

# Palladium-Catalyzed $\beta$ -Allylation of 2,3-Disubstituted Indoles

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## Experimental Section.

**General.** Reactions were run in oven dried glassware under N<sub>2</sub> atmosphere in degassed solvent. Methylene chloride was purified by passage over activated alumina. Reactions were monitored by TLC on Whatman silica gel 60 Å F<sub>254</sub> plates visualized by anisaldehyde and ceric ammonium molybdate staining solutions. Flash column chromatography was performed on Dynamic Adsorbents 32-63  $\mu$  Flash silica gel. NMR spectra were measured on Bruker DRX and DMX spectrometers at 500 MHz for <sup>1</sup>H spectra and 125 MHz for <sup>13</sup>C spectra and calibrated from residual solvent signal. Infrared spectra were measured on a Nicolet 6700 FT-IR spectrometer on NaCl plates. Mass spectral analysis was performed by the College of Sciences Major Instrumentation Cluster at Old Dominion University (Norfolk, VA) directed by Susan Hatcher.

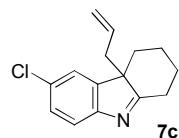
**Typical procedure for allylation of indoles.** To a solution of Pd<sub>2</sub>(dba)<sub>3</sub> (5.7 mg, 0.0063 mmol) and P(2-furyl)<sub>3</sub> (2.9 mg, 0.013 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.3 mL) at rt was added allyl methyl carbonate (57  $\mu$ L, 0.50 mmol). After 10 min, a solution of the appropriate indole (0.250 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.3 mL) was added. When indole starting material had disappeared (monitored by TLC), the reaction mixture was concentrated. The residue was purified by flash chromatography to afford the desired 3-allylated products.



**4a-Allyl-6-methyl-2,3,4,4a-tetrahydro-1H-carbazole (7a).** R<sub>f</sub> 0.38 (3:1 hexanes : EtOAc); IR: 2934, 2860, 1583, 1462, 1449, 821 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz):  $\delta$  7.45 (d, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.09 (s, 1H), 5.16 (ddt, *J* = 17.1, 10.1, 7.3 Hz, 1H), 4.95 (d, *J* = 17.0 Hz, 1H), 4.85 (d, *J* = 10.0 Hz, 1H), 2.85 (d, *J* = 13.2 Hz, 1H), 2.48-2.63 (m, 3H), 2.39 (s, 3H), 2.31 (dq, *J* = 13.3, 2.6 Hz, 1H), 2.18 (m, 1H), 1.81 (qt, *J* = 13.7, 3.7 Hz, 1H), 1.67 (d, *J* = 13.3 Hz, 1H), 1.41 (qt, *J* = 13.5, 4.4 Hz, 1H), 1.14 (td, *J* = 13.5, 4.0 Hz, 1H); <sup>13</sup>C NMR (125 MHz)  $\delta$  187.8, 152.6, 144.7, 134.3, 132.2, 128.1, 122.6, 119.5, 117.8, 57.4, 37.6, 37.0, 30.1, 28.8, 21.4, 21.0; HRMS (FAB+) Calcd for C<sub>16</sub>H<sub>20</sub>N (M+H)<sup>+</sup>: 226.1590, Found: 226.1585.

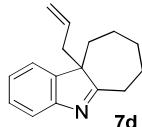


**4a-Allyl-6-methoxy-2,3,4,4a-tetrahydro-1H-carbazole (7b).** R<sub>f</sub> 0.16 (1:1 hexanes : EtOAc); IR: 2935, 1585, 1469, 1269, 1197 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz):  $\delta$  7.47 (d, *J* = 8.3 Hz, 1H), 6.82-6.86 (m, 2H), 5.18 (ddt, *J* = 17.0, 10.1, 7.3 Hz, 1H), 4.95 (d, *J* = 17.0 Hz, 1H), 4.86 (d, *J* = 10.1 Hz, 1H), 3.82 (s, 3H), 2.83 (d, 13.1 Hz, 1H), 2.57 (m, 2H), 2.52 (td, *J* = 13.2, 5.2 Hz, 1H), 2.30 (dq, *J* = 13.5, 2.5 Hz, 1H), 2.17 (m, 1H), 1.81 (qt, *J* = 13.8, 3.9 Hz, 1H), 1.16 (td, *J* = 13.5, 4.2 Hz, 1H); <sup>13</sup>C NMR (125 MHz)  $\delta$  186.8, 157.5, 148.6, 146.2, 132.1, 120.2, 118.0, 112.0, 108.8, 57.8, 55.7, 37.7, 37.0, 30.0, 28.9, 21.1, 17.0; HRMS (FAB+) Calcd for C<sub>16</sub>H<sub>20</sub>NO (M+H)<sup>+</sup>: 242.1539, Found: 242.1530.

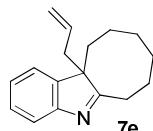


**4a-Allyl-6-chloro-2,3,4,4a-tetrahydro-1H-carbazole (7c).** R<sub>f</sub> 0.22 (3:1 hexanes : EtOAc); IR: 2936, 2861, 1581, 1448 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz):  $\delta$  7.49 (d, *J* = 8.2 Hz, 1H), 7.29 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.27 (d, *J* = 2.2 Hz, 1H), 5.16 (ddt, *J* = 17.0, 10.0, 7.3 Hz, 1H), 4.97 (dq, *J* = 17.0, 1.7 Hz, 1H), 4.89 (d, *J* = 9.9 Hz,

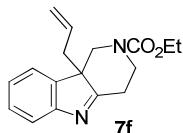
1H), 2.86 (d,  $J = 13.2$  Hz, 1H), 2.58 (m, 2H), 2.54 (td,  $J = 13.5, 5.8$  Hz, 1H), 2.33 (dq,  $J = 13.6, 3.2$  Hz, 1H), 2.20 (d,  $J = 3.4$  Hz, 1H), 1.82 (qt,  $J = 13.8, 3.8$  Hz, 1H), 1.70 (m, 1H), 1.42 (qt,  $J = 13.2, 4.2$  Hz, 1H), 1.16 (td,  $J = 13.6, 4.2$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz)  $\delta$  189.3, 153.4, 146.3, 131.5, 130.5, 127.7, 122.4, 120.9, 118.4, 58.1, 37.4, 36.8, 30.1, 28.7, 20.9; HRMS (FAB+) Calcd for  $\text{C}_{15}\text{H}_{16}\text{ClN}$  ( $\text{M}+\text{H}$ ) $^+$ : 246.1044, Found: 246.1048.



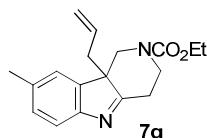
**10a-Allyl-6,7,8,9,10,10a-hexahydro-cyclohepta[b]indole (7d).**  $R_f$  0.20 (3:1 hexanes : EtOAc); IR: 2927, 2854, 1690, 1455  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz):  $\delta$  7.50 (d,  $J = 7.3$  Hz, 1H), 7.29 (t,  $J = 7.3$  Hz, 1H), 7.22 (d,  $J = 7.3$  Hz, 1H), 7.18 (t,  $J = 7.3$  Hz, 1H), 5.21 (ddt,  $J = 16.4, 10.0, 7.2$  Hz, 1H), 4.91 (d,  $J = 16.3$  Hz, 1H), 4.85 (d,  $J = 9.9$  Hz, 1H), 2.92 (ddd,  $J = 13.5, 6.0, 4.1$  Hz, 1H), 2.57-2.65 (m, 2H), 2.45 (dd,  $J = 13.5, 7.8$  Hz, 1H), 2.00-2.11 (m, 2H), 1.71-1.82 (m, 2H), 1.55-1.67 (m, 2H), 1.47 (m, 1H), 0.73 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz)  $\delta$  190.6, 154.9, 143.7, 132.4, 127.7, 124.9, 121.8, 119.7, 118.0, 62.1, 41.6, 35.0, 31.5, 30.5, 28.6, 24.6; HRMS (FAB+) Calcd for  $\text{C}_{16}\text{H}_{20}\text{N}$  ( $\text{M}+\text{H}$ ) $^+$ : 226.1590, Found: 226.1587.



**11a-Allyl-7,8,9,10,11,11a-hexahydro-6H-cycloocta[b]indole (7e).**  $R_f$  0.20 (3:1 hexanes : EtOAc); IR: 2924, 2853, 1566, 1456, 1445  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz):  $\delta$  7.54 (d,  $J = 7.6$  Hz, 1H), 7.30 (dd,  $J = 7.6, 2.1$  Hz, 1H), 7.17-7.23 (m, 2H), 5.12 (ddt,  $J = 17.0, 10.1, 7.3$  Hz, 1H), 4.86 (d,  $J = 17.0$  Hz, 1H), 4.82 (d,  $J = 10.0$  Hz, 1H), 2.81 (ddd,  $J = 13.3, 6.2, 4.8$  Hz, 1H), 2.61 (ddd,  $J = 14.4, 10.1, 4.4$  Hz, 1H), 2.54 (dd,  $J = 13.5, 6.6$  Hz, 1H), 2.35 (dd,  $J = 14.0, 8.0$  Hz, 1H), 2.26 (ddd,  $J = 14.9, 11.9, 3.4$  Hz, 1H), 2.14 (ddd,  $J = 14.9, 5.3, 3.9$  Hz, 1H), 2.03-2.11 (m, 1H), 1.91 (m, 1H), 1.56-1.68 (m, 1H), 1.40-1.49 (m, 1H), 1.23-1.40 (m, 2H), 0.84-0.95 (m, 1H), 0.95-1.06 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz)  $\delta$  192.3, 155.1, 141.6, 132.3, 127.7, 124.8, 121.9, 119.9, 117.9, 61.8, 42.5, 31.8, 30.5, 30.0, 25.7, 25.2, 23.8; HRMS (FAB+) Calcd for  $\text{C}_{17}\text{H}_{21}\text{NNa}$  ( $\text{M}+\text{Na}$ ) $^+$ : 240.1747, Found: 240.1741.

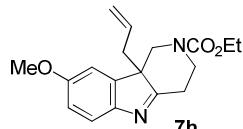


**9b-Allyl-1,3,4,9b-tetrahydro-pyrido[4,3-b]indole-2-carboxylic acid ethyl ester (7f).**  $R_f$  0.21 (1:1 hexanes : EtOAc); IR: 2979, 1701, 1430, 1230, 1132  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ , 353 K):  $\delta$  7.50 (d,  $J = 7.7$  Hz, 1H), 7.48 (d,  $J = 7.4$  Hz, 1H), 7.33 (td,  $J = 7.6, 1.0$  Hz, 1H), 7.20 (t,  $J = 7.4$  Hz, 1H), 5.12 (ddt,  $J = 17.0, 10.1, 7.5$  Hz, 1H), 4.89 (dd,  $J = 17.0, 1.3$  Hz, 1H), 4.80 (dd,  $J = 10.1, 0.8$  Hz, 1H), 4.63 (dd,  $J = 13.0, 2.0$  Hz, 1H), 4.48-5.54 (m, 1H), 4.17 (m, 1H), 2.71-2.82 (m, 4H), 2.42 (dd,  $J = 14.1, 7.7$  Hz, 1H), 2.29 (d,  $J = 13.0$  Hz, 1H), 1.27 (t,  $J = 7.1$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO}-d_6$ , 353 K)  $\delta$  184.1, 155.1, 154.9, 140.1, 131.8, 127.8, 124.5, 122.6, 119.6, 117.7, 61.0, 58.6, 52.1, 44.9, 35.9, 29.6, 14.2; HRMS (FAB+) Calcd for  $\text{C}_{17}\text{H}_{20}\text{N}_2\text{O}_2\text{Na}$  ( $\text{M}+\text{Na}$ ) $^+$ : 307.1417, Found: 307.1418.

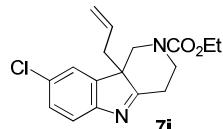


**8-Methyl-1,3,4,5-tetrahydro-pyrido[4,3-b]indole-2-carboxylic acid ethyl ester (7g).**  $R_f$  0.23 (1:1 hexanes : EtOAc); IR: 2980, 2922, 1703, 1469, 1431, 1234  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{PhMe}-d_8$ , 340 K):  $\delta$  7.50 (d,  $J = 7.8$  Hz, 1H), 6.95 (d,  $J = 7.9$  Hz, 1H), 6.89 (s, 1H), 5.17 (dddd,  $J = 16.9, 10.3, 7.8, 6.5$  Hz, 1H), 4.77 (dq,  $J = 16.9, 1.6$  Hz, 1H), 4.69 (d,  $J = 10.3$  Hz, 1H), 4.64 (d,  $J = 12.1$  Hz, 1H), 4.43 (br s, 1H), 4.08

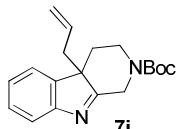
(m, 2H), 2.60 (dq,  $J$  = 13.0, 1.7 Hz, 1H), 2.56 (d,  $J$  = 6.5 Hz, 1H), 2.50 (td,  $J$  = 12.3, 6.2 Hz, 1H), 2.40 (dt,  $J$  = 12.6, 3.6 Hz, 1H), 2.34 (dd,  $J$  = 13.9, 7.5 Hz, 1H), 2.19 (s, 3H), 1.99 (d,  $J$  = 13.1 Hz, 1H), 2.50 (t,  $J$  = 17.1 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz, PhMe- $d_8$ , 340 K):  $\delta$  181.0, 158.1, 155.1, 150.0, 142.0, 132.0, 120.8, 117.5, 113.1, 109.4, 61.1, 59.1, 54.9, 52.6, 45.4, 36.5, 30.0, 14.2; HRMS (FAB+) Calcd for  $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 299.1754, Found: 299.1753.



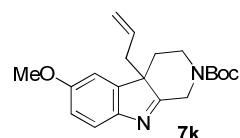
**9b-Allyl-8-methoxy-1,3,4,9b-tetrahydro-pyrido[4,3-b]indole-2-carboxylic acid ethyl ester (7h).**  $R_f$  0.19 (1:1 hexanes : EtOAc); IR: 2978, 2931, 1700, 1471, 1431, 1264, 1228  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz, PhMe- $d_8$ , 340 K):  $\delta$  7.50 (d,  $J$  = 8.4 Hz, 1H), 6.78 (d,  $J$  = 2.5 Hz, 1H), 6.71 (dd,  $J$  = 8.3, 2.5 Hz, 1H), 5.22 (dddd,  $J$  = 16.9, 10.1, 7.8, 6.6 Hz, 1H), 4.78 (dq,  $J$  = 17.0, 1.6 Hz, 1H), 4.72 (d,  $J$  = 10.1 Hz, 1H), 4.63 (d,  $J$  = 11.6 Hz, 1H), 4.44 (br s, 1H), 4.08 (m, 2H), 3.44 (s, 3H), 2.52-2.62 (m, 2H), 2.50 (td,  $J$  = 12.9, 5.9 Hz, 1H), 2.40 (td,  $J$  = 12.4, 3.4 Hz, 1H), 2.33 (dd,  $J$  = 13.9, 7.7 Hz, 1H), 2.02 (d,  $J$  = 13.0 Hz, 1H), 1.10 (t,  $J$  = 7.1 Hz, 3H).



**9b-Allyl-8-chloro-1,3,4,9b-tetrahydro-pyrido[4,3-b]indole-2-carboxylic acid ethyl ester (7i).**  $R_f$  0.22 (1:1 hexanes : EtOAc); IR: 2979, 2929, 1701, 1470, 1432, 1231  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz, PhMe- $d_8$ , 340 K):  $\delta$  7.34 (d,  $J$  = 8.2 Hz, 1H), 7.10 (dd,  $J$  = 8.3, 2.3 Hz, 1H), 7.07 (d,  $J$  = 2.2 Hz, 1H), 5.09 (dddd,  $J$  = 17.2, 9.9, 7.5, 6.7 Hz, 1H), 4.71 (d,  $J$  = 17.1 Hz, 1H), 4.67 (d,  $J$  = 10.0 Hz, 1H), 4.53 (d,  $J$  = 12.0 Hz, 1H), 4.39 (br s, 1H), 4.07 (m, 2H), 2.53 (dq,  $J$  = 12.6, 1.7 Hz, 1H), 2.45 (d,  $J$  = 6.8 Hz, 1H), 2.42 (td,  $J$  = 12.1, 6.1 Hz, 1H), 2.30 (td,  $J$  = 12.5, 3.4 Hz, 1H), 2.22 (dd,  $J$  = 13.9, 7.8 Hz, 1H), 1.85 (d,  $J$  = 13.1 Hz, 1H), 1.09 (t,  $J$  = 7.1 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz, PhMe- $d_8$ , 340 K)  $\delta$  184.0, 155.0, 154.7, 142.3, 131.4, 130.8, 128.3, 127.7, 124.8, 122.8, 121.3, 117.9, 61.2, 59.4, 52.2, 45.2, 36.2, 30.1, 14.1; HRMS (FAB+) Calcd for  $\text{C}_{17}\text{H}_{20}\text{ClN}_2\text{O}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 319.1208, Found: 319.1209.

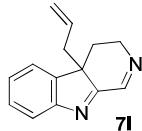


**4a-Allyl-1,3,4,4a-tetrahydro-β-carboline-2-carboxylic acid tert-butyl ester (7j).**  $R_f$  0.28 (10:1 hexanes : EtOAc); IR: 2977, 2932, 1694, 1455, 1412, 1365, 1265, 1160  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , 353 K):  $\delta$  7.64 (d,  $J$  = 7.5 Hz, 1H), 7.37 (dt,  $J$  = 7.5, 1.5 Hz, 1H), 7.34 (d,  $J$  = 7.5 Hz, 1H), 7.25 (dt,  $J$  = 7.5, 1.0 Hz, 1H), 5.19 (ddt,  $J$  = 17.0, 10.0, 7.5 Hz, 1H), 5.00 (s, 1H), 4.99 (dd,  $J$  = 17.0, 1.5 Hz, 1H), 4.93 (dd,  $J$  = 10.0, 1.0 Hz, 1H), 4.12 (br s, 1H), 3.99 (d,  $J$  = 14.5 Hz, 1H), 4.93 (dd,  $J$  = 10.0, 1.0 Hz, 1H), 4.12 (br s, 1H), 3.99 (d,  $J$  = 14.5 Hz, 1H), 3.31 (br s, 1H), 2.69 (dd,  $J$  = 14.0, 6.5 Hz, 1H), 2.59 (dd,  $J$  = 13.5, 7.5 Hz, 1H), 2.32 (d,  $J$  = 13.5 Hz, 1H), 1.47 (s, 9H), 1.52-1.41 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ , 353 K)  $\delta$  181.2, 154.4, 153.7, 143.5, 131.8, 127.5, 125.1, 122.1, 120.1, 117.8, 79.3, 55.9, 44.9, 38.7, 35.8, 35.1, 27.8; HRMS (FAB+) Calcd for  $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_2\text{Na}$  ( $\text{M}+\text{Na}^+$ ): 295.1417, Found: 295.1404.

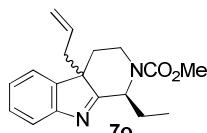


**4a-Allyl-6-methoxy-1,3,4,4a-tetrahydro-β-carboline-2-carboxylic acid tert-butyl ester (7k).**  $R_f$  0.17 (4:1 hexanes : EtOAc); IR: 2976, 2932, 1696, 1591, 1470, 1413, 1159, 1030, 921, 867, 762  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , 353 K):  $\delta$  7.40 (d,  $J$  = 8.4 Hz, 1H), 7.02 (d,  $J$  = 2.5 Hz, 1H), 6.87 (dd,  $J$  = 8.4, 2.6 Hz, 1H), 5.09 (ddt,  $J$  = 17.0, 9.8, 7.0 Hz, 1H), 4.95 (dd,  $J$  = 17.0, 2.1 Hz, 1H), 4.81 (dd,  $J$  = 10.0, 2.1 Hz,

1H), 4.69 (dd,  $J$  = 14.2, 1.1 Hz, 1H), 4.02 (d,  $J$  = 14.2 Hz, 1H), 3.86-3.82 (m, 1 H), 3.78 (s, 3H), 3.36 (ddd,  $J$  = 13.9, 12.6, 3.0 Hz, 1H), 2.68 (d,  $J$  = 7.07 Hz, 2H), 2.32 (td,  $J$  = 13.5, 2.79 Hz, 1H), 1.40 (s, 9H), 1.19 (dt,  $J$  = 12.9, 5.0 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz, DMSO-*d*<sub>6</sub>, 353 K)  $\delta$  179.0, 157.7, 153.7, 148.0, 145.1, 131.9, 120.4, 117.7, 112.8, 108.8, 79.2, 56.0, 55.4, 44.9, 38.7, 35.8, 35.2, 27.8; HRMS (FAB+) Calcd for C<sub>20</sub>H<sub>26</sub>N<sub>2</sub>O<sub>3</sub>Na (M+Na<sup>+</sup>): 365.1836, Found: 365.1834.



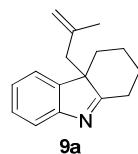
**4a-Allyl-4,4a-dihydro-3H-β-carboline (7l).** R<sub>f</sub> 0.15 (5:1 CH<sub>3</sub>Cl : MeOH); IR: 1639, 1455, 1412, 1301, 1170, 1160 cm<sup>-1</sup>;  $^1\text{H}$  NMR (500 MHz):  $\delta$  8.06 (dd,  $J$  = 8.0, 1.0 Hz, 1H), 7.57 (d,  $J$  = 7.0 Hz, 1H), 7.29 (td,  $J$  = 8.0, 1.5 Hz, 1H), 7.25 (td,  $J$  = 7.5, 1.5 Hz, 1H), 5.97 (s, 1H), 5.95 (dddd,  $J$  = 17.0, 10.0, 8.5, 4.0 Hz, 1H), 5.18 (d, 17.5 Hz, 1H), 5.12 (dt,  $J$  = 10.0, 1.0 Hz), 3.65 (dd,  $J$  = 14.5, 6.5 Hz, 1H), 3.39-3.49 (m, 2H), 3.04 (dddd,  $J$  = 18.0, 11.0, 6.0, 1.0 Hz, 1H), 2.86 (dd,  $J$  = 14.0, 9.0, 1H), 2.63 (ddd,  $J$  = 16.5, 6.0, 2.0 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz)  $\delta$  139.9, 136.2, 130.8, 129.7, 122.7, 121.3, 118.7, 117.1, 113.6, 110.5, 69.7, 46.1, 44.4, 16.1; HRMS (FAB+) Calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub> (M+H<sup>+</sup>): 211.1230, Found: 211.1228.



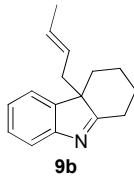
**(±)-(1S,4aS)-4a-Allyl-1-ethyl-1,3,4,4a-tetrahydro-β-carboline-2-carboxylic acid methyl ester and (±)-(1S,4aR)-4a-allyl-1-ethyl-1,3,4,4a-tetrahydro-β-carboline-2-carboxylic acid methyl ester (7o).**

First eluting diastereomer: R<sub>f</sub> 0.23 (3:1 hexanes : EtOAc); IR: 2955, 1703, 1456, 1402 cm<sup>-1</sup>;  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.59 (d,  $J$  = 7.7 Hz, 1H), 7.32 (t,  $J$  = 7.6 Hz, 1H), 7.29 (d,  $J$  = 7.2 Hz, 1H), 7.21 (t,  $J$  = 7.2 Hz, 1H), 5.06-5.16 (m, 2H), 4.94 (d,  $J$  = 16.8 Hz, 1H), 4.87 (d,  $J$  = 9.9 Hz), 4.11 (br s, 1H), 3.82 (s, 3H), 2.75 (ddd,  $J$  = 14.2, 10.5, 7.0 Hz, 1H), 2.63 (dd,  $J$  = 13.9, 6.2 Hz, 1H), 2.44-2.53 (m, 1H), 2.41 (dd,  $J$  = 13.9, 8.1 Hz, 1H), 2.30 (dq,  $J$  = 14.9, 7.6, 4.9 Hz, 1H), 1.87 (qd,  $J$  = 14.9, 7.5 Hz, 1H), 1.75 (ddd,  $J$  = 13.1, 6.7, 2.7 Hz, 1H), 1.04 (t,  $J$  = 7.5 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  187.0, 156.7, 154.9, 144.4, 132.1, 127.9, 125.5, 121.9, 120.6, 118.7, 57.7, 56.9, 52.9, 42.1, 39.1, 32.3, 24.4, 10.0.

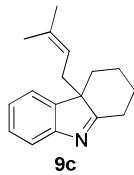
Second eluting diastereomer: R<sub>f</sub> 0.15 (3:1 hexanes : EtOAc); 2953, 2876, 1701, 1447, 1404 cm<sup>-1</sup>;  $^1\text{H}$  NMR (500 MHz, PhMe-*d*<sub>8</sub>, 340 K):  $\delta$  7.57 (d,  $J$  = 7.6 Hz, 1H), 7.11 (t,  $J$  = 7.6 Hz, 1H), 6.99 (t,  $J$  = 7.5 Hz, 1H), 6.94 (d,  $J$  = 7.5 Hz, 1H), 5.34 (br s, 1H), 5.05 (ddt,  $J$  = 17.1, 10.4, 7.0 Hz, 1H), 4.71 (d,  $J$  = 17.1 Hz, 1H), 4.69 (d,  $J$  = 10.5 Hz, 1H), 4.07 (br s, 1H), 3.45 (s, 3H), 3.06 (td,  $J$  = 14.6, 1.8 Hz, 1H), 2.46 (dd,  $J$  = 14.3, 7.1 Hz, 1H), 2.39 (dd,  $J$  = 14.3, 7.1 Hz, 1H), 1.75-1.82 (m, 2H), 1.71 (sext.,  $J$  = 7.5 Hz, 1H), 1.10 (td,  $J$  = 13.2, 4.4 Hz, 1H), 0.93 (t,  $J$  = 7.6 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz, PhMe-*d*<sub>8</sub>, 340 K):  $\delta$  181.3, 155.2, 155.0, 143.7, 132.2, 127.6, 124.9, 121.3, 121.1, 117.6, 59.7, 56.3, 51.7, 37.6, 35.8, 35.7, 23.3, 10.5.



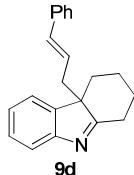
**4a-(2-Methyl-allyl)-2,3,4,4a-tetrahydro-1H-carbazole (9a).** R<sub>f</sub> 0.29 (3:1 hexanes : EtOAc); IR: 2934, 2860, 1580, 1454 cm<sup>-1</sup>;  $^1\text{H}$  NMR (500 MHz):  $\delta$  7.58 (d,  $J$  = 7.7 Hz, 1H), 7.31 (td,  $J$  = 7.6, 1.2 Hz, 1H), 7.28 (d,  $J$  = 7.5 Hz, 1H), 7.18 (td,  $J$  = 7.2, 0.7 Hz, 1H), 4.50 (t,  $J$  = 1.6 Hz, 1H), 4.45 (s, 1H), 2.92 (m, 1H), 2.88 (d,  $J$  = 13.9 Hz, 1H), 2.65 (td,  $J$  = 13.1, 5.8 Hz, 1H), 2.34 (dq,  $J$  = 2.5, 13.5 Hz, 1H), 2.22 (m, 1H), 1.86 (qt,  $J$  = 13.8, 3.8 Hz, 1H), 1.68 (m, 1H), 1.44 (qt,  $J$  = 13.3, 4.3 Hz, 1H), 1.15 (s, 3H), 1.12 (td,  $J$  = 13.6, 3.9 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz)  $\delta$  189.3, 154.9, 144.9, 141.2, 127.5, 124.4, 122.0, 120.2, 113.5, 58.0, 41.7, 39.8, 30.7, 29.3, 23.2, 21.3; HRMS (FAB+) Calcd for C<sub>16</sub>H<sub>20</sub>N (M+H)<sup>+</sup>: 226.1590, Found: 226.1585.



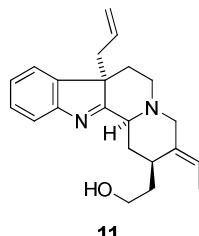
**((E)-4a-But-2-enyl)-2,3,4,4a-tetrahydro-1H-carbazole (9b).**  $R_f$  0.21 (4:1 hexanes : EtOAc); IR: 2934, 2858, 1582, 1453, 967  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz):  $\delta$  7.58 (d,  $J = 7.6$  Hz, 1H), 7.32 (t,  $J = 7.6$  Hz, 1H), 7.28 (d,  $J = 7.4$  Hz, 1H), 7.18 (t,  $J = 7.5$  Hz, 1H), 5.38 (sext.,  $J = 6.4$  Hz, 1H), 4.84 (dddd,  $J = 14.9, 9.5, 6.7, 1.6$  Hz, 1H), 2.86 (dt,  $J = 13.3, 2.5$ , 1H), 2.56 (qd,  $J = 15.4, 7.0$  Hz, 1H), 2.54 (td,  $J = 13.3, 5.4$  Hz, 1H), 2.45 (dd,  $J = 14.2, 7.9$  Hz, 1H), 2.35 (dq,  $J = 15.8, 2.5$  Hz, 1H), 2.19 (m, 1H), 1.82 (qt,  $J = 13.8, 3.8$  Hz, 1H), 1.67 (d,  $J = 14.2$  Hz, 1H), 1.48 (d,  $J = 6.3$  Hz, 3H), 1.42 (qt,  $J = 13.1, 4.1$  Hz, 1H), 1.13 (td,  $J = 13.5, 4.3$ , 1H);  $^{13}\text{C}$  NMR (125 MHz)  $\delta$  189.2, 154.9, 144.9, 128.6, 127.5, 127.4, 124.5, 121.9, 120.0, 57.8, 36.7, 36.4, 30.1, 28.8, 21.0, 17.8.



**4a-(3-Methylbut-2-enyl)-2,3,4,4a-tetrahydro-1H-carbazole (9c).**  $R_f$  0.24 (4:1 hexanes : EtOAc);  $^1\text{H}$  NMR (500 MHz):  $\delta$  7.57 (d,  $J = 7.6$  Hz, 1H), 7.31 (t,  $J = 7.6$  Hz, 1H), 7.28 (d,  $J = 7.5$  Hz, 1H), 7.16 (t,  $J = 7.5$  Hz, 1H); 4.52 (t,  $J = 7.1$  Hz, 1H), 2.86 (d,  $J = 12.5$ , 1H), 2.55 (d,  $J = 13.3, 7.1$  Hz, 1H), 2.50 (d,  $J = 13.3, 7.1$  Hz, 1H), 2.37 (dq,  $J = 13.5, 1.8$ , 1H), 2.19 (d,  $J = 12.5$ , 1H), 1.83 (qt,  $J = 13.7, 3.3$  Hz, 1H), 1.65-1.75 (m, 2H), 1.51 (s, 3H), 1.50 (s, 3H), 1.41 (qt,  $J = 13.3, 4.2$  Hz, 1H), 1.13 (td,  $J = 13.3, 4.2$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz)  $\delta$  189.5, 154.9, 145.1, 134.3, 127.4, 124.5, 121.9, 120.0, 117.7, 57.9, 36.9, 31.6, 30.1, 28.9, 25.7, 21.3, 18.0; HRMS (FAB+) Calcd for  $\text{C}_{17}\text{H}_{22}\text{N}$  ( $\text{M}+\text{H}$ ) $^+$ : 240.1747, Found: 240.1744.

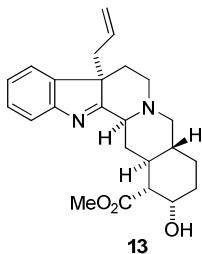


**4a-((E)-3-Phenylallyl)-2,3,4,4a-tetrahydro-1H-carbazole (9d).** mp 86-88 °C;  $R_f$  0.17 (3:1 hexanes : EtOAc); IR: 3024, 2933, 2859, 1582, 1449, 965, 745  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.61 (d,  $J = 7.8$  Hz, 1H), 7.31-7.36 (m, 2H), 7.19-7.25 (m, 3H), 7.13-7.19 (m, 3H), 6.33 (d,  $J = 15.6$  Hz, 1H), 5.64 (dt,  $J = 15.6, 7.2$  Hz, 1H), 2.91 (d,  $J = 13.3$  Hz, 1H), 2.81 (dd,  $J = 14.0, 7.1$  Hz, 1H), 2.58-2.66 (m, 2H), 2.43 (dq,  $J = 13.6, 2.7$  Hz, 1H), 2.22, (d,  $J = 13.1$  Hz, 1H), 1.88 (qt,  $J = 13.8, 3.6$  Hz, 1H), 1.72 (d,  $J = 14.5$  Hz, 1H), 1.46 (qt,  $J = 13.1, 4.3$  Hz, 1H), 1.17 (td,  $J = 13.6, 4.1$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz)  $\delta$  188.8, 154.9, 144.6, 137.0, 133.2, 128.5, 128.4, 127.7, 127.2, 126.4, 126.1, 124.7, 123.9, 122.0, 120.3, 57.8, 36.6, 30.2, 28.8, 21.1; HRMS (FAB+) Calcd for  $\text{C}_{21}\text{H}_{22}\text{N}$  ( $\text{M}+\text{H}$ ) $^+$ : 288.1747, Found: 288.1742.

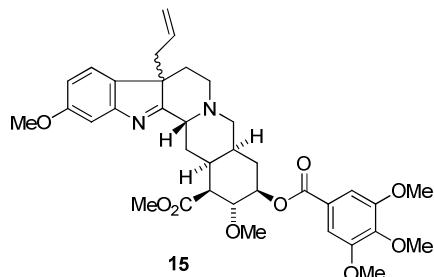


**Allylgeissoschizol 11.** mp 160 °C;  $R_f$  0.25 (5:1  $\text{CH}_3\text{Cl}$  : MeOH); IR: 3362, 2866, 1573, 1455, 748  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{MeOH}-d_4$ ):  $\delta$  7.37 (d,  $J = 8.0$  Hz, 1H), 7.25 (d,  $J = 8.5$  Hz, 1H), 7.04 (dt,  $J = 8.0, 1.0$  Hz, 1H), 6.94 (dt,  $J = 8.0, 1.0$  Hz, 1H), 6.07 (ddt,  $J = 17.5, 10.0, 7.0$  Hz, 1H), 5.81 (q,  $J = 7.0$  Hz, 1H), 5.64-5.60 (m, 1H), 4.61 (br s, 1H), 4.08 (d,  $J = 13.0$  Hz, 1H), 4.01 (dd,  $J = 13.0, 7.0$  Hz, 1H), 3.93 (dd,  $J = 14.0, 7.5$  Hz, 1H), 3.71-3.57 (m, 2H), 3.37-3.31 (m, 2H), 3.22 (s, 1H), 3.14-2.96 (m, 3H), 2.54 (ddd,  $J =$

15.5, 6.5, 4.0 Hz, 1H), 2.23 (td,  $J$  = 15.0, 6.5 Hz, 1H), 1.69 (dd,  $J$  = 7.0, 1.5 Hz, 3H), 1.46 (td,  $J$  = 13.0, 6.5 Hz, 1H), 1.25 (td,  $J$  = 13.5, 7.5 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz, MeOH- $d_4$ )  $\delta$  138.6, 133.4, 130.3, 129.6, 128.9, 127.1, 126.1, 123.8, 120.8, 119.3, 112.5, 105.6, 64.6, 62.6, 60.3, 57.3, 36.9, 31.6, 30.9, 18.3, 13.8.



**Allyl yohimbine 13.**  $R_f$  0.30 (95:5 CH<sub>2</sub>Cl<sub>2</sub> : MeOH); IR: 3292, 2926, 1740, 1713, 1455, 1437, 1210, 1154, 913, 732 cm<sup>-1</sup>;  $^1\text{H}$  NMR (500 MHz)  $\delta$  7.52 (d,  $J$  = 7.6 Hz, 1H), 7.29 (t,  $J$  = 7.6 Hz, 1H), 7.25 (d,  $J$  = 7.4 Hz, 1H), 7.17 (t,  $J$  = 7.4 Hz, 1H), 5.22 (ddt,  $J$  = 17.0, 9.9, 7.5 Hz, 1H), 4.92 (d,  $J$  = 17.0 Hz, 2H), 4.85 (d,  $J$  = 10.0 Hz, 1H), 4.18 (s, 1H), 3.73 (s, 3H), 3.55 (br s, 1H), 3.29 (dd,  $J$  = 11.9, 2.5, 1H), 3.06 (dd,  $J$  = 13.9, 7.1 Hz, 1H), 2.98 (ddd,  $J$  = 12.1, 9.2, 3.2 Hz, 1H), 2.83-2.90 (m, 2H), 2.45 (dt,  $J$  = 13.3, 8.2 Hz, 1H), 2.30 (d,  $J$  = 12.1 Hz, 1H), 2.25 (dt,  $J$  = 12.1, 8.1 Hz, 1H), 2.05 (t,  $J$  = 10.5 Hz, 1H), 1.91-2.02 (m, 3H), 1.45-1.65 (m, 5H), 1.38 (d,  $J$  = 11.9 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz)  $\delta$  188.3, 175.9, 154.9, 144.4, 133.1, 127.6, 125.1, 122.0, 120.1, 118.5, 66.5, 65.9, 60.2, 56.6, 52.2, 52.0, 49.4, 41.8, 40.4, 37.2, 36.1, 31.1, 29.8, 23.2; HRMS (FAB+) Calcd for C<sub>24</sub>H<sub>31</sub>N<sub>2</sub>O<sub>3</sub> (M+H)<sup>+</sup>: 395.2329, Found: 395.2327.



### Allyl reserpines 15.

Analytically pure samples were obtained by preparative HPLC purification (Agilent Zorbax RX-Sil 7  $\mu\text{m}$  column, 7%  $^3\text{PrOH}$  in hexanes).

First eluting diastereomer (8.5 min):  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 (s, 2H), 7.22 (d,  $J$  = 2.4 Hz, 1H), 7.14 (d,  $J$  = 8.1 Hz, 1H), 6.77 (dd,  $J$  = 8.2, 2.4 Hz, 1H), 5.04 (ddt,  $J$  = 16.9, 10.0, 7.0 Hz, 1H), 4.89 (dd,  $J$  = 16.9, 1.6 Hz, 1H), 4.83 (dd,  $J$  = 10.1, 1.6 Hz, 1H), 4.06 (d,  $J$  = 5.2 Hz, 1H) 3.91 (s, 9H), 3.86 (s, 3H), 3.84 (s, 3H), 3.52 (s, 3H), 3.37 (td,  $J$  = 14.4, 2.7 Hz, 1H), 3.01 (sext,  $J$  = 4.7 Hz, 1H), 2.75 (dd,  $J$  = 11.3, 5.0 Hz, 1H), 2.64 (m, 2H), 2.57 (m, 2H), 2.29 (d,  $J$  = 12.4 Hz, 1H), 2.00-2.18 (m, 4H), 1.94 (d,  $J$  = 12.2 Hz, 1H), 1.87 (dt,  $J$  = 12.6, 4.1 Hz, 1H), 1.82 (td,  $J$  = 13.8, 4.5 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  184.4, 172.6, 165.4, 159.8, 155.7, 152.3, 142.1, 135.9, 131.9, 125.4, 121.9, 118.1, 111.5, 106.6, 78.0, 77.9, 60.9, 60.8, 60.3, 56.6, 56.2, 55.5, 54.9, 52.0, 51.9, 50.2, 49.3, 38.1, 34.8, 34.4, 31.2, 29.6, 22.5, 21.0, 14.1.

Second eluting diastereomer (10.3 min):  $^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.32 (s, 2H), 7.24 (d,  $J$  = 2.3 Hz, 1H), 7.19 (d,  $J$  = 8.3 Hz, 1H), 6.75 (dd,  $J$  = 8.3, 2.3 Hz, 1H), 5.46 (ddt,  $J$  = 17.0, 10.1, 7.3 Hz, 1H), 5.18 (br s, 1H), 5.04 (td,  $J$  = 10.1, 6.4 Hz, 1H), 4.99 (d,  $J$  = 10.1 Hz, 1H), 4.96 (d,  $J$  = 17.0 Hz, 1H), 4.03 (dd,  $J$  = 11.0, 9.4 Hz, 1H), 3.93 (s, 6H), 3.89 (s, 3H), 3.83 (s, 3H), 3.78 (s, 3H), 3.39 (dd,  $J$  = 11.6, 2.1 Hz, 1H), 3.32 (td,  $J$  = 12.1, 4.1 Hz, 1H), 3.21 (br s, 1H), 3.02 (dd,  $J$  = 11.5, 5.3 Hz, 1H), 2.94 (dd,  $J$  = 11.9, 2.3 Hz, 1H), 2.77 (dd,  $J$  = 11.0 Hz, 4.8 Hz, 1H), 2.56 (dd,  $J$  = 13.8, 8.0 Hz, 1H), 2.33 (dd,  $J$  = 13.9, 3.0 Hz, 1H), 2.20-2.36 (m, 1H), 2.18 (dd,  $J$  = 13.9, 6.9 Hz, 1H), 1.91-2.01 (m, 2H), 1.55 (td,  $J$  = 13.1, 5.7 Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  180.5, 172.2, 165.6, 160.1, 156.4, 152.9, 142.1, 136.8, 134.7, 131.7, 125.3, 122.6, 119.0, 111.5, 106.7, 106.4, 94.8, 77.6, 77.4, 60.9, 60.8, 56.3, 55.5, 54.6, 53.8, 51.9, 51.6, 46.4, 36.4, 35.9, 32.1, 30.5, 29.1.

