

Electronic Supplementary Information

A new entry into *cis*-3-amino-2-methylpyrrolidines via ring expansion of 2-(2-hydroxyethyl)-3-methylaziridines

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***N*-(4-Acetoxy-2-chloro-1-methylbutylidene)*tert*-butylamine 8b**

Bp. 58-59 °C/0.01 mmHg. ¹H NMR (270 MHz, CDCl₃): δ 1.27 (9H, s); 2.03 and 2.06 (6H, 2×s); 2.05-2.20 (2H, m); 4.08-4.30 (2H, m); 4.36 (1H, d×d, J = 8.6, 5.9 Hz). ¹³C NMR (68 MHz, CDCl₃): δ 16.7, 20.9, 30.0, 34.2, 55.2, 61.3, 65.4, 162.3, 170.7. IR (NaCl): ν_{C=O} = 1740 cm⁻¹, ν_{C=N} = 1665 cm⁻¹. MS (70 eV): m/z (%): no M⁺; 218 (3); 198 (2); 158 (7); 149 (7); 147 (17); 136 (5); 118 (6); 104 (6); 98 (20); 91 (7); 82 (5); 76 (7); 57 (100).

***N*-(4-Acetoxy-2-chloro-1-methylbutylidene)benzylamine 8c**

¹H NMR (270 MHz, CDCl₃): δ 2.04 (3H, s); 2.05 (3H, s); 2.12-2.43 (2H, m); 4.16-4.33 (2H, m); 4.51 and 4.53 (2H, 2×d, J = 15.8 Hz); 4.56 (1H, d×d, J = 9.4, 5.5 Hz); 7.20-7.39 (5H, m). ¹³C NMR (68 MHz, CDCl₃): δ 14.5, 20.7, 33.9, 55.1, 61.1, 63.5, 126.7, 127.6, 128.4, 139.6, 167.0, 170.6. IR (NaCl): ν_{C=O} = 1729 cm⁻¹, ν_{C=N} = 1656 cm⁻¹. MS (70 eV): m/z (%): 267/9 (M⁺, 0.5); 232 (2); 194 (1); 181/3 (22); 172 (2); 171 (1); 160 (1); 146 (8); 132 (5); 106 (3); 91 (100); 89 (3); 77 (3); 65 (13); 51 (3).

***cis*-2-(2-Acetoxyethyl)-1-*tert*-butyl-3-methylaziridine *cis*-9b**

¹H NMR (270 MHz, CDCl₃): δ 0.96 (9H, s); 1.11 (3H, d, J = 5.6 Hz); 1.54-1.82 (4H, m); 2.06 (3H, s); 4.13-4.20 (2H, m). ¹³C NMR (68 MHz, CDCl₃): δ 14.0, 21.0, 26.8, 27.9, 30.6, 33.2, 52.8, 63.5, 171.1. IR (NaCl): ν_{C=O} = 1738 cm⁻¹. MS (70 eV): m/z (%): 199 (M⁺, 6); 184 (5); 156 (4); 143 (5); 142 (11); 140 (6); 100 (7); 82 (100); 72 (4); 70 (26); 68 (11); 57 (19); 56 (12); 55 (18); 54 (7).

***trans*-2-(2-Acetoxyethyl)-1-*tert*-butyl-3-methylaziridine *trans*-9b**

¹H NMR (270 MHz, CDCl₃): δ 1.13 (9H, s); 1.33 (3H, d, J = 5.9 Hz); 1.62-1.89 (4H, m); 2.07 (3H, s); 4.17 (2H, d×d, J = 7.1, 5.8 Hz). ¹³C NMR (68 MHz, CDCl₃): δ 15.5, 21.0, 29.8, 31.9, 36.8, 53.6, 63.4, 171.1. IR (NaCl): ν_{C=O} = 1739 cm⁻¹. MS (70 eV): m/z (%): 199 (M⁺, 3); 184 (3); 156 (2); 143 (3); 142 (7); 140 (3); 124 (7); 100 (5); 82 (100); 70 (29); 68 (11); 57 (23); 56 (14); 55 (21). Anal. Calcd for C₁₁H₂₁NO₂: C 66.29, H 10.62, N 7.03. Found: C 66.36, H 10.78, N 7.17.

2-(2-Acetoxyethyl)-1-benzyl-3-methylaziridine 9c

¹H NMR (270 MHz, CDCl₃): δ 1.18 and 1.33 (6H, 2×d, J = 5.9 Hz); 1.35-1.98 (8H, m); 2.01 (3H, s); 2.02 (3H, s); 3.42 and 3.52 (2H, 2×d, J = 13.3 Hz); 3.48 and 3.77 (2H, 2×d, J = 13.7 Hz); 3.82-4.22 (4H, m); 7.21-7.42 (10H, m). ¹³C NMR (68 MHz, CDCl₃): δ_{cis-9c} 13.3, 20.8, 27.4, 39.0, 40.6, 63.0, 64.7, 127.0, 128.0, 128.3, 139.3, 170.9. δ_{trans-9c} 11.3, 20.9, 32.2, 38.2, 43.2, 55.4, 62.7, 126.8, 128.1, 128.4, 140.0, 170.9. IR (NaCl): ν_{C=O} = 1749-1741 cm⁻¹. MS (70 eV): m/z (%): 233 (M⁺, 2); 190 (3); 174 (4); 173 (6); 160 (7); 142 (15); 117 (4); 104 (3); 91 (53); 82 (100); 70 (6); 68 (5); 65 (11); 55 (7); 51 (5). Anal. Calcd for C₁₄H₁₉NO₂: C 72.07, H 8.21, N 6.00. Found: C 72.31, H 8.42, N 6.16.

1-*tert*-Butyl-2-(2-hydroxyethyl)-3-methylaziridine 10b

Bp. 59-60 °C/0.01 mmHg. ¹H NMR (270 MHz, CDCl₃): δ 0.98 (9H, s); 1.12-1.14 (3H, m); 1.14 (9H, s); 1.36 (3H, d, J = 6.3 Hz); 1.45-2.08 (8H, m); 3.62-3.88 (4H, m). ¹³C NMR (68 MHz, CDCl₃): δ 13.8, 15.0, 26.7, 29.7, 30.6, 33.2, 33.8, 35.6, 52.8, 53.7, 60.5, 60.8. IR (NaCl): ν_{OH} = 3560-3030 cm⁻¹. MS (70 eV): m/z _{cis-10b} (%): 157 (M⁺, 5); 142 (17); 113 (8); 98 (38); 72 (8); 70 (7); 57 (100); 56 (49). m/z _{trans-10a} (%): 157 (M⁺, 6); 142 (18); 113 (8); 112 (5); 100 (22); 98 (34); 96 (5); 86 (6); 85 (7); 84 (6); 80 (8); 72 (10); 70 (44); 57 (100); 56 (94); 54 (8); 53 (7). Anal. Calcd for C₉H₁₉NO: C 68.74, H 12.18, N 8.91. Found: C 68.92, H 12.30, N 9.14.

1-Benzyl-2-(2-hydroxyethyl)-3-methylaziridine 10c

¹H NMR (270 MHz, CDCl₃): δ 1.19 (3H, d, J = 5.6 Hz); 1.31 (3H, d, J = 6.3 Hz); 1.47-2.29 (8H, m); 1.47-2.29 (8H, m); 3.39 and 3.71 (2H, 2×d, J = 13.1 Hz); 3.48-3.67 (6H, m); 7.23-7.40 (10H, m). ¹³C NMR (68 MHz, CDCl₃): δ_{cis-10c} 13.2, 30.2, 38.9, 41.2, 60.7, 64.6, 127.0, 128.1, 128.3, 139.0. δ_{trans-10a} 11.2, 33.4, 36.8, 44.2, 55.1, 60.1, 126.9, 127.9, 128.3, 139.6. IR (NaCl): ν_{OH} = 3510-3020 cm⁻¹. MS (70 eV): m/z (%): 191 (M⁺, 3); 160 (10); 147 (6); 146

(10); 132 (8); 100 (75); 91 (100); 89 (5); 77 (5); 70 (65); 65 (21); 56 (99). Anal. Calcd for C₁₂H₁₇NO: C 75.35, H 8.96, N 7.32. Found: C 75.50, H 9.11, N 7.18.

***cis*-3-Bromo-1-*tert*-butyl-2-methylpyrrolidine *cis*-11b**

R_f 0.17 (hexane/EtOAc/MeOH 90/7/3). ¹H NMR (270 MHz, CDCl₃): δ 1.06 (9H, s); 1.20 (3H, d, J = 6.6 Hz); 2.18-2.31 (2H, m); 2.66 (1H, t×d, J = 9.5, 7.0 Hz); 2.89-2.99 (1H, m); 3.25 (1H, d×q, J = 7.3, 6.6 Hz); 4.08 (1H, t×d, J = 10.2, 7.3 Hz). ¹³C NMR (68 MHz, CDCl₃): δ 22.5, 26.6, 34.5, 45.4, 51.1, 53.8, 54.9. IR (NaCl): ν_{max} = 2965, 1369, 1360, 1228 cm⁻¹. MS (70 eV): m/z (%): 219/21 (M⁺, 12); 204/6 (60); 148/50 (12); 140 (31); 124 (12); 84 (100); 82 (10); 70 (35); 69 (16); 68 (13); 67 (18); 58 (15); 57 (45); 56 (16); 55 (19). Anal. Calcd for C₉H₁₈BrN: C 49.10, H 8.24, N 6.36. Found: C 49.16, H 8.32, N 6.24.

***trans*-3-Bromo-1-*tert*-butyl-2-methylpyrrolidine *trans*-11b**

R_f 0.23 (hexane/EtOAc/MeOH 90/7/3). ¹H NMR (270 MHz, CDCl₃): δ 1.10 (3H, d, J = 6.6 Hz); 1.12 (9H, s); 2.05 (1H, d×d×d, J = 13.8, 5.0, 1.0 Hz); 2.25-2.46 (1H, m); 3.01-3.19 (2H, m); 3.43 (1H, q, J = 6.6 Hz); 4.09 (1H, d, J = 5.0 Hz). ¹³C NMR (68 MHz, CDCl₃): δ 26.3, 27.4, 34.5, 46.5, 52.9, 57.1, 62.6. IR (NaCl): ν_{max} = 2965-2930, 1361, 1230, 1208 cm⁻¹. MS (70 eV): m/z (%): 219/21 (M⁺, 12); 204/6 (100); 148/50 (57); 140 (4); 124 (18); 109 (5); 84 (72); 82 (13); 70 (39); 69 (25); 68 (18); 67 (18); 58 (14); 57 (45); 55 (19). Anal. Calcd for C₉H₁₈BrN: C 49.10, H 8.24, N 6.36. Found: C 49.16, H 8.32, N 6.24.

***cis*-1-Benzyl-3-bromo-2-methylpyrrolidine *cis*-11c**

R_f 0.29 (hexane/EtOAc 96/4). ¹H NMR (270 MHz, CDCl₃): δ 1.26 (3H, d, J = 6.3 Hz); 2.19-2.51 (3H, m); 2.56 (1H, pent, J = 5.4 Hz); 3.02-3.14 (1H, m); 3.34 and 3.99 (2H, 2×d, J = 13.4 Hz); 4.41-4.50 (1H, m); 7.19-7.37 (5H, m). ¹³C NMR (68 MHz, CDCl₃): δ 17.5, 34.9, 51.3, 56.7, 57.1, 62.5, 127.0, 128.3, 128.8. IR (NaCl): ν_{max} = 1590, 1452, 1373, 1290 cm⁻¹. MS (70 eV): m/z (%): 253/5 (M⁺, 8); 252/4 (5); 239/41 (6); 238/40 (28); 176/8 (5); 174 (9); 162/4 (5); 159 (6); 147 (5); 146 (5); 132 (6); 105 (6); 91 (100); 89 (6); 82 (5); 65 (18); 56 (35). Anal. Calcd for C₁₂H₁₆BrN: C 56.71, H 6.35, N 5.51. Found: C 56.93, H 6.52, N 5.64.

***trans*-1-Benzyl-3-bromo-2-methylpyrrolidine *trans*-11c**

R_f 0.24 (hexane/EtOAc 96/4). ¹H NMR (270 MHz, CDCl₃): δ 1.25 (3H, d, J = 6.2 Hz); 1.96-2.13, 2.33-2.51 and 2.81-2.94 (4H, 3×m); 2.73 (1H, pent, J = 6.2 Hz); 3.25 and 4.03 (2H, 2×d, J = 12.9 Hz); 3.80-3.90 (1H, m); 7.22-7.34 (5H, m). ¹³C NMR (68 MHz, CDCl₃): δ 17.0, 33.6,

51.8, 53.4, 58.1, 68.8, 127.1, 128.3, 128.9, 138.7. IR (NaCl): $\nu_{\max} = 1450, 1376, 1207 \text{ cm}^{-1}$. MS (70 eV): m/z (%): 253/5 (M^+ , 4); 238/40 (25); 91 (100); 65 (11); 56 (17). Anal. Calcd for $C_{12}H_{16}BrN$: C 56.71, H 6.35, N 5.51. Found: C 56.88, H 6.61, N 5.59.

***cis*-3-Azido-1-*tert*-butyl-2-methylpyrrolidine *cis*-14b**

R_f 0.23 (hexane/EtOAc/MeOH 76/19/5). 1H NMR (270 MHz, $CDCl_3$): δ 1.06 (9H, s); 1.06 (3H, d, $J = 6.6$ Hz); 1.86-2.11 (2H, m); 2.68 (1H, t \times d, $J = 10.1, 6.3$ Hz); 2.98-3.05 (1H, m); 3.19 (1H, d \times q, $J = 7.6, 6.6$ Hz); 3.73 (1H, d \times d \times d, $J = 10.7, 7.6, 6.6$ Hz). ^{13}C NMR (68 MHz, $CDCl_3$): δ 19.8, 26.5, 28.9, 44.5, 53.9, 54.4, 63.1. IR (NaCl): $\nu_{N_3} = 2090 \text{ cm}^{-1}$. MS (70 eV): m/z (%): 182 (M^+ , 10); 167 (20); 139 (20); 137 (6); 112 (11); 111 (12); 96 (7); 84 (56); 83 (13); 82 (18); 81 (15); 80 (23); 71 (35); 70 (90); 68 (15); 57 (100); 56 (65); 55 (25). Anal. Calcd for $C_9H_{18}N_4$: C 59.31, H 9.95, N 30.74. Found: C 59.11, H 9.79, N 30.88.

***cis*-3-Azido-1-benzyl-2-methylpyrrolidine *cis*-14c**

R_f 0.32 (hexane/EtOAc 93/7). 1H NMR (270 MHz, $CDCl_3$): δ 1.25 (3H, d, $J = 6.2$ Hz); 1.81-2.22 (3H, m); 2.55 (1H, pent, $J = 6.2$ Hz); 2.93-3.04 (1H, m); 3.15 (1H, d, $J = 13.2$ Hz); 3.61-3.72 (1H, m); 4.02 (1H, d, $J = 13.2$ Hz); 7.19-7.33 (5H, m). ^{13}C NMR (68 MHz, $CDCl_3$): δ 13.9, 29.0, 51.5, 57.2, 63.3, 64.2, 126.9, 128.2, 128.7, 138.8. IR (NaCl): $\nu_{N_3} = 2091 \text{ cm}^{-1}$. MS (70 eV): m/z (%): no M^+ ; 171 (5); 160 (11); 132 (5); 104 (5); 92 (11); 91 (100); 84 (6); 65 (12); 63 (6); 55 (9); 54 (6); 51 (5); 49 (5). Anal. Calcd for $C_{12}H_{16}N_4$: C 66.64, H 7.46, N 25.90. Found: C 66.75, H 7.61, N 25.84.

***cis*-3-Amino-1-*tert*-butyl-2-methylpyrrolidine *cis*-16b**

R_f 0.12 (CH_2Cl_2 /MeOH/ NH_4OH (25%) 49.3/16.3/1). 1H NMR (270 MHz, $CDCl_3$): δ 1.10 (3H, s); 1.11 (9H, s); 1.59-2.04 (2H, m); 1.80-2.10 (2H, s_{broad}); 2.66 (1H, d \times d \times d, $J = 11.0, 9.5, 5.9$ Hz); 2.99 (1H, m); 3.07 (1H, pent, $J = 7.8$ Hz); 3.20 (1H, d \times d \times d, $J = 10.8, 7.8, 5.7$ Hz). ^{13}C NMR (68 MHz, $CDCl_3$): δ 18.4, 26.4, 33.2, 45.1, 54.6, 55.3. IR (NaCl): $\nu_{NH_2} = 3020-2575 \text{ cm}^{-1}$. MS (70 eV): m/z (%): 156 (M^+ , 7); 141 (34); 113 (8); 98 (12); 85 (19); 84 (17); 80 (13); 72 (10); 70 (26); 57 (100); 56 (64); 51 (10); 49 (17). Anal. Calcd for $C_9H_{20}N_2$: C 69.17, H 12.90, N 17.93. Found: C 68.95, H 12.76, N 17.77.