.1 (CMe\textsubscript{3}), 31.5 (C(5)), 32.7 (NMe), 50.6 (C(2)), 55.2 (OMe), 58.9 (C(3)), 61.9 (C(\alpha)), 72.4 (C(1′)), 80.9 (CMe\textsubscript{3}), 113.7 (Ar), 115.2 (C(7)), 115.5 (C(3′)), 128.7 (Ar), 137.9 (C(6)), 138.2 (Ar), 140.0 (C(2′)), 158.8 (Ar), 171.9 (C(1)); m/z (ESI\textsuperscript{+}) 829 ([2M+Na]\textsuperscript{+}, 100%), 426 ([M+Na]\textsuperscript{+}, 15%), 404 ([M+H]\textsuperscript{+}, 75%); HRMS (ESI\textsuperscript{+}) \textsubscript{C}_{20}H_{38}NO\textsubscript{4}\textsuperscript{+} ([M+H]\textsuperscript{+}) requires 404.2795; found 404.2780.

tert-Butyl (1S,2S,7\textsubscript{R},\textsubscript{aR})-2-hydroxy-7-[N-methyl-N-(\alpha-methyl-p-methoxybenzyl)amino]cyclohept-3-ene-1-carboxylate 13

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\text{Method A (from 9):} \quad \text{Grubbs I catalyst (526 mg, 0.64 mmol) was added to a stirred solution of 9 (1.20 g, 3.20 mmol, >99:1 dr) in degassed CH}_2\text{Cl}_2 (120 mL) at 30 °C. The resultant mixture was stirred at 30 °C for 12 h then allowed to cool to rt and concentrated in vacuo. The residue was dissolved in CH}_2\text{Cl}_2 (70mL) and P(CH}_2\text{OH})_3 (7.94 g, 64.0 mmol), Et}_3\text{N (0.89 mL, 6.40 mmol) and excess silica were added sequentially. The resultant mixture was left to stir at rt for a further 12 h, then filtered and concentrated in vacuo. Purification via flash column chromatography (eluent 30–40 °C petrol/EtOAc, 10:1) gave 13 as a white solid (1.05 g, 95%, >99:1 dr); mp 97–103 °C; [\alpha]_D^{20} +29.4 (c 1.2 in CHCl\textsubscript{3}); \nu\textsubscript{max} (KBr) 3440 (O−H), 2972, 2932 (C−H), 1708 (C=O), 1654 (C=C); \delta\textsubscript{H} (400 MHz, CDCl\textsubscript{3}) 1.13–1.23 (1H, m, C(6)H\textsubscript{A}), 1.30 (3H, d, J 6.7, C(\alpha)Me), 1.51 (9H, s, CMe\textsubscript{3}), 1.62–1.67 (1H, m, C(6)H\textsubscript{B}), 1.80–1.88 (1H, m, C(5)H\textsubscript{A}), 1.97 (3H, s, NMe), 2.13–2.20 (1H, m, C(5)H\textsubscript{B}), 2.66 (1H, app t, J 10.6, C(1)H), 2.76–2.87 (1H, br s, OH), 3.35 (1H, app td, J 10.6, 2.8, C(7)H), 3.52 (1H, q, J 6.7, C(a)H), 3.77 (3H, s, OMe), 4.51–4.58 (1H, m, C(2)H), 5.71–5.81 (2H, m, C(3)H, C(4)H), 6.79 (2H, d, J 8.6, Ar), 7.19 (2H, d, J 8.6, Ar); \delta\textsubscript{C} (100 MHz, CDCl\textsubscript{3}) 21.9 (C(\alpha)Me), 23.3 (C(6)), 25.1 (C(5)), 28.3 (CMe\textsubscript{3}), 33.1 (NMe), 55.2 (OMe), 57.9 (C(1)), 60.9 (C(7)), 61.6 (C(\alpha)), 71.2 (C(2)), 80.3 (CMe\textsubscript{3}), 113.3, 128.4, 137.0 (Ar), 129.6, 138.2 (C(3), C(4)), 158.3 (Ar), 173.1 (CO\textsubscript{2}Bu); m/z (ESI\textsuperscript{+}) 376 ([M+H]\textsuperscript{+}, 100%); HRMS (ESI\textsuperscript{+}) \textsubscript{C}_{20}H_{38}NO\textsubscript{4}\textsuperscript{+} ([M+H]\textsuperscript{+}) requires 376.2482; found 376.2486.

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\text{Method B (from 6):} \quad \text{BuLi (2.30 M in hexanes, 8.62 mL, 19.8 mmol) was added dropwise via syringe to a stirred solution of (R)-N-methyl-N-(\alpha-methyl-p-methoxybenzyl)amine (3.43 g, 20.8 mmol) in THF (25 mL) at –78 °C.}


°C. After stirring for 30 min a solution of 6⁸ (3.44 g, 18.9 mmol, >99:1 dr) in THF (25 mL) at −78 °C was added dropwise via cannula. The reaction mixture was left to stir for a further 2 h, before addition of acrolein (2.52 mL, 37.7 mmol). The resultant mixture was allowed to warm to rt over 2 h then concentrated in vacuo. The residue was then partitioned between CH₂Cl₂ (30 mL) and 10% aq citric acid (30 mL). The aqueous layer was extracted with CH₂Cl₂ (2 × 30 mL) and the combined organic extracts were washed sequentially with satd aq NaHCO₃ (50 mL), H₂O (50 mL) and brine (50 mL), then dried and concentrated in vacuo. The residue was dissolved in degassed CH₂Cl₂ (600 mL) and Grubbs I catalyst (2.60 g, 3.16 mmol) was added. The resultant mixture was stirred at 30 °C for 12 h then allowed to cool to rt and concentrated in vacuo. The residue was dissolved in CH₂Cl₂ (150 mL) and P(CH₂OH)₃ (39.2 g, 316 mmol), 9Et₃N (5.27 mL, 37.8 mmol) and excess silica were added sequentially. The resultant mixture was left to stir at rt for a further 12 h, then filtered and concentrated in vacuo. Purification via flash column chromatography (eluent 30–40 °C petrol/acetone, 30:1) gave 13 as a white solid (4.68 g, 66%, >99:1 dr); mp 100–104 °C; [α]D²⁰ +28.9 (c 0.3 in CHCl₃).

tert-Butyl (1S,2R,7R,aR)-2-hydroxy-7-[N-methyl-N-(α-methyl-p-methoxybenzyl)amino]cyclohept-3-ene-1-carboxylate 14

Grubbs I catalyst (12 mg, 0.01 mmol) was added to a stirred solution of 10 (30 mg, 0.07 mmol, >99:1 dr) in degassed CH₂Cl₂ (3 mL) at 30 °C. The resultant mixture was stirred at 30 °C for 12 h then allowed to cool to rt and concentrated in vacuo. The residue was dissolved in CH₂Cl₂ (5 mL) and P(CH₂OH)₃ (124 mg, 1.00 mmol), 9Et₃N (0.02 mL, 0.14 mmol) and excess silica were added sequentially. The resultant mixture was left to stir at rt for a further 12 h, then filtered and concentrated in vacuo. Purification via flash column chromatography (eluent 30–40 °C petrol/acetone, 10:1) gave 14 as a yellow oil (27 mg, 97%, >99:1 dr); [α]D²⁰ −12.7 (c 0.4 in MeOH); νmax (film) 3493 (O−H), 2971, 2931, 2836 (C−H), 1725, 1700 (C=O); δH (400 MHz, CDCl₃) 1.33 (3H, d, J₆,₇, C(α)Me), 1.44–1.56 (1H, m, C(6)H₆A) overlapping 1.48 (9H, s, CMe₃), 1.69–1.76 (1H, m, C(6)H₆B), 2.07 (3H, s, NMe), 2.11–2.23 (2H, m, C(5)H₂), 2.79 (1H, dd, J 9.3, 1.4, C(1)H), 3.57 (1H, q, J 6.7, C(α)H), 3.67 (1H, d, J 3.8, OH), 3.79 (3H, s, OMe), 3.91 (1H, app td, J 9.3, 3.4, C(7)H), 4.53–4.57 (1H, m, C(2)H), 5.78 (1H, dd, J 11.3, 6.0, 1.7, C(3)H), 5.86–5.92 (1H, m, C(4)H), 6.81 (2H, d, J 8.5, Ar), 7.20 (2H, d, J 8.5, Ar); δC (100 MHz, CDCl₃) 21.4 (C(α)Me), 25.2, 25.5 (C(5), C(6)), 28.2 (CMe₃), 33.0 (NMe), 384.

⁸ Davies, S. G.; Fletcher, A. M.; Roberts, P. M.; Smith, A. D. Tetrahedron 2009, 65, 10192.
53.8 (C(1)), 55.2 (OMe), 56.5 (C(7)), 61.7 (C(a)), 67.6 (C(2)), 81.1 (CMe₃), 113.4, 128.3 (Ar), 130.9 (C(3)), 134.7 (C(4)), 138.0, 158.4 (Ar), 175.2 (CO₂Bu); m/z (ESI⁺) 773 ([M+Na]⁺, 95%), 398 ([M+Na]⁺, 100%), 376 ([M+H]⁺, 70%); HRMS (ESI⁺) C₂₂H₃₄NO₄⁺ ([M+H]⁺) requires; 376.2482, found 376.2476.

tert-Butyl (1R,2S,3S,4R,5S)-3-hydroxy-4-iodo-N(8)-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate 17

I₂ (365 mg, 1.44 mmol) was added to a stirred solution of 14 (180 mg, 0.48 mmol, >99:1 dr) in CH₂Cl₂ (15 mL) at rt. The resultant mixture was allowed to stir at rt for 12 h then Na₂S₂O₃ (excess) was added. The reaction mixture was stirred at rt for 15 min then filtered and concentrated in vacuo. The residue was dissolved in THF (5 mL) and K₂CO₃ (74 mg, 0.53 mmol) was added. The resultant mixture was left to stir for 1 h at rt then filtered through Celite® (eluent THF) and concentrated in vacuo. Purification via flash column chromatography (eluent 30–40 °C petrol/acetone, 10:1 increased to 2:1) gave 17 as a brown solid (19 mg, 11%, >99:1 dr);¹¹ mp 105–109 °C (dec); δH (500 MHz, CDCl₃) 1.47 (9H, s, CMe₃), 1.86–1.96 (1H, m, C(6)H₁₈), 2.40–2.48 (1H, m, C(7)H₁₈), 2.42 (3H, s, NMe), 2.98 (2H, m, C(6)H₈), 2.72–2.84 (1H, m, C(6)H₈), 2.55–2.68 (1H, m, C(7)H₈) overlapping 2.42 (3H, s, NMe), 3.08 (1H, app d, J 2.5, C(2)H), 3.42 (1H, br s, C(5)H), 3.56 (1H, br s, C(1)), 4.23 (1H, app q, J 3.8, C(3)H), 4.71 (1H, br s, C(4)H); δC (125 MHz, CDCl₃) [selected peaks] 23.4, 23.8 (C(6), C(7)), 28.1 (CMe₃), 39.6 (NMe), 66.6 (C(5)), 68.1 (C(3)), 81.8 (CMe₃), 170.6 (CO₂Bu); m/z (FI⁺) 367 ([M⁺], 100%); HRMS (FI⁺) C₁₃H₂₂NO₅⁺ ([M⁺]) requires 367.0639; found 367.0365.

tert-Butyl (1R,2S,3R,4R,5S)-3-hydroxy-4-iodo-N(8)-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate hydroiodide 20-HI

I₂ (203 mg, 0.80 mmol) was added to a stirred solution of 13 (100 mg, 0.27 mmol, >99:1 dr) in CH₂Cl₂ (10 mL) at rt. The reaction mixture was allowed to stir at rt for 12 h then Na₂S₂O₃ (excess) was added. The reaction mixture was stirred at rt for 15 min then filtered and concentrated in vacuo to give a mixture of 18 and 20-HI. Purification via direct crystallisation from CH₂Cl₂/Et₂O gave 20-HI as a white solid (95 mg, 72%, >99:1

¹¹ Compound 17 was found to be susceptible to decomposition, especially in solution, resulting in the formation of a complex mixture of products.
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do; mp 147–150 °C; [α]_D^{20} -5.7 (c 0.44 in MeOH); ν_max (KBr) 3364 (O–H), 2836, 2714, 2579 (C–H), 1724 (C=O); δ_H (500 MHz, D_2O) 1.40 (9H, s, CMe_3), 2.10–2.15 (1H, m, CH_A), 2.22–2.36 (2H, m, CH_A, CH_B), 2.43–2.48 (1H, m, CH_B), 2.80 (3H, s, NMe), 2.91 (1H, d, J 9.1, C(2)H), 4.17–4.27 (4H, m, C(1)H, C(3)H, C(4)H, C(5)H); δ_C (125 MHz, D_2O) 21.5, 22.5 (C(6), C(7)), 27.4 (CMe_3), 30.2 (C(4)), 38.9 (NMe), 53.2 (C(2)), 64.9, 69.0, 69.4 (C(1), C(3), C(5)), 85.2 (CMe_3), 168.7 (CO_2^Bu); m/z (F^+) 367 ([M]^+, 100%); HRMS (F^+) C_{13}H_{22}INO_3^+ ([M]^+) requires 367.0644; found 367.0637.

tert-Butyl (1R,2S,3R,4R,5S)-3-hydroxy-4-iodo-N(8)-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate 20

Method A: I_2 (202 mg, 0.80 mmol) was added to a stirred solution of 13 (100 mg, 0.26 mmol, >99:1 dr) in CH_2Cl_2 (10 mL) at rt. The resultant mixture was allowed to stir at rt for 12 h then Na_2S_2O_3 (excess) was added. The reaction mixture was then stirred at rt for 15 min then filtered and concentrated in vacuo. The residue was dissolved in CHCl_3 (10 mL) and the resultant solution was washed with 1.0 M aq KOH (10 mL), then dried and concentrated in vacuo. Purification via flash column chromatography (eluent 30–40 °C petrol/acetone, 100:1 increased to 2:1) gave 20 as a yellow oil (45 mg, 46%, >99:1 dr); [α]_D^{20} -7.6 (c 1.1 in CHCl_3); ν_max (film) 3127 (O–H), 2973 (C–H), 1721 (C=O); δ_H (400 MHz, CDCl_3) 1.46 (9H, s, CMe_3), 1.59–1.65 (1H, m, C(7)H_A), 1.91–2.03 (2H, m, C(6)H_A, C(7)H_B), 2.06–2.14 (1H, m, C(6)H_B), 2.45 (3H, s, NMe), 2.82 (1H, dd, J 9.6, 3.8, C(2)H), 3.49–3.51 (1H, m, C(5)H), 3.53–3.55 (1H, m, C(1)H), 4.08 (1H, app t, J 9.9, C(3)H), 4.32 (1H, dd, J 9.9, 2.3, C(4)H); δ_C (100 MHz, CDCl_3) 24.6, 24.8 (C(6), C(7)), 28.1 (CMe_3), 37.1 (NMe), 39.3 (C(4)), 52.9 (C(2)), 62.1 (C(5)), 67.8 (C(1)), 71.2 (C(3)), 81.8 (CMe_3), 171.25 (CO_2^Bu); m/z (F^+) 367 ([M]^+, 100%); HRMS (F^+) C_{13}H_{22}INO_3^+ ([M]^+) requires 367.0644; found 367.0651.

Method B: I_2 (203 mg, 0.80 mmol) was added to a stirred solution of 13 (100 mg, 0.27 mmol, >99:1 dr) in CH_2Cl_2 (10 mL) at rt. The resultant mixture was allowed to stir at rt for 12 h then Na_2S_2O_3 (excess) was added. The reaction mixture was then stirred at rt for 15 min then filtered and concentrated in vacuo. The residue was dissolved in THF (5 mL) and K_2CO_3 (74 mg, 0.53 mmol) was added. The resultant mixture was left to stir at rt for 4 h then filtered through Celite® (eluent THF) and concentrated in vacuo. Purification via flash column chromatography (eluent 30–40 °C petrol/acetone, 100:1 increased to 2:1) gave 20 as a yellow oil (90 mg, 92%, >99:1 dr); [α]_D^{25} -7.3 (c 0.9 in CHCl_3).
**tert-Butyl (1R,2S,3S,5S)-3-hydroxy-N(8)-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate 21**

*Method A (from 20):* AIBN (128 mg, 0.78 mmol) and Bu₃SnH (0.42 mL, 1.56 mmol) were added to a solution of 20 (287 mg, 0.78 mmol, >99:1 dr) in PhMe/MeOH (v/v, 5:1, 12 mL). The reaction mixture was then heated at reflux for 5 h, then allowed to cool to rt and concentrated *in vacuo*. Purification via flash column chromatography (on silica doped with 10% KF, eluent 30–40 °C petrol/acetone, 100:1 increased to 100% acetone) gave 21 as a yellow oil (124 mg, 66%, >99:1 dr); [α]D³⁰ +34.2 (c 1.0 in CHCl₃); νmax (film) 3136 (O–H), 2973, 2883, 2800 (C–H), 1720 (C=O); δH (400 MHz, CDCl₃) 1.46 (9H, s, CMe₃), 1.48–1.53 (2H, m, C(6)H₆, C(7)H₆), 1.66–1.72 (1H, m, C(4)H₆), 1.77 (1H, ddd, J 12.6, 6.6, 3.0, C(4)H₆B), 1.85–1.93 (1H, m, C(7)H₆B), 1.96–2.03 (1H, m, C(6)H₆B), 2.36 (3H, s, NMe), 2.58 (1H, dd, J 10.2, 3.0, C(2)H), 3.00 (1H, br s, OH), 3.17–3.21 (1H, m, C(5)H), 3.40 (1H, app dd, J 6.6, 2.5, C(1)H), 4.04 (1H, app td, J 10.2, 6.6, C(3)H); δC (100 MHz, CDCl₃) 24.8 (C(7)), 27.0 (C(6)), 28.1 (CMe₃), 36.0 (C(4)), 37.8 (NMe), 52.5 (C(2)), 60.0 (C(5)), 61.9 (C(1)), 64.5 (C(3)), 81.3 (CMe₃), 173.3 (CO₂Bu); m/z (ESI⁺) 505 ([2M+Na]⁺, 100%), 483 ([2M+H]⁺, 35%), 264 ([M+Na]⁺, 75%), 242 ([M+H]⁺, 90%); HRMS (ESI⁺) C₁₃H₂₄NO₃⁺ ([M+H]⁺) requires 242.1751; found 242.1751.

*Method B (from 13):* I₂ (608 mg, 2.40 mmol) was added to a stirred solution of 13 (300 mg, 0.80 mmol, >99:1 dr) in CH₂Cl₂ (30 mL) at rt. The resultant mixture was allowed to stir at rt for 12 h then Na₂S₂O₃ (excess) was added. The reaction mixture was then stirred at rt for 15 min then filtered and concentrated *in vacuo*. The residue was dissolved in PhMe/MeOH (v/v, 5:1, 10 mL) and AIBN (131 mg, 0.80 mmol) and Bu₃SnH (0.43 mL, 1.60 mmol) were added to the resultant solution. The reaction mixture was then heated at reflux for 5 h, then allowed to cool to rt and concentrated *in vacuo*. Purification via flash column chromatography (on silica doped with 10% KF, eluent 30–40 °C petrol/acetone, 100:1 increased to 100% acetone) gave 21 as a yellow oil (150 mg, 78%, >99:1 dr); [α]D³⁰ +34.2 (c 1.0 in CHCl₃).

Methyl (1R,2S,3S,5S)-3-hydroxy-N(8)-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate

[(+)-pseudoecgonine methyl ester] 22

SOCl₂ (0.12 mL, 1.66 mmol) was added to a stirred solution of 21 (200 mg, 0.83 mmol, >99:1 dr) in MeOH (5 mL) at 0 °C and the resultant mixture was heated at 50 °C for 5 h. The reaction mixture was then allowed to
cool to rt and concentrated in vacuo. The residue was dissolved in THF/MeOH (v/v 10:1, 5 mL) and the resultant solution was left to stir with K₂CO₃ (230 mg, 1.66 mmol) for 4 h before being filtered through Celite® (elucent CH₂Cl₂) and concentrated in vacuo. Purification via flash column chromatography (elucent 30–40 °C petrol/acetone, 10:1 increased to 100% acetone) gave 22 as a white solid (90 mg, 55%, >99:1 dr); mp 111–113 °C; [lit.¹³ mp 114–116 °C; lit.¹⁴ mp 113–114 °C; lit.¹⁵ for ent-22: mp 114–115 °C]; [α]ᵩ₂⁰ +17.5 (c 0.4 in H₂O); [lit.¹⁶ [α]ᵩ₂⁰ +22.8 (c 1.7 in H₂O); lit.¹⁷ [α]ᵩ²³ +23.1 (c 1 in H₂O); lit.¹⁸ for ent-22: [α]ᵩ²⁴ −22.5 (c 1 in H₂O)]; δH (400 MHz, CDCl₃) 1.50–1.57 (2H, m, C(6)H₆), 1.84–1.94 (1H, m, C(7)H₇), 1.96–2.06 (1H, m, C(6)H₆), 2.37 (3H, s, NMe), 2.71 (1H, dd, J 10.1, 2.8, C(2)H), 2.85–2.95 (1H, br s, OH), 3.19–3.24 (1H, m, C(3)H), 3.45 (1H, app dd, J 6.8, 2.8, C(1)H), 3.72 (3H, s, OMe), 4.11 (1H, td, J 10.1, 6.6, C(3)H); δC (100 MHz, CDCl₃) 24.9, 27.1 (C(6), C(7)), 36.1 (C(4)), 37.7 (NMe), 51.8, 51.9 (C(2), OMe), 60.0 (C(5)), 61.8 (C(1)), 64.3 (C(3)), 174.3 (CO₂Me).

Methyl (1R,2S,3S,5S)-3-benzoyloxy-N(8)-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate hydrochloride ([+)-pseudococaine hydrochloride] 2·HCl

Method A (from 22): PhCOCl (0.02 mL, 0.15 mmol) was added to a stirred solution of 22 (21 mg, 0.11 mmol, >99:1 dr), NEt₃ (0.07 mL, 0.53 mmol) and DMAP (2 mg, cat.) in CH₂Cl₂ (2 mL) and the resultant mixture was left to stir at rt for 12 h. The reaction mixture was then diluted with CH₂Cl₂ (2 mL) and the resultant solution was washed sequentially with 2.0 M aq NaOH (2 × 4 mL), H₂O (2 × 4 mL) and brine (4 mL), then dried and concentrated in vacuo. Purification via flash column chromatography (elucent CH₂Cl₂/MeOH/NEt₃, 100:1:0.1) gave 2 as a colourless oil (24 mg, 75%, >99:1 dr);¹⁹ [α]ᵩ₂⁰ +24.3 (c 0.5 in CHCl₃); νmax (film) 2949, 2882, 2850 (C–H), 1734, 1718 (C=O); δH (500 MHz, CDCl₃) 1.75–1.81 (2H, m, C(4)H₆, C(6)H₆), 1.84–1.89 (1H, m, C(7)H₇), 1.92–1.99 (1H, m, C(7)H₇), 2.05–2.14 (2H, m, C(4)H₆, C(6)H₆), 2.45 (3H, s, NMe), 3.14 (1H, dd, J 10.7, 2.8, C(2)H), 3.26–3.29 (1H, m, C(5)H), 3.49–3.51 (1H, m, C(1)H), 3.66 (3H, s, OMe), 5.54 (1H, app td, J

10.7, 6.6, C(3)H, 7.42 (2H, app t, J 7.6, Ph), 7.54 (1H, app t, J 7.25, Ph), 7.99 (2H, app d, J 6.9, Ph); δC (125 MHz, CDCl₃) 24.1 (C(7)), 26.9, 33.8 (C(4), C(6)), 37.7 (NMe), 48.7 (C(2)), 51.9 (OMe), 59.8 (C(5)), 62.7 (C(1)), 67.9 (C(3)), 128.3, 129.6, 130.3, 132.8 (Ph), 165.6 (OCOPh), 172.8 (CO₂Me); m/z (ESI⁺) 629 ([M+Na]⁺, 45%), 326 ([M+Na]⁺, 40%), 304 ([M+H]⁺, 100%); HRMS (ESI⁺) C₁₇H₂₂NO₄⁺ ([M+H]⁺) requires 304.1543; found 304.1539. (+)-Pseudococaine 2 (24 mg, 0.08 mmol) was then dissolved in 1.25 M HCl in MeOH (2 mL) and the resultant solution was stirred at rt for 5 min then concentrated in vacuo. This co-evaporation process was then repeated to give 2-HCl as a white solid (27 mg, quant); mp 209–211 °C; {lit.²⁰ for ent-2-HCl: mp 210–212 °C}; [α]D²⁰ +43.7 (c 0.2 in H₂O); {lit.²¹ [α]D²⁰ +42 (c 1.5 in H₂O); lit.²² for ent-2-HCl: [α]D²⁴ –42.3 (c 1.0 in H₂O)); νmax (KBr) 3480 (N−H), 2814, 2681, 2568 (C−H), 1738, 1712 (C=O); δH (500 MHz, MeOH-d₄) 2.18–2.24 (2H, m, C(4)H₂, C(6)H₂), 2.30–2.40 (2H, m, C(7)H₂), 2.41–2.48 (1H, m, C(6)H₃), 2.52 (1H, ddd, J 13.9, 6.4, 2.8, C(4)H₂), 2.93 (3H, s, NMe), 3.58 (1H, dd, J 10.9, 2.5, C(2)H), 3.70 (3H, s, OMe), 4.07–4.10 (1H, m, C(5)H), 4.29–4.31 (1H, m, C(1)H), 5.65 (1H, td, J 10.9, 6.4, C(3)H), 7.49–7.52 (2H, m, Ph), 7.63–7.67 (1H, m, Ph), 8.00–8.02 (2H, m, Ph); δC (125 MHz, MeOH-d₄) 23.1 (C(7)), 25.4 (C(6)), 35.3 (C(4)), 38.9 (NMe), 49.5 (C(2)), 53.3 (OMe), 64.7 (C(5)), 65.3 (C(1)), 66.5 (C(3)), 129.7, 130.7, 130.7, 131.7, 134.7 (Ph), 166.9, 170.5 (OCOPh, CO₂Me).

**Method B (from 21)** – Step 1: SOCl₂ (0.09 mL, 1.24 mmol) was added to a stirred solution of 21 (150 mg, 0.62 mmol) in MeOH (3 mL) at 0 °C and the resultant mixture was heated at 50 °C for 5 h. The reaction mixture was then allowed to cool to rt and concentrated in vacuo to give 22-HCl a pale brown solid (177 mg, quant);²³ mp 205–208 °C; {lit.²⁴ mp 209.5 °C); [α]D²⁰ +21.2 (c 0.1 in H₂O); {lit.²⁵ [α]D²⁰ +23.4 (c 2.2 in H₂O); νmax (KBr) 3374 (O–H), 2949, 2883, 2805 (C–H), 1729 (C=O); δH (500 MHz, D₂O) 1.78–1.83 (1H, m, C(4)H₆), 1.95–2.00 (1H, m, C(6)H₆), 2.04–2.11 (1H, m, C(7)H₆), 2.13–2.29 (3H, m, C(4)H₅, C(6)H₅, C(7)H₅), 2.74 (3H, s, NMe), 2.92 (1H, dd, J 10.6, 2.5, C(2)H), 3.69 (3H, s, OMe), 3.90–3.92 (1H, m, C(5)H), 4.08–4.09 (1H, m, C(1)H), 4.28 (1H, app td, J 10.6, 6.3, C(3)H); δC (125 MHz, D₂O) 21.5 (C(7)), 23.8 (C(6)), 36.9 (C(4)), 38.3 (NMe), 52.1 (C(2)), 53.0 (OMe), 61.7 (C(3)), 63.8, 64.0 (C(1), C(5)), 171.3 (CO₂Bu); m/z (ESI⁺) 200 ([M+H]⁺, 100%); HRMS (ESI⁺) C₁₉H₁₈NO₃⁺ ([M+H]⁺) requires 200.1281; found 200.1281.

**Method B (from 21)** – Step 2: PhCOCl (0.02 mL, 0.15 mmol) was added to a stirred solution of 22-HCl (72 mg, 0.31 mmol), NEt₃ (0.21 mL, 1.53 mmol) and DMAP (2 mg, cat.) in CH₂Cl₂ (3 mL) and the resultant mixture

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was left to stir at rt for 12 h. The reaction mixture was then diluted with CH₂Cl₂ (5 mL) and the resultant solution was washed sequentially with 2.0 M aq NaOH (2 × 10 mL), H₂O (2 × 10 mL) and brine (10 mL), then dried and concentrated in vacuo. Purification via flash column chromatography (eluent CH₂Cl₂/MeOH/NEt₃, 100:1:0.1) gave 2 as a colourless oil (62 mg, 66%, >99:1 dr). The residue (62 mg, 0.20 mmol) was then dissolved in 1.25 M HCl in MeOH (2 mL) and the resultant solution was stirred at rt for 5 min then concentrated in vacuo. This co-evaporation process was then repeated to give 2·HCl as a white solid (69 mg, quant); mp 209–211 °C; {lit.²⁶ for ent-2·HCl: mp 210–212 °C}; [α]D₂₀ +43.7 (c 0.2 in H₂O); {lit.²⁷ [α]D₂₀ +42 (c 1.5 in H₂O); lit.²⁸ for ent-2·HCl: [α]D₂₀ −42.3 (c 1.0 in H₂O)).

X-ray crystal structure determination for 9, 13, 17, 20·HI and 22

Data were collected using either a Nonius κ-CCD diffractometer with graphite monochromated Mo-Kα radiation, or an Oxford Diffraction SuperNova diffractometer with graphite monochromated Cu-Kα radiation, using standard procedures at 150 K. The structures were solved by direct methods (SIR92); all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions.

The structure was refined using CRYSTALS.29,30

X-ray crystal structure data for 9 [C24H37NO4]: M = 403.56, triclinic, space group P 1, a = 5.6229(3) Å, b = 8.7918(4) Å, c = 12.5901(6) Å, α = 81.487(4)°, β = 82.616(4)°, γ = 76.535(4)°, V = 595.75(5) Å³, Z = 1, μ = 0.599 mm⁻¹, colourless block, crystal dimensions = 0.11 × 0.17 × 0.25 mm. A total of 8922 unique reflections were measured for 4 < θ < 76 and 7575 reflections were used in the refinement. The final parameters were wR₂ = 0.164 and R₁ = 0.063 [(I > −3.0σ(I)], with Flack enantiopole = −0.1(2).31

X-ray crystal structure data for 13 [C22H33NO4]: M = 751.02, monoclinic, space group P 2₁, a = 10.5891(2) Å, b = 10.1907(2) Å, c = 20.7473(4) Å, β = 103.0723(8)°, V = 2180.83(7) Å³, Z = 4, μ = 0.078 mm⁻¹, colourless block, crystal dimensions = 0.21 × 0.24 × 0.27 mm. A total of 5228 unique reflections were measured for 5 < θ < 27 and 4301 reflections were used in the refinement. The final parameters were wR₂ = 0.110 and R₁ = 0.057 [(I > −3.0σ(I)].

X-ray crystal structure data for 17 [C13H22INO4]: M = 367.23, orthorhombic, space group P 2₁ 2₁ 2₁, a = 10.5822(4) Å, b = 11.4387(6) Å, c = 12.8091(8) Å, V = 1550.51(13) Å³, Z = 4, μ = 16.24 mm⁻¹, colourless block, crystal dimensions = 0.05 × 0.05 × 0.05 mm. A total of 3217 unique reflections were measured for 5 < θ < 77 and 1357 reflections were used in the refinement. The final parameters were wR₂ = 0.061 and R₁ = 0.050 [(I > 3.0σ(I)], with Flack enantiopole = −0.04(3).32

X-ray crystal structure data for 20·HI [C13H23I2NO3]: M = 495.14, monoclinic, space group P 2₁, a = 11.7106(5) Å, b = 7.0979(4) Å, c = 11.9661(7) Å, β = 116.827(2)°, V = 887.58(8) Å³, Z = 2, μ = 3.547 mm⁻¹, colourless block, crystal dimensions = 0.04 × 0.06 × 0.22 mm. A total of 3940 unique reflections were measured and R₁ = 0.050 [(I > 3.0σ(I)].

30 Crystallographic data (excluding structure factors) for compounds 9, 11, 15, 18·HI and 20 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 883481–883485, respectively. Copies of these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif
measured for $5 < \theta < 27$ and 3940 reflections were used in the refinement. The final parameters were $wR_2 = 0.101$ and $R_1 = 0.082$ [$I > 3.0 \sigma(I)$], with Flack enantiopole = $-0.01(7)$.$^{33}$

X-ray crystal structure data for 22 [C$_{10}$H$_{17}$NO$_3$]: $M = 199.25$, orthorhombic, space group P 2$_1$ 2$_1$ 2$_1$,

\[
a = 6.3402(2) \text{ Å}, \quad b = 8.2496(3) \text{ Å}, \quad c = 18.8623(6) \text{ Å}, \quad V = 986.58(6) \text{ Å}^3, \quad Z = 4, \quad \mu = 0.098 \text{ mm}^{-1},
\]

colourless prism, crystal dimensions = $0.11 \times 0.13 \times 0.25$ mm. A total of 1323 unique reflections were measured for $5 < \theta < 27$ and 1323 reflections were used in the refinement. The final parameters were $wR_2 = 0.105$ and $R_1 = 0.048$ [$I > 3.0 \sigma(I)$].

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2. Copies of $^1$H and $^{13}$C NMR spectra

*tert*-Butyl $(R,R)$-3-$[N$-methyl-$N$-(α-methyl-$p$-methoxybenzyl)amino]hept-6-enoate 8 (400 MHz $^1$H, CDCl$_3$)
tert-Butyl (R,R)-3-[N-methyl-N-(α-methyl-p-methoxybenzyl)amino]hept-6-enoate 8 (100 MHz $^{13}$C, CDCl$_3$)
tert-Butyl (2S,3R,aR,1'S)-2-(1'-hydroxyprop-2'-en-1'-yl)-3-[N-methyl-N-(a-methyl-p-methoxybenzyl)amino]hept-6-enoate 9 (400 MHz $^1$H, CDCl$_3$)
**tert-Butyl (2S,3R,aR,1'S)-2-(1'-hydroxyprop-2'-en-1'-yl)-3-[N-methyl-N-(α-methyl-p-methoxybenzyl)amino]hept-6-enoate 9 (100 MHz $^{13}$C, CDCl$_3$)**
tert-butyl (2S,3R,aR,1'R)-2-(1'-hydroxyprop-2'-en-1'-yl)-3-[N-methyl-N-(a-methyl-p-methoxybenzyl)amino]hept-6-enoate 10 (400 MHz ¹H, CDCl₃)
tert-butyl (2S,3R,αR,1'R)-2-(1'-hydroxyprop-2'-en-1'-yl)-3-[N-methyl-N-(α-methyl-p-methoxybenzyl)amino]hept-6-enoate 10 (100 MHz $^{13}$C, CDCl$_3$)
tert-Butyl (1S,2S,7R,αR)-2-hydroxy-7-[[N-methyl-N-(α-methyl-p-methoxybenzyl)amino]cyclohept-3-ene-1-carboxylate 13 (400 MHz $^1$H, CDCl$_3$)
tert-Butyl (1S,2S,7R,αR)-2-hydroxy-7-[N-methyl-N-(α-methyl-p-methoxybenzyl)amino]cyclohept-3-ene-1-carboxylate 13 (100 MHz $^{13}$C, CDCl$_3$)
tert-Butyl (1S,2R,7αR)-2-hydroxy-7-[N-methyl-N-(α-methyl-p-methoxybenzyl)amino]cyclohept-3-ene-1-carboxylate 14 (400 MHz $^1$H, CDCl$_3$)
tert-Butyl (1S,2R,7R,αR)-2-hydroxy-7-[N-methyl-N-(α-methyl-p-methoxybenzyl)amino]cyclohept-3-ene-1-carboxylate 14 (100 MHz $^{13}$C, CDCl$_3$)
** tert-Butyl (1R,2S,3R,4R,5S)-3-hydroxy-4-iodo-N(8)-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate hydroiodide 20·HI (500 MHz $^1$H, D$_2$O) **

[Chemical structure and spectrum image]
tert-Butyl (1R,2S,3R,4R,5S)-3-hydroxy-4-iodo-N(8)-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate hydroiodide 20·HI (125 MHz $^{13}$C, D$_2$O)
**tert-Butyl (1R,2S,3R,4R,5S)-3-hydroxy-4-iodo-N(8)-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate 20**

(400 MHz $^1$H, CDCl$_3$)
tert-Butyl \((1R,2S,3R,4R,5S)-3\text{-}\text{hydroxy-}4\text{-}\text{iodo-}N(8)\text{-}\text{methyl-8-azabicyclo[3.2.1]octane-2-carboxylate 20 (100 MHz }^{13}\text{C, CDCl}_3\)
**tert-Butyl (1R,2S,3S,5S)-3-hydroxy-N(8)-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate 21 (400 MHz $^1$H, CDCl$_3$)**

![NMR Spectrum](image)
tert-Butyl (1R,2S,3S,5S)-3-hydroxy-N(8)-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate 21 (100 MHz $^{13}$C, CDCl$_3$)
Methyl (1R,2S,3S,5S)-3-hydroxy-N(8)-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate [(+)-pseudoeccgonine methyl ester] 22 (400 MHz $^1$H, CDCl$_3$)
Methyl (1R,2S,3S,5S)-3-hydroxy-N(8)-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate [(+)-pseudoecgonine methyl ester] 22 (100 MHz $^{13}$C, CDCl$_3$)
Methyl (1R,2S,3S,5S)-3-hydroxy-N(8)-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate hydrochloride [(+)-pseudoecgonine methyl ester hydrochloride] 22·HCl (500 MHz ¹H, D₂O)
Methyl (1R,2S,3S,5S)-3-hydroxy-N(8)-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate hydrochloride [(+)-pseudoecgonine methyl ester hydrochloride] 22·HCl (125 MHz $^{13}$C, D$_2$O)
Methyl (1R,2S,3S,5S)-3-benzoyloxy-N(8)-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate [(+)-pseudococaine] 2 (500 MHz $^1$H, CDCl$_3$)
Methyl \((1R,2S,3S,5S)-3\text{-}\text{benzoyloxy}\text{-}N(8)\text{-}\text{methyl}\text{-}8\text{-}\text{azabicyclo}[3.2.1]\text{octane-2-carboxylate [(+)-pseudococaine]}\) 2 (125 MHz \(^{13}\text{C}, \text{CDCl}_3\))
Methyl \((1R,2S,3S,5S)-3\text{-benzoyloxy-N}(8)\text{-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate hydrochloride} [(+)-pseudococaine hydrochloride] 2\text{HCl}\) (500 MHz \(^1\text{H}, \text{MeOH-}d_4\))
(125 MHz $^{13}$C, MeOH-$d_4$)