

## Supporting Information

### An Concise Synthesis of Physostigmine from Skatole and Activated Aziridine *via* Alkylative Cyclization

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#### Synthesis of dimethyl-1-benzyloxycarbonyl-3a,8-1,2,3,3a,8,8a-hexahydroindolo[2,3-b]-indole (**8**) from **5b** and **6**.

To a suspension of Sc(OTf)<sub>3</sub> (246 mg, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 ml), was added a solution of **5b** (72.6 mg, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.3 ml), TMSCl (27.2 mg, 0.25 mmol), and a solution of **6** (44.5 mg, 0.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.3 ml) at -30 °C and the mixture was stirred for 9 h. The mixture was treated with sat. NaHCO<sub>3</sub> aq. and extracted with CH<sub>2</sub>Cl<sub>2</sub>. Combined organic layers were washed, and dried over MgSO<sub>4</sub>. After evaporation of the solvent, a residue was purified by column chromatography on silica gel (hexane/ethyl acetate 10/1-5/1) and afforded **8** (72.5 mg, 90 %) and recovered **5b** (30.1 mg, 42 %).

**8** : colorless oil.; IR (neat) cm<sup>-1</sup>: 2956, 2886, 1700, 1608, 1489, 1406, 1362, 1203, 1092, 995, 905, 878, 742, 697.; <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, 150 °C): δ 1.38 (3H, s, C3aCH<sub>3</sub>), 1.94 (1H, ddd, *J*=11.0, 7.8, 3.7 Hz, 3-H), 2.05 (1H, ddd, *J*=11.0, 8.8, 7.0 Hz, 3-H), 2.87 (3H, s, N-Me), 3.04 (1H, ddd, *J*=12.0, 6.9, 3.6 Hz, 2-H), 3.77 (1H, ddd, *J*=12.0, 8.5, 7.8 Hz, 2-H), 5.12 (1H, s, 8a-H), 5.16 (2H, s, CH<sub>2</sub>Ph), 6.39 (1H, d, *J*=7.6 Hz, Ar-H), 6.63 (1H, t, *J*=7.4 Hz, Ar-H), 7.02-7.06 (2H, m, Ar-H), 7.29-7.40 (5H, m, Ar-H).; <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 55 °C, two sets of rotomers): δ (24.38, 24.70), (32.52, 33.12), (38.46, 38.89), (46.12, 46.33), (51.64, 62.82), (66.86, 67.27), (88.16, 88.93), (105.89, 106.06), 117.48, 121.77, 127.75, 127.93, 128.25, 128.44, (133.92, 134.08), (136.27, 136.61), (150.13, 150.30), (154.81, 155.73).; LRMS (EI), *m/z* 322 (M<sup>+</sup>, 100 % base peak).; HRMS (FAB), calcd for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>; 322.1681, found 322.1678.

**Desoxyeseroline<sup>1</sup> (3)**: colorless oil.; IR (neat)  $\text{cm}^{-1}$  : 2957, 2864, 1605, 1492, 1451, 1346, 1299, 1255, 1191, 1124, 1034, 957, 897, 737.; <sup>1</sup>H-NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.43 (3H, s, C3a- $\text{CH}_3$ ), 1.94-1.97 (2 H, m, 3-H), 2.55 (3H, *N*1- $\text{CH}_3$ ), 2.60-2.74 (2H, m, 2-H), 2.95 (3H, s, *N*8- $\text{CH}_3$ ), 4.10 (1H, s, 8a-H), 6.40 (1H, d,  $J=7.8$  Hz, Ar-H), 6.66 (1H, t,  $J=7.4$  Hz, Ar-H), 6.98 (1H, d,  $J=7.8$  Hz, Ar-H), 7.07 (1H, t,  $J=7.6$  Hz, Ar-H).; <sup>13</sup>C-NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  27.32, 36.46, 38.45, 40.81, 52.57, 53.18, 97.47, 106.49, 117.43, 122.14, 127.61, 136.63, 151.90.; LRMS (EI),  $m/z$  202 ( $\text{M}^+$ , 20 %), 158 (100 % base peak).; HRMS (FAB), calcd for  $\text{C}_{13}\text{H}_{18}\text{N}_2$ : 202.1470, found: 202.1465.

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<sup>1</sup> Wijnberg, J. B.; Speckamp, W. N. *Tetrahedron* **1978**, *34*, 2399-2404.