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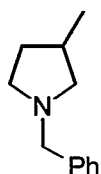
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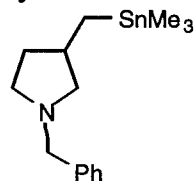
Supporting Information for :**Anionic Cyclizations of α -Aminoorganolithiums.
Determination of the Stereoselectivity at the Carbanion Center
and the Synthesis of (+)-Pseudoheliotridane.****Iain Coldham,* Richard Hufton and David J. Snowden***Department of Chemistry, University of Exeter, Stocker Road, Exeter, EX4 4QD, U.K.*A procedure for the anionic cyclization, electrophilic quench of aminomethylstannane **1** and spectroscopic data for compounds **3a-i**, **5-7** and **8a-d** (8 pages):**Anionic cyclization-electrophilic quench of aminomethylstannane **1**:**

n-Butyllithium (0.44 cm³, 0.64 mmol, 1.48 mol dm⁻³ in hexanes) was added to aminomethylstannane **1** (160 mg, 0.34 mmol) in dry hexane-diethylether (2 cm³, 10:1) at -78 °C under argon. After 10 min. the mixture was warmed to room temperature over 30 min. and allowed to stand for 3 h. The mixture was cooled to -78 °C and quenched with the electrophile (3.20 mmol). The solvents were removed under reduced pressure and the residue was purified by column chromatography on silica gel, eluting with CH₂Cl₂-EtOH-NH₃ (200:3:2) or EtOAc-light petroleum (b.p. 40-60°C) (1:10) to give the pyrrolidine **3**.

Pyrrolidine **3a** (quench with methanol, 74%):*R*_F [hexane-ethyl acetate (7:1)] 0.09.IR (neat) 1605 and 1495 cm⁻¹ (Ph).

¹H NMR (300 MHz, CDCl₃) δ 7.43-7.18 (5H, m, C₆H₅), 3.62 (2H, ABq, *J* 12.8 Hz, CH₂Ph), 2.83 [1H, dd, *J* 9.0 and 7.5 Hz, NCH_AH_BCH(CH₃)], 2.71 (1H, ddd, *J* 9.0, 7.9 and 5.7 Hz, NCH_CH_DCH₂), 2.47 (1H, td, *J* 9.0 and 6.4 Hz, NCH_CH_DCH₂), 2.26 [1H, ddqdd, *J* 12.0, 8.4, 7.5, 7.3 and 6.2 Hz, CH(CH₃)], 2.04 (1H, dtd, *J* 12.0, 9.0 and 6.2 Hz, NCH₂CH_EH_F), 2.01 [1H, dd, *J* 9.0 and 7.3 Hz, NCH_AH_BCH(CH₃)], 1.35 (1H, dtd, *J* 12.0, 9.0 and 6.2 Hz, NCH₂CH_EH_F) and 1.03 (3H, d, *J* 6.7 Hz, CHCH₃).

¹³C NMR (75 MHz, CDCl₃) δ 139.37, 128.55, 128.16, 126.81, 62.13, 60.80, 54.10, 32.65, 31.88 and 20.37.

HRMS (EI) (Found: *M*⁺, 175.1360. C₁₂H₁₇N requires *M*, 175.1361).*m/z* 175 (38%, *M*⁺), 160 (2, *M*-CH₃), 91 (100, CH₂Ph) and 84 (21, *M*-CH₂Ph).Pyrrolidine **3b** (quench with Me₄Sn, 68%)*R*_F [hexane-ethyl acetate (7:3)] 0.27.

IR (neat) 1605 and 1496 cm^{-1} (Ph).

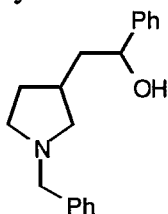
^1H NMR (300 MHz, CDCl_3) δ 7.36-7.21 (5H, m, C_6H_5), 3.59 (2H, ABq, J 13 Hz, CH_2Ph), 2.84 [1H, dd, J 8.5 and 7.0 Hz $\text{NCH}_A\text{H}_B\text{C}(\text{H})\text{CH}_2\text{Sn}$], 2.73-2.64 (1H, m, $\text{NCH}_C\text{H}_D\text{CH}_2$), 2.50-2.37 [2H, m, $\text{CH}(\text{CH}_2\text{Sn})$ and $\text{NCH}_C\text{H}_D\text{CH}_2$], 2.20-2.11 (1H, m, $\text{NCH}_2\text{CH}_E\text{HF}$), 2.01 [1H, dd, J 8.5 and 7.5 Hz, $\text{NCH}_A\text{H}_B\text{C}(\text{H})\text{CH}_2\text{Sn}$], 1.31 (1H, dtd, J 12.5, 9.0 and 6.0 Hz, $\text{NCH}_2\text{CH}_E\text{HF}$), 0.97 (2H, d, J 7.5 Hz, CH_2Sn) and 0.06 [9H, s, $\text{Sn}(\text{CH}_3)_3$].

^{13}C NMR (75 MHz, CDCl_3) δ 139.32, 128.87, 128.15, 126.80, 64.15, 60.84, 54.06, 36.05, 34.47, 18.37 and -9.67.

HRMS (EI) (Found: M^+ - CH_3 , 324.0786. $\text{C}_{14}\text{H}_{22}\text{NSn}$ requires M - CH_3 , 324.0774).

m/z 324 (75%, M^+), 174 [97, $M-(\text{CH}_3)_3\text{Sn}$] and 91 (100, CH_2Ph).

Pyrrolidine **3c** (quench with benzaldehyde, 90%)



Two diastereomers (1:1), R_F (CH_2Cl_2 -EtOH-conc. NH_3 , 100:8:1) 0.45.

IR (neat) 3360 (O-H), 1600 and 1495 cm^{-1} (Ph).

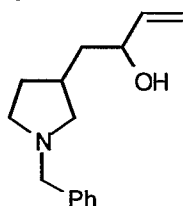
^1H NMR (300 MHz, CDCl_3) δ 7.44-7.15 [10H, m, $\text{CH}_2\text{C}_6\text{H}_5$ and $\text{CH}(\text{OH})\text{C}_6\text{H}_5$], 4.72 (0.5H, dd, J 9.1 and 4.4 Hz, CHOH), 4.66 (0.5H, dd, J 8.2 and 5.3 Hz, $\text{CH}'\text{OH}$), 3.95 (1H, broad s, CHOH), 3.71 (1H, ABq, J 12.6 Hz, CH_2Ph), 3.68 (1H, ABq, J 12.6 Hz, $\text{CH}_2\text{Ph}'$), 2.88-2.68 (1H, m, $\text{NCH}_A\text{H}_B\text{CH}(\text{CH}_2)$ and $\text{NCH}_A\text{H}_B\text{CH}(\text{CH}_2)'$), 2.71-2.58 (2H, m, NCH_2CH_2 and $\text{NCH}_2'\text{CH}_2'$), 2.53-3.0 [2H, m, $\text{NH}_A\text{CH}_B\text{CH}(\text{CH}_2)$, $\text{NCH}_A\text{H}'_B\text{CH}(\text{CH}_2)'$, $\text{NCH}_2\text{CH}(\text{CH}_2)$ and $\text{NCH}_2'\text{CH}(\text{CH}_2)'$], 2.12-1.93 (1H, m, $\text{NCH}_2\text{CH}_C\text{H}_D$ and $\text{NCH}_2'\text{CH}'_C\text{H}'_D$), 1.91-1.64 (2.5H, m, CH_2CHOH , $\text{CH}_2'\text{CHOH}'$ and $\text{NCH}_2\text{CH}_C\text{H}_D$) and 1.59-1.44 (0.5H, m, $\text{NCH}_2\text{CH}_C\text{H}'_D$).

^{13}C NMR (75 MHz, CDCl_3) δ 145.29, 145.17, 138.89, 138.45, 128.94, 128.89, 128.38, 128.35, 128.29, 128.26, 128.19, 127.35, 127.14, 127.12, 126.97, 125.92, 125.86, 73.19, 71.77, 60.57, 60.45, 60.41, 60.03, 53.66, 53.43, 45.08, 34.61, 34.24, 30.94 and 28.64.

HRMS (EI) (Found: M^+ , 281.1786. $\text{C}_{19}\text{H}_{23}\text{NO}$ requires M , 281.1780).

m/z 281 (12%, M^+), 190 (5, $M-\text{CH}_2\text{Ph}$), 174 [4, $M-\text{CH}(\text{OH})\text{C}_6\text{H}_5$], 159 (14, $M-\text{C}_8\text{H}_8\text{O}$), 120 (80, $\text{C}_8\text{H}_8\text{O}$), 91 (100, CH_2Ph) and 77 (8, C_6H_5).

Pyrrolidine **3d** (quench with acrolein, 65%)



Two diastereomers (1:1), R_F (CH_2Cl_2 -EtOH-conc. NH_3 , 100:8:1) 0.32 and 0.23.

IR (neat) 3370 (O-H), 1640 (C=C), 1605 and 1495 cm^{-1} (Ph).

^1H NMR (300 MHz, CDCl_3) δ 7.39-7.20 (5H, m, C_6H_5), 5.95-5.78 (1H, m, $\text{CH}=\text{CH}_2$ and $\text{CH}'=\text{CH}_2'$), 5.28-5.03 (2H, m, $\text{CH}=\text{CH}_2$ and $\text{CH}=\text{CH}_2'$), 4.23-4.04 (1H, m, CHOH and $\text{CH}'\text{OH}$), 3.77-3.46 (2H, 2 x ABq, J 12.7 and 13 Hz, CH_2Ph and $\text{CH}_2\text{Ph}'$), 2.85-2.71 [1H, m, $\text{NCH}_A\text{H}_B\text{CH}(\text{CH}_2)$ and $\text{NCH}_A'\text{H}_B'\text{CH}(\text{CH}_2)'$], 2.64-2.22

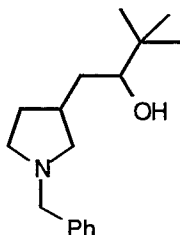
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[4H, m, $\text{NCH}_A\text{H}_B\text{CH}(\text{CH}_2-)$, $\text{NCH}_A\text{H}'_B\text{CH}(\text{CH}_2)'$, NCH_2CH_2 and $\text{NCH}'_2\text{CH}'_2$], 2.15-1.93 (1.5H, m, $\text{NCH}_2\text{CH}_C\text{H}_D$, $\text{NCH}_2\text{CH}'_C\text{H}'_D$ and $\text{NCH}_2\text{CH}_C\text{H}'_D$) and 1.71-1.43 (2.5H, m, CH_2CHOH , $\text{CH}'_2\text{CHOH}'$ and $\text{NCH}_2\text{CH}_C\text{H}_D$).

HRMS (EI) (Found: M^+ , 231.1628. $\text{C}_{15}\text{H}_{21}\text{NO}$ requires M , 231.1623).

m/z 231 (17%, M^+), 214 (2, $M-\text{OH}$), 174 [10, $M-\text{CH}(\text{OH})\text{CH}=\text{CH}_2$], 160 (10, $M-\text{CH}_2\text{CH}(\text{OH})\text{CH}=\text{CH}_2$] and 91 (100, CH_2Ph).

Pyrrolidine **3e** (quench with pivalaldehyde, 52%)



Two diastereomers (1:1), R_F (hexane-ethyl acetate 1:1) 0.02.

IR (neat) 3410 (O-H), 1605 and 1495 cm^{-1} (Ph).

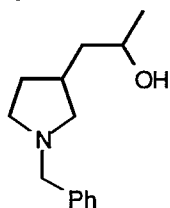
^1H NMR (300 MHz, CDCl_3) δ 7.40-7.18 (5H, m, C_6H_5), 3.74-3.57 (2H, m, CH_2Ph and $\text{CH}_2\text{Ph}'$), 3.21 (1H, dd, J 10.9 and 10.9 Hz, CHOH and $\text{CH}'\text{OH}'$), 2.91 (1H, broad s, CHOH), 2.90-2.28 (6H, m, 3 x CH_2 ring protons), 2.15-1.97 [1H, m, $\text{NCH}_2\text{CH}(\text{CH}_2)$ and $\text{NCH}_2\text{CH}(\text{CH}_2)'$], 1.65-1.32 (2H, m, CH_2CHOH and $\text{CH}'_2\text{CHOH}'$) and 0.80 [9H, s, $\text{C}(\text{CH}_3)_3$].

^{13}C NMR (75 MHz, CDCl_3) δ 133.05, 132.81, 123.84, 123.76, 123.10, 122.00, 121.91, 73.16, 55.20, 55.14, 55.06, 54.82, 48.40, 48.35, 31.63, 31.59, 29.62, 29.60, 29.52, 29.52, 29.46, 25.65, 25.33, 24.50, 20.63 and 20.46.

HRMS (EI) (Found: M^+ , 261.2097. $\text{C}_{17}\text{H}_{27}\text{NO}$ requires M , 261.2093).

m/z 261 (26%, M^+), 204 (27, $M-\text{C}_4\text{H}_9$), 120 (100, $\text{CH}_2\text{NHCH}_2\text{Ph}$) and 57 (27, C_4H_9).

Pyrrolidine **3f** (quench with acetaldehyde, 68%)



Two diastereomers (2:1), R_F (hexane-ethyl acetate. 1:1) 0.01.

IR (neat) 3370 (O-H), 1605 and 1495 cm^{-1} (Ph).

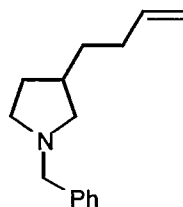
^1H NMR (300 MHz, CDCl_3) δ 7.41-7.13 (5H, m, C_6H_5), 3.70-3.62 (3H, m, CH_2Ph , $\text{CH}_2\text{Ph}'$, CHOH and $\text{CH}'\text{OH}'$), 3.20 (1H, broad s, CHOH), 2.87-1.88 [7H, m, 3 x CH_2 ring protons, $\text{NCH}_2\text{CH}(\text{CH}_2)$ and $\text{NCH}_2\text{CH}'(\text{CH}_2)'$], 1.80-1.42 (2H, m, CH_2CHOH and $\text{CH}'_2\text{CHOH}'$) and 1.20-1.13 (3H, m, CH_3 and CH_3').

^{13}C NMR (75 MHz, CDCl_3) δ 138.43, 138.30, 128.97, 128.80, 128.40, 128.32, 128.30, 127.22, 127.14, 127.11, 67.17, 66.58, 60.46, 60.37, 60.15, 57.94, 53.67, 53.56, 44.75, 44.35, 38.87, 34.56, 34.20, 30.92, 26.96, 23.82 and 23.60.

HRMS (EI) (Found: M^+ , 219.1623. $\text{C}_{14}\text{H}_{21}\text{NO}$ requires M , 219.1623).

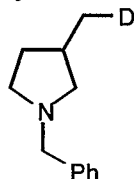
m/z 219 (4%, M^+), 204 (1, $M-\text{CH}_3$), 174 (2, $M-\text{CH}_3\text{CHOH}$), 91 (100, CH_2Ph), 128 (4, $M-\text{CH}_2\text{Ph}$) and 77 (5, C_6H_5).

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Pyrrolidine **3g** (quench with allyl bromide, 58%) R_F (hexane-ethyl acetate 1:1) 0.20.IR (neat) 1605 and 1495 cm^{-1} (Ph).

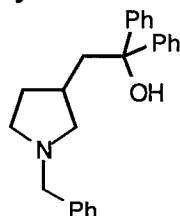
^1H NMR (300 MHz, CDCl_3) δ 7.39-7.18 (5H, m, C_6H_5), 5.81 (1H, ddt, J 17.0, 10.5 and 6.5 Hz, $\text{CH}_2=\text{CH}$), 5.00 (1H, dq, J 18.0 and 2.0 Hz, $\text{CH}_A\text{H}_B=\text{CH}$), 4.94 (1H, d, J 10.0 Hz, $\text{CH}_C\text{H}_D=\text{CH}$), 3.61 (2H, ABq, J 12.0 Hz, CH_2Ph), 2.83 [1H, dd, J 8.5 and 7.5 Hz, $\text{NCH}_C\text{H}_D\text{CH}(\text{CH}_2)$], 2.71 (1H, ddd, J 9.0, 7.9 and 5.5 Hz, $\text{NCH}_E\text{H}_F\text{CH}_2$), 2.44 (1H td, J 8.9 and 6.5, $\text{NCH}_E\text{H}_F\text{CH}_2$), 2.26-2.10 [1H, m, $\text{CH}(\text{CH}_2)$], 2.10-1.94 [4H, m, $\text{NCH}_A\text{H}_B\text{CH}(\text{CH}_2)$, $\text{NCH}_2\text{CH}_G\text{H}_H$ and $\text{CH}_2=\text{CHCH}_2$], 1.47 (2H, ABq, J 7.5 Hz, $\text{CH}_2=\text{CHCH}_2\text{CH}_2$) and 1.50-1.35 (1H, m, $\text{NCH}_2\text{CH}_G\text{H}_H$).

^{13}C NMR (75 MHz, CDCl_3) δ 139.37, 138.75, 128.81, 128.17, 126.81, 114.33, 60.82, 60.49, 53.92, 37.08, 34.95, 32.54 and 30.77.

HRMS (EI) (Found: M^+ , 215.1672. $\text{C}_{15}\text{H}_{21}\text{N}$ requires M , 215.1674). m/z 215 (19%, M^+), 174 (13, $M-\text{C}_3\text{H}_5$), 138 (9, $M-\text{C}_6\text{H}_5$) and 91 (100, CH_2Ph).Pyrrolidine **3h** (quench with CD_3OD , 73%) R_F (hexane-ethyl acetate 1:1) 0.09.IR (neat) 1605 and 1495 cm^{-1} (Ph).

^1H NMR (300 MHz, CDCl_3) δ 7.39-7.20 (5H, m, C_6H_5), 3.62 (2H, ABq, J 12.0 Hz, CH_2Ph), 2.83 [1H, dd, J 8.7 and 7.5 Hz, $\text{NCH}_A\text{H}_B\text{CH}(\text{CH}_2\text{D})$], 2.71 (1H, ddd, J 9.0, 8.0 and 5.5 Hz, $\text{NCH}_C\text{H}_D\text{CH}_2$), 2.48 (1H ddd, J 9.0, 8.0 and 5.5 Hz $\text{NCH}_C\text{H}_D\text{CH}_2$), 2.26 [1H, broad m, $\text{CH}(\text{CH}_2\text{D})$], 2.12-1.96 [2H, m, $\text{NCH}_2\text{CH}_E\text{H}_F$ and $\text{NCH}_A\text{H}_B\text{CH}(\text{CH}_2\text{D})$] and 1.02 (2H, m, CHCH_2D).

^{13}C NMR (75 MHz, CDCl_3) δ 139.57, 128.91, 128.25, 126.88, 62.22, 60.84, 54.14, 32.71, 31.87, 20.38, 20.08 and 19.77.

HRMS (EI) (Found: M^+ , 176.1424. $\text{C}_{12}\text{H}_{16}\text{DN}$ requires M , 176.1425). m/z 176 (17%, M^+), 91 (64, CH_2Ph), 84 (18, $M-\text{CH}_2\text{Ph}$), 77 (12, C_6H_5) and 55 (100, C_4H_7).Pyrrolidine **3i** (quench with benzophenone, 82%) R_F (CHCl_3 -MeOH 20:1) 0.27.IR (neat) 3340 (O-H), 1600 and 1490 cm^{-1} (Ph).

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^1H NMR (400 MHz, CDCl_3) δ 7.55-7.25 (15H, m, 3xPh) 3.61 (2H, ABq, J 15.0 Hz, CH_2Ph), 2.69 [1H, dd, J 8.0 and 6.0 Hz, $\text{NCH}_\text{A}\text{H}_\text{B}\text{CH}(\text{CH}_2)$], 2.60-2.50 (2H, m, NCH_2CH_2), 2.46 [2H, dd, J 5.5 and 1.5 Hz, $\text{CH}_2\text{C}(\text{OH})$], 2.36-2.23 [2H, m, $\text{NCH}_\text{A}\text{H}_\text{B}\text{CH}(\text{CH}_2)$ and $\text{NCH}_\text{A}\text{H}_\text{B}\text{CH}(\text{CH}_2)$], 1.92-1.81 (1H, m, $\text{NCH}_2\text{CH}_\text{C}\text{H}_\text{D}$) and 1.52-1.41 (1H, m, $\text{NCH}_2\text{CH}_\text{C}\text{H}_\text{D}$).

^{13}C NMR (100 MHz, CDCl_3) δ 147.64, 147.37, 137.46, 129.24, 128.36, 128.11, 127.35, 126.79, 126.73, 126.06, 126.04, 78.01, 60.57, 60.21, 53.13, 46.87, 33.56 and 31.70.

HRMS (EI) (Found: M^+ , 357.2076. $\text{C}_{25}\text{H}_{27}\text{NO}$ requires M , 357.2092).

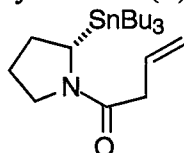
m/z 357 (3%, M^+), 174 [15, $\text{M}-\text{C}(\text{OH})\text{Ph}_2$], 159 [79, $\text{M}-\text{CH}_2\text{C}(\text{OH})\text{Ph}_2$], 91 (100, CH_2Ph) and 77 (22, C_6H_5).

Pyrrolidine (-)-4 and the corresponding Mosher amide were prepared according to the procedure described by Beak.^{1b}

Pyrrolidine (-)-4 (94%ee)

$[\alpha]_\text{D}^{23}$ -136 (c 2.7 in CHCl_3).

Pyrrolidine (+)-5 (61%)



R_F [light petroleum (b.p. 40-60°C) : EtOAc (9:1)] 0.29.

$[\alpha]_\text{D}^{23}$ +189 (c 2.8 in EtOH).

IR (neat) 1640 (C=C), 1605 cm^{-1} (C=O).

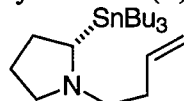
^1H NMR (400 MHz, C_6D_6) δ 6.13 (1H, ddt, J 17, 10, 7 Hz, $\text{CH}_2=\text{CH}$), 5.10 (1H, ddd, J 9, 3.5, 1.5 Hz, $\text{CHH}=\text{CH}$), 5.05 (1H, dd, J 4 and 1.5 Hz, $\text{CHH}=\text{CH}$), 3.19 (1H, t, J 7 Hz, NCHSn), 3.01 (1H, t, J 10 Hz, CHHN), 2.93 (1H, t, J 8 Hz, CHHN), 2.87 (2H, d, J 7 Hz, $\text{O}=\text{CCH}_2$), 1.96-1.45 (4H, m, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.73 [6H, m, $(\text{CH}_2)_3\text{Sn}$], 1.49 [6H, sextet, J 7.5 Hz, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{Sn}$], 1.09 [6H, m, $(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{Sn}$], and 1.04 [9H, t, J 7.5 Hz, $[\text{CH}_3(\text{CH}_2)_3]_3\text{Sn}$].

^{13}C NMR (100 MHz, C_6D_6) δ 166.95, 132.51, 116.62, 46.48, 39.71, 29.67, 29.46, 27.82, 27.61, 13.77 and 10.90.

HRMS (EI) (Found: M^+ , 429.2068. $\text{C}_{20}\text{H}_{39}\text{NOSn}^{119}$ requires M , 429.2054).

m/z 429 (0.5%, M^+), 372 (62, $\text{M}-\text{Bu}$), 70 (100, $\text{C}_4\text{H}_6\text{O}$).

Pyrrolidine (+)-6 (89%)



R_F [light petroleum (b.p. 40-60°C) : EtOAc (4:1)] 0.15.

$[\alpha]_\text{D}^{23}$ +107 (c 2.6 in EtOAc).

IR (neat) 2870 (C-H), 1640 cm^{-1} (C=C).

^1H NMR (400 MHz, C_6D_6) δ 6.00 (1H, ddt, J 17, 10, 6 Hz, $\text{CH}_2=\text{CH}$), 5.17 (1H, d, J 16 Hz, $\text{CHH}=\text{CH}$), 5.11 (1H, d, J 10 Hz, $\text{CHH}=\text{CH}$), 3.07-2.97 (2H, m, $\text{CH}_2\text{CH}=\text{CH}_2$), 2.51 (2H, dd, J 10 and 7 Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}$), 2.45-2.23 (2H, m, $\text{NCH}_2\text{CH}_2\text{CH}=\text{CH}_2$), 2.10-1.92 (4H, m, $\text{NCH}_2\text{CH}_2\text{CH}_2$), 1.88 (1H, t, J 9 Hz,

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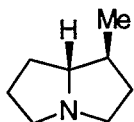
NCHSn), 1.71 [6H, m, (CH₂)₃Sn], 1.47 [6H, sextet, *J* 8 Hz, (CH₃CH₂CH₂CH₂)₃Sn], 1.08 [6H, m, (CH₃CH₂CH₂CH₂)₃Sn] and 1.04 {9H, t, *J* 7 Hz, [CH₃(CH₂)₃]₃Sn}.

¹³C NMR (100 MHz, C₆D₆) δ 137.19, 115.00, 57.51, 56.46, 53.66, 33.86, 29.71, 29.54, 27.72, 24.97, 13.68 and 9.22.

HRMS (EI) (Found: *M*⁺, 415.2257. C₂₀H₄₁NSn¹¹⁹ requires *M*, 415.2261).

m/z 415 (0.1%, *M*⁺), 124 (100, *M*-SnBu₃), 55 (72, C₄H₇).

Pseudoheliotridane (+)-7 (87%), data corresponds with lit.¹⁰



M.p. 230-234 °C of picrate salt.

R_F [CH₂Cl₂-MeOH-NH₃ (9:1:0.1)] 0.10.

[α]_D²³ +6.8 (*c* 0.5 in EtOH, free base).

IR (KBr disk, picrate salt) 2990 (C-H), 1560 cm⁻¹ (NO₂).

¹H NMR (400 MHz, CDCl₃, picrate salt) δ 8.85 (2H, s, C₆H₂ of picrate), 4.04-4.00 (1H, m, NCHCHMe), 3.95-3.85 (1H, m, NCHHCH₂CHMe), 3.74-3.64 (1H, m, NCHHCH₂CHMe), 3.13-3.03 (1H, m, NCHHCH₂CH₂), 2.92-2.83 (1H, m, NCHHCH₂CH₂), 2.33-2.26 (1H, m, CHHCHMe), 2.27-2.17 (2H, m, NCH₂CHHCH₂ and CHHCHMe), 2.16-2.07 (1H, m, NCH₂CHHCH₂), 2.07-1.98 (1H, m, NCH₂CH₂CHH), 1.98-1.91 (1H, m, CHMe), 1.91-1.80 (1H, m, NCH₂CH₂CHH) and 1.21 (3H, d, *J* 6.5 Hz, CH₃).

¹³C NMR (100 MHz, CDCl₃, picrate salt) δ 162.08, 141.60, 128.55, 126.60, 74.07, 55.63, 55.45, 40.02, 33.89, 29.31, 24.78 and 16.69.

HRMS (EI, free base) (Found: *M*⁺, 125.1201. C₈H₁₅N requires *M*, 125.1204).

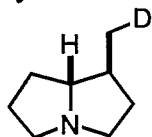
HRMS (EI, picrate salt) (Found: *M*⁺+H, 355.1243. C₁₄H₁₉N₄O₇ requires *M*, 355.1254).

m/z 355 (1.3%, *M*⁺), 229 (4, picric acid), 125 (51, C₈H₁₅N), 83 (100, C₅H₉N).

Found: C, 47.47; H, 5.04; N, 15.51. C₁₄H₁₈N₄O₇ requires C, 47.46; H, 5.12; N, 15.81.

The Pirkle solvating agent (0.03 mmol) splits and shifts the CH₃ group of the free base, pseudoheliotridane (5 mg, 0.04 mmol) in CDCl₃ (0.7 cm³) from δ 1.02 (3H, d, *J* 6.5 Hz) to δ 0.69 (3H, d, *J* 4 Hz) and δ 0.67 (3H, d, *J* 4 Hz).

Pyrrolizidine (±)-8a (quench with CD₃OD, 50%)



M.p. 235-236 °C of picrate salt.

R_F [CH₂Cl₂-MeOH (9:1)] 0.60.

IR (CDCl₃, picrate salt) 2960 (C-H), 1570 cm⁻¹ (NO₂).

¹H NMR (400 MHz, CDCl₃, picrate salt) δ 8.82 (2H, s, C₆H₂ of picrate), 4.05-3.99 (1H, m, NCHCHCH₂D), 3.95-3.85 (1H, m, NCHHCH₂CHCH₂D), 3.74-3.64 (1H, m, NCHHCH₂CHCH₂D), 3.13-3.03 (1H, m, NCHHCH₂CH₂), 2.93-2.83 (1H, m, NCHHCH₂CH₂), 2.33-2.26 (1H, m, CHHCHCH₂D), 2.27-2.17 (2H, m, NCH₂CHHCH₂ and CHHCHCH₂D), 2.16-2.07 (1H, m, NCH₂CHHCH₂), 2.07-1.98 (1H, m, CHCH₂D), 1.98-1.91 (1H, m, NCH₂CH₂CHH), 1.91-1.82 (1H, m, NCH₂CH₂CHH) and 1.25-1.15 (2H, dt, *J* 2 and 6.5 Hz, CH₂D).

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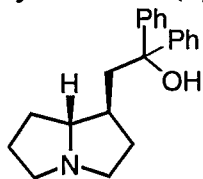
^{13}C NMR (100 MHz, CDCl_3 , picrate salt) δ 162.38, 141.71, 128.07, 126.58, 74.08, 55.62, 55.45, 39.91, 33.86, 29.30, 24.78, 16.60, 16.41 and 16.21.

HRMS (EI, picrate salt) (Found: M^+ , 355.1244. $\text{C}_{14}\text{H}_{17}\text{DN}_4\text{O}_7$ requires M , 355.1238).

m/z 355 (0.1%, M^+), 229 (23, picric acid), 126 (25, $\text{C}_8\text{H}_{16}\text{N}$), 83 (100, $\text{C}_5\text{H}_9\text{N}$).

Found: C, 47.80; H, 5.18; N, 15.62. $\text{C}_{14}\text{H}_{17}\text{DN}_4\text{O}_7$ requires C, 47.32; H, 4.82; N, 15.77.

Pyrrolizidine (+)-**8b** (quench with benzophenone, 62%)



M.p. 164-166 °C.

R_F [CH_2Cl_2 -MeOH (9:1)] 0.11.

$[\alpha]_D^{23} +19.6$ (c 0.5 in EtOH).

IR (KBr disk) 3420 (O-H), 2960 cm^{-1} (C-H).

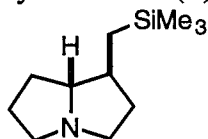
^1H NMR (400 MHz, CD_3OD) δ 7.47-7.13 (10H, m, 2xPh), 3.08 (1H, dt, J 5 and 8 Hz, $\text{NCHHCH}_2\text{CHCH}_2\text{CO}$), 3.00-2.92 (1H, m, $\text{NCHCHCH}_2\text{CO}$), 2.80 (1H, dt, J 11 and 6.5 Hz, $\text{NCHHCH}_2\text{CH}_2$), 2.55-2.45 (2H, m, $\text{NCH}_2\text{CH}_2\text{CHCH}_2\text{CO}$), 2.42-2.32 (1H, m, $\text{NCHHCH}_2\text{CH}_2$), 2.32-2.24 (1H, m, $\text{NCHHCH}_2\text{CHCH}_2\text{CO}$), 1.82-1.58 (5H, m, $\text{NCH}_2\text{CH}_2\text{CH}_2$ and CHCH_2CO) and 1.47-1.31 (2H, m, CH_2CO).

^{13}C NMR (100 MHz, CD_3OD) δ 148.09, 148.03, 127.50, 127.47, 126.07, 126.05, 125.88, 77.09, 71.05, 54.54, 54.40, 45.29, 41.45, 34.88, 30.36 and 24.68.

HRMS (EI) (Found: M^+ , 307.1941. $\text{C}_{21}\text{H}_{25}\text{NO}$ requires M , 307.1936).

m/z 307 (1%, M^+), 183 (4.5, Ph_2COH), 124 (100, $\text{C}_8\text{H}_{14}\text{N}$).

Pyrrolizidine ($\pm$)-**8c** (quench with TMSCl , 63%)



M.p. 145-146 °C of picrate salt.

R_F [CH_2Cl_2 -MeOH (9:1)] 0.64.

IR (CDCl_3 , picrate salt) 2960 (C-H), 1565 cm^{-1} (NO_2).

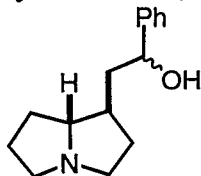
^1H NMR (400 MHz, CDCl_3 , picrate salt) δ 8.87 (2H, s, C_6H_2 of picrate), 4.08-3.97 (1H, m, $\text{NCHCHCH}_2\text{Si}$), 3.95-3.84 (1H, m, $\text{NCHHCH}_2\text{CHCH}_2\text{Si}$), 3.74-3.63 (1H, m, $\text{NCHHCH}_2\text{CHCH}_2\text{Si}$), 3.11-3.03 (1H, m, $\text{NCHHCH}_2\text{CH}_2$), 2.92-2.79 (1H, m, $\text{NCHHCH}_2\text{CH}_2$), 2.29-1.82 (7H, m, $\text{NCH}_2\text{CH}_2\text{CH}_2$ and $\text{CH}_2\text{CHCH}_2\text{Si}$), 1.59 (1H, s, NH), 0.88 (1H, dd, J 16 and 5 Hz, CHHSi), 0.70 (1H, dd, J 16 and 5 Hz, CHHSi) and 0.06 (9H, s, Me_3Si).

^{13}C NMR (100 MHz, CDCl_3 , picrate salt) δ 162.35, 141.71, 128.00, 126.54, 75.48, 55.65, 55.40, 41.85, 34.11, 29.26, 24.71, 19.83 and -1.06.

HRMS (EI) (Found: M^+ , 197.1600. $\text{C}_{11}\text{H}_{23}\text{NSi}$ requires M , 197.1601).

m/z 197 (9.2%, M^+), 126 (49, $\text{C}_8\text{H}_{16}\text{N}$), 83 (100, $\text{C}_5\text{H}_9\text{N}$).

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Pyrrolizidine ($\pm$)-**8d** (quench with PhCHO, 41%)

Two diastereomers (1:1).

M.p. 140-143 °C of picrate salt.

 R_F [CH_2Cl_2 -MeOH (9:1)] 0.55.IR (CDCl_3 , picrate salt) 2965 (C-H), 1565 cm^{-1} (NO_2).

^1H NMR (400 MHz, CDCl_3 , picrate salt) δ 8.84 (2H, s, C_6H_2 of picrate), 7.39-7.26 (5H, m, Ph), 4.79-4.71 (1H, m, CHOH), 4.18-4.08 (0.5H, m, $\text{NCHCHCH}_2\text{CO}$), 4.08-4.00 (0.5H, m, $\text{NCHCHCH}_2\text{CO}$), 4.00-3.89 (1H, m, $\text{NCHHCH}_2\text{CHCH}_2\text{CO}$), 3.74-3.57 (1H, m, $\text{NCHHCH}_2\text{CHCH}_2\text{CO}$), 3.13-3.00 (1H, m, $\text{NCHHCH}_2\text{CH}_2$), 2.83-2.79 (1H, m, $\text{NCHHCH}_2\text{CH}_2$), 2.34-1.87 (10H, m, $\text{NCH}_2\text{CH}_2\text{CH}_2$, $\text{CH}_2\text{CHCH}_2\text{CO}$, NH, CHHCHOH), 1.89 (0.5H, ddd, J 15, 9 and 3 Hz, CHHCO) and 1.23 (0.5H, ddd, J 18, 12 and 6 Hz, CHHCO).

^{13}C NMR (100 MHz, CDCl_3 , picrate salt) δ 162.27, 143.96, 143.75, 141.64, 128.82, 128.77, 128.23, 128.07, 128.05, 126.60, 125.59, 125.57, 73.01, 72.81, 72.76, 72.62, 55.39, 55.32, 55.22, 55.15, 42.41, 41.92, 41.38, 41.20, 32.69, 32.14, 30.13, 29.86, 25.00 and 24.82.

HRMS (EI) (Found: M^+ , 231.1622. $\text{C}_{15}\text{H}_{21}\text{NO}$ requires M , 231.1624). m/z 231 (84%, M^+), 214 (100, M-OH), 124 (94, $\text{C}_8\text{H}_{14}\text{N}$).