SUPPORTING INFORMATION FOR:
Ring-Opening/Ring-Closing Metathesis (RORCM) Reactions of 7-Azanorbornene
Derivatives. An Entry into Perhydroindolines.

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Experimental protocols and spectroscopic data for compounds **6**, **7**, **8**, **10**, **11**, **13**,
31, and **33**.

5-But-3-enyl-5-(toluene-4-sulfonyl)-7-aza-bicyclo[2.2.1]hept-2-ene-7-carboxylic acid *tert*-butyl ester **6** (from *endo*-**5**): To a solution of **5** (140 mg, 0.400 mmol) in THF (20 mL) and HMPA (1.0 mL) at -78 °C was added 4-bromo-1-butene (146 μ L, 2.4 mmol) followed by LDA (10 mL of a 0.40 M solution in THF, 4.0 mmol). After stirring for 3 h, the reaction mixture was quenched with saturated NH_4Cl (20 mL) and the aqueous phase was extracted with diethyl ether (3 x 30 mL). The extracts were dried (Na_2SO_4) and concentrated. Flash chromatography (6:1, hexanes:ethyl acetate) gave 130 mg (81%) of **6** as a colorless oil which consisted of a 1:2.8 mixture of *exo*:*endo* isomers, respectively.

From *exo*-**5**: To a solution of **5** (190 mg, 0.54 mmol) in THF (80 mL) and HMPA (2.0 mL) at -78 °C was added 4-bromo-1-butene (300 μ L, 3.44 mmol) followed by LDA (13 mL of a 0.48 M solution, 6.2 mmol). After stirring at -78°C for 3 h, the reaction was quenched with saturated NH_4Cl (80 mL) and the aqueous phase was extracted with diethyl ether (3 x 60 mL). The extracts were dried (Na_2SO_4), and concentrated. Flash

chromatography (6:1 hexanes:ethyl acetate) gave 180 mg (82%) of **6** as a colorless oil which consisted of a 1:1.4 mixture of exo and endo isomers, respectively. IR (neat) 3074, 2976, 1706, 1451, 1365, 1292, 1167, 1141 cm^{-1} ; LRMS (CI) calc'd for $\text{C}_{22}\text{H}_{30}\text{NO}_4\text{S}$ $[\text{M}+\text{H}]^+$ 404.2, found, 404.1.

5-But-3-enyl-7-aza-bicyclo[2.2.1]hept-2-ene-7-carboxylic acid *tert*-butyl ester (**7**) and 3-But-3-enyl-2-aza-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid *tert*-butyl ester (**8**). To a solution of **6** (228 mg, 0.653 mmol) in MeOH (7 mL) at 0 °C was added NaH_2PO_4 (630 mg, 5.48 mmol) and 5% sodium amalgam (3.00 g, 6.53 mmol). After stirring at 0°C for 6 h, the reaction mixture was filtered through a celite plug using pentane. The solution was concentrated and the resulting residue was purified by flash chromatography (20:1, pentane:ether) to give 57 mg (40%) of **7** and 58 mg (41%) of **8**, each as a viscous oil.

7: ^1H NMR (500 MHz, CDCl_3) δ 6.33 (broad s, 1 H), 6.18 (broad s, 1H), 5.83-5.73 (m, 1 H), 5.02 (broad d, $J = 17.1$ Hz, 1 H), 4.94 (broad d, $J = 10.3$ Hz, 1 H), 4.56 (broad s, 2 H), 2.30-1.98 (m, 4 H), 1.41 (s, 9 H), 1.24-1.16 (m, 2 H), 0.65 (dd, $J = 10.8, 3.4$ Hz, 1 H); IR (neat) 2973, 2927, 1705, 1452, 1170 cm^{-1} ; LRMS (CI) calc'd for $\text{C}_{15}\text{H}_{24}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 250.2, found, 250.2.

8: ^1H NMR (500 MHz, CDCl_3) δ 6.36 (broad s, 0.5 H), 6.25 (broad s, 0.5 H), 6.13 (d, $J = 5.3$ Hz, 1 H), 5.90 – 5.82 (dddd, $J = 17.1, 10.8, 6.6, 6.6$ Hz, 1 H), 5.05 (dd, $J = 17.1, 1.5$ Hz, 1 H), 4.98 (d, $J = 10.3$ Hz, 1 H), 4.68 (br. s, 0.5 H), 4.54 (br. s, 0.5 H), 3.22 (d, $J = 8.8$ Hz, 1 H), 2.70-2.52 (m, 1 H), 2.24-2.09 (m, 2 H), 1.90-1.73 (m, 2 H), 1.52-1.35 (m,

2 H), 1.43 (s, 9 H); IR (neat) 2975, 2920, 1696, 1390, 1178 cm^{-1} ; LRMS (CI) calc'd for $\text{C}_{15}\text{H}_{24}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 250.2, found 250.2.

2-Vinyl-2,3,3a,4,5,7a-hexahydro-indole-1-carboxylic acid *tert*-butyl ester (**10**). To a solution of **7** (12.4 mg, 0.050 mmol) in CH_2Cl_2 (4 mL) under ethylene (1 atm) at rt was added a solution of Grubbs 2 catalyst **9** (2.1 mg, 0.0025 mmol) in CH_2Cl_2 (1 mL). After stirring for 12 h, the reaction mixture was concentrated. Flash chromatography (15:1 hexanes:ethyl acetate) gave 8.5 mg (69%) of **10** as a colorless oil.

10: ^1H NMR (500 MHz, CDCl_3) δ 5.76-5.64 (m, 3 H), 5.18-4.91 (m, 2 H), 4.24 (broad s, 1 H), 4.16 (broad s, 1 H), 2.41-2.33 (m, 1 H), 2.20-1.91 (m, 3 H), 1.81-1.74 (m, 1 H), 1.68-1.61 (m, 2 H), 1.43 (s, 9 H); IR (neat) 2973, 2927, 1692, 1385, 1174 cm^{-1} ; LRMS (CI) calc'd for $\text{C}_{15}\text{H}_{24}\text{NO}_2$ $[\text{M}+\text{H}]^+$ 250.2, found, 250.2.

2-Vinyl-2,3,3a,4,5,7a-hexahydro-1*H*-indole (**10H**). To a solution of **10** (7.5 mg, 0.03 mmol) in CH_2Cl_2 (4 mL) at rt was added TFA (0.3 mL). The mixture was stirred for 2h and then neutralized with 1 M NaOH (2 mL). The aqueous phase was extracted with CH_2Cl_2 (3 X 5 mL), dried (Na_2SO_4), and concentrated. Flash chromatography (gradient

of ethyl acetate (neat) to 4:1, ethyl acetate:methanol) gave 4.5 mg (96%) of amine **10H** as a viscous oil.

10H: ^1H NMR (500 MHz, CDCl_3) : δ 6.08-6.06 (m, 1 H), 5.93 (ddd, $J = 17.1, 10.1, 7.6$ Hz, 1 H), 5.76 (ddd, $J = 10.2, 1.5, 1.5$ Hz, 1 H), 5.35 (d, $J = 17.1$ Hz, 1 H), 5.25 (d, $J = 10.2$ Hz, 1 H), 4.03 (ddd, $J = 8.6, 8.6, 8.6$ Hz, 1 H), 3.92 (br. d, $J = 3.9$ Hz, 1 H), 2.52 - 2.45 (m, 1 H), 2.35 (ddd, $J = 13.1, 7.8, 7.8$ Hz, 1 H), 2.15-2.10 (m, 1 H), 2.05-1.96 (m, 1 H), 1.79 (dddd, $J = 13.4, 5.2, 5.2, 5.2$ Hz, 1 H), 1.71-1.59 (m, 2 H); ^{13}C NMR (125 MHz, CDCl_3) δ 134.4, 134.2, 121.7, 120.3, 61.3, 56.7, 36.0, 35.4, 24.4, 22.8; IR (neat) 3397, 2921, 1736, 1604, 1070 cm^{-1} ; LRMS (CI) calc'd for $\text{C}_{10}\text{H}_{16}\text{N}$ $[\text{M}+\text{H}]^+$ 150.1, found, 150.1.

COSY summary: the following crossing peaks were observed: H(1) and H(2), H(2) and H(3), H(3) and H(4), H(3) and H(4'), H(4), H(4') and H(5), H(5) and H(6), H(5) and H(6'), H(6), H(6') and H(7), H(6), H(6') and H(7'), H(7), H(7') and H(8), H(8) and H(9), H(9) and H(10), H(10) and H(5).

3-Vinyl-2-aza-spiro[4.4]non-6-ene-2-carboxylic acid *tert*-butyl ester (**11**). To a solution of **7** (47 mg, 0.189 mmol) in CH_2Cl_2 (15 mL) under ethylene (1 atm) at rt was

added a solution of Grubbs 2 catalyst **9** (9.6 mg, 0.0113 mmol) in 2 mL CH₂Cl₂. After stirring for 5 h the solvent was removed. The resulting residue was purified by flash chromatography (15:1 hexanes:ethyl acetate) to give **11** (45 mg, 96%) as a viscous oil.

11: ¹H NMR (500 MHz, CDCl₃) δ 5.86-5.67 (m, 1 H), 5.75 (ddd, *J* = 3.2, 2.2, 2.2 Hz, 1 H), 5.52 (ddd, *J* = 5.7, 2.0, 2.0 Hz, 1 H), 5.19-4.97 (m, 2 H), 4.24 (br. s, 0.5 H), 4.19 (br. s, 0.5 H), 3.44 (broad s, 0.5 H), 3.35 (broad s, 0.5 H), 3.20 (broad d, *J* = 10.4 Hz, 1 H), 2.44-2.34 (m, 2 H), 1.93 (ddd, *J* = 12.5, 7.3, 1.5 Hz, 1 H), 1.88-1.68 (m, 3 H), 1.43 (s, 9 H); IR (neat) 2974, 2852, 1696, 1391, 1164 cm⁻¹; LRMS (CI) calc'd for C₁₅H₂₄NO₂ [M+H]⁺ 250.1, found 250.1.

3-Vinyl-2-aza-spiro[4.4]non-6-ene (**11H**). To a solution of **11** (8.0 mg, 0.032 mmol) in 4 mL CH₂Cl₂ at rt was added TFA (0.3 mL). After stirring for 3h the mixture was neutralized with 1M NaOH (2 mL). The aqueous phase was extracted with CH₂Cl₂ (3 X 5 mL) dried (Na₂SO₄), and concentrated. Flash chromatography (gradient of ethyl acetate to 4:1, hexanes:ethyl acetate) gave 4.6 mg (97%) of amine **11H** as a viscous oil.

11H: ¹H NMR (500 MHz, CDCl₃) δ 5.96 (ddd, *J* = 17.1, 10.3, 7.8 Hz, 1 H), 5.81 (ddd, *J* = 5.1, 2.4, 2.4 Hz, 1 H), 5.55 (ddd, *J* = 4.6, 2.0, 2.0 Hz, 1 H), 5.38 (d, *J* = 17.1 Hz, 1 H), 5.26 (d, *J* = 10.2 Hz, 1 H), 4.05 (m, 1 H), 3.20 (d, *J* = 11.6 Hz, 1 H), 3.04 (d, *J* = 11.7 Hz, 1 H), 2.45-2.40 (m, 2 H), 2.04-1.98 (m, 1 H), 1.95-1.85 (m, 3 H); ¹³C NMR (125 MHz, CDCl₃) δ 133.8, 133.5, 132.6, 121.7, 62.2, 55.7, 54.4, 43.8, 37.2, 32.0; IR (neat) 3381, 2920, 2851, 1604, 1070 cm⁻¹; LRMS (CI) calc'd for C₁₀H₁₆N [M+H]⁺ 150.1, found, 150.1.

COSY summary: the following crossing peaks are observed: H(1), H(1') and H(2), H(2) and H(3), H(2) and H(5), H(2) and H(6), H(3) and H(4), H(3) and H(4'), H(5) and

H(6), H(6) and H(7), H(6) and H(7'), H(7), H(7') and H(8), H(7), H(7') and H(8'), H(8) and H(8'), H(9) and H(9').

2-(Toluene-4-sulfonyl)-3-vinyl-2-aza-spiro[4.4]non-6-ene (**11Ts**). To a solution of amine **11H** (4.6 mg, 0.0031 mmol) in CH₂Cl₂ (1 mL) at 0°C was added NaOH (3.8 mg, 0.096 mmol). After stirring for 0.5 h, TsCl (9.2 mg, 0.047 mmol) was added to the resulting mixture. Following an additional 3 h, the reaction mixture was diluted with brine (2 mL) and the aqueous phase was extracted with CH₂Cl₂ (3 X 3 mL). The extracts were dried and concentrated. Flash chromatography (15:1 hexanes:ethyl acetate) gave 8.0 mg (86%) of **11Ts** as a white solid.

11Ts: mp = 80°C; ¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, *J* = 8.3 Hz, 2 H), 7.31 (d, *J* = 8.3 Hz, 2 H), 5.87 (ddd, *J* = 17.1, 9.7, 7.3 Hz, 1 H), 5.72 (ddd, *J* = 5.2, 2.4, 2.4 Hz, 1 H), 5.48 (ddd, *J* = 3.4, 1.9, 1.9 Hz, 1 H), 5.22 (d, *J* = 17.1 Hz, 1 H), 5.10 (d, *J* = 10.3 Hz, 1 H), 4.06 (ddd, *J* = 7.5 Hz, 1 H), 3.34 (d, *J* = 10.7 Hz, 1 H), 3.26 (d, *J* = 10.7 Hz, 1 H), 2.44 (s, 3 H), 2.26 (ddd, *J* = 4.9, 1.8, 1.8 Hz, 2 H), 1.82-1.76 (m, 2 H), 1.40 (dt, *J* = 14.2, 7.3, 7.3 Hz, 1 H), 1.34 (dt, *J* = 13.2, 6.9, 6.9 Hz, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ 143.4, 139.6, 134.7, 132.5, 129.7, 127.8, 115.7, 63.0, 59.0, 54.8, 45.9, 35.8, 31.7, 21.8; IR (neat) 3052, 2928, 2855, 1346, 1160 cm⁻¹; LRMS (CI) calc'd for C₁₇H₂₂NO₂S [M+H]⁺ 304.1, found, 304.0.

X-ray (**11Ts**)

3-But-3-enyl-7-aza-bicyclo[2.2.1]hepta-2,5-diene-2,7-dicarboxylic acid 7-*tert*-butyl ester 2-ethyl ester (**13**). To a solution of **12** (0.370 g, 0.880 mmol) in THF (3 mL) at 0 °C was added 4-butenylmagnesium bromide (2 mL of a 1.0 M solution in diethyl ether, 2 mmol). The mixture was stirred for 3 h before the reaction was quenched with saturated NH₄Cl (5 mL). The aqueous phase was extracted with CH₂Cl₂ (3 X 10 mL) and the extracts were dried (Na₂SO₄). Concentration and flash chromatography (15:1, hexanes:ethyl acetate) gave 240 mg of 7-azanorbornene **13** (85%) as a viscous oil.

13: ¹H NMR (500 MHz, CDCl₃) δ 7.13 (broad s, 0.5 H), 7.07 (broad s, 0.5 H), 6.95 (broad s, 0.5 H), 6.90 (broad s, 0.5 H), 5.82-5.75 (m, 1 H), 5.42 (broad s, 0.5 H), 5.36 (broad s, 0.5 H), 5.13-4.98 (m, 3 H), 4.19 (broad s, 2 H), 2.86-2.80 (m, 1 H), 2.76-2.69 (m, 1 H), 2.27-2.15 (m, 2 H), 1.39 (s, 9 H), 1.29 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃) δ 171.1, 171.1, 164.3, 154.4, 154.4, 145.6, 145.6, 141.4, 141.4, 140.2, 140.2, 137.2, 115.6, 80.9, 71.0, 71.0, 67.5, 67.5, 60.3, 30.8, 28.9, 28.3, 14.3; IR (neat) 2979, 1707, 1636, 1334, 1167 cm⁻¹; LRMS (CI) calc'd for C₁₈H₂₆NO₄ [M+H]⁺ 320.2, found, 320.2.

3-But-3-enyl-7-aza-bicyclo[2.2.1]hept-5-ene-2,7-dicarboxylic acid 7-*tert*-butyl ester 2-ethyl ester (**14**) and 3-But-3-enyl-7-aza-bicyclo[2.2.1]hept-5-ene-2,7-dicarboxylic acid 7-*tert*-butyl ester 2-ethyl ester (**15**). To a solution of **13** (70 mg, 0.219 mmol) in MeOH (4 mL) at 0 °C was added activated Mg (84 mg, 3.5 mmol). The reaction was allowed to warm to rt over 2 h and then was quenched with saturated NH₄Cl (5 mL). The aqueous phase was extracted with CH₂Cl₂ (3 X 10 mL) and the extracts were dried (Na₂SO₄). Concentration and flash chromatography (gradient of 25:1 to 10:1 hexanes:ethyl acetate) gave 41 mg (58%) of **14** and 20.2 mg (28%) of **15** each as a viscous oil

14: ¹H NMR (500 MHz, CDCl₃) δ 6.52-6.24 (m, 2 H), 5.84-5.74 (m, 1 H), 5.01 (d, *J* = 17.1 Hz, 1 H), 4.95 (d, *J* = 9.7 Hz, 1 H), 4.88-4.81 (broad m, 1 H), 4.68-4.59 (broad m, 1 H), 4.17 (q, *J* = 7.3, 2 H), 2.62 (broad s, 1 H), 2.10-2.04 (m, 2 H), 1.84-1.82 (m, 1 H), 1.39 (s, 9 H), 1.40-1.20 (partially obscured m, 5 H); IR (neat) 2978, 2927, 1735, 1709, 1370, 1171 cm⁻¹; LRMS (CI) calc'd for C₁₈H₂₈NO₄ [M + H]⁺ 322.2; found 322.1.

15: ¹H NMR (500 MHz, C₆D₆) δ 6.66 (broad s, 1 H), 6.11 (broad s, 0.5 H), 6.02 (broad s, 0.5 H), 5.71-5.61 (m, 1 H), 5.03-4.94 (m, 2 H), 4.84 (broad s, 1 H), 4.62 (broad s, 1 H), 3.86 (broad s, 2 H), 3.29-3.17 (m, 1 H), 2.59 (broad s, 1 H), 1.81 (broad s, 2 H), 1.55 (broad s, 1 H), 1.42 (s, 9 H), 0.93 (t, *J* = 6.9 Hz, 3 H), 1.02-0.82 (partially obscured m, 1 H); IR (neat) 2978, 2928, 1730, 1709, 1368, 1173 cm⁻¹; LRMS (CI) calc'd for C₁₈H₂₈NO₄ [M + H]⁺ 322.2; found 322.2.

2-Vinyl-2,3,3a,4,5,7a-hexahydro-indole-1,3-dicarboxylic acid 1-*tert*-butyl ester 3-ethyl ester (**16**). To a solution of **14** (32.1 mg, 0.1 mmol) and ethylene (1 atm) in CH₂Cl₂ (15 mL) at rt was added a solution of **9** (9.0 mg, 0.011 mmol) in CH₂Cl₂ (2 mL). The reaction mixture was stirred for 16 h and concentrated. Flash chromatography (10:1 hexanes:ethyl acetate) gave 22.5 mg (70%) of **16** as a colorless oil.

16: ¹H NMR (500 MHz, CDCl₃) : δ 5.71 (broad s, 2 H), 5.24-4.94 (m, 2 H), 4.44 (broad s, 2 H), 4.19 (q, *J* = 7.2 Hz, 2 H), 2.77 (t, *J* = 9.5 Hz, 1 H), 2.56 (broad s, 1 H), 2.13-1.95 (m, 2 H), 1.79 (d, *J* = 2.9 Hz, 2 H), 1.43 (m, 10 H), 1.26 (t, *J* = 7.1 Hz, 3 H); IR: 2978, 2928, 1735, 1697, 1377, 1173 cm⁻¹; LRMS (CI) calc'd for C₁₇H₂₈NO₄ [M+H]⁺ 322.2, found, 322.2.

2-Vinyl-2,3,3a,4,5,7a-hexahydro-1*H*-indole-3-carboxylic acid ethyl ester (**16H**). To a solution of **16** (5.6 mg, 0.017 mmol) in CH₂Cl₂ (1 mL) at rt was added TFA (0.2 mL). After stirring for 3 h, the mixture was neutralized with saturated Na₂CO₃ (3 mL). The aqueous phase was extracted with CH₂Cl₂ (3 X 5 mL), dried (Na₂SO₄), and concentrated. Flash chromatography (gradient of ethyl acetate (neat) to 4:1, ethyl acetate:hexanes) gave 3.7 mg (96%) of amine **16H** as a viscous oil.

16H: ^1H NMR (500 MHz, C_6D_6) δ 5.91 (ddd, $J = 17.1, 10.2, 6.3$, Hz, 1 H), 5.73-5.70 (m, 1 H), 5.66-5.62 (m, 1 H), 5.28 (ddd, $J = 17.1, 1.5, 1.5$ Hz, 1 H), 4.99 (ddd, $J = 10.3, 1.5, 1.5$ Hz, 1 H), 4.00-3.94 (m, 3 H), 3.50-3.46 (m, 1 H), 2.47-2.39 (m, 2 H), 1.80-1.74 (m, 1 H), 1.72-1.64 (m, 1 H), 1.56-1.49 (m, 1 H), 1.36 (m, 1 H), 0.94 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3) δ 173.9, 137.8, 130.8, 126.4, 117.1, 64.9, 60.9, 56.6, 56.1, 42.4, 25.2, 23.7, 14.5; IR 3334, 2921, 2851, 1730, 1171 cm^{-1} ; LRMS (CI) calc'd for $\text{C}_{13}\text{H}_{20}\text{NO}_2$ $[\text{M}+1]^+$ 222.1, found, 222.1.

COSY summary: the following crossing peaks are observed: terminal alkene (H(1)) and H(2), H(2) and H(3), H(3) and H(4), H(4) and H(5), H(5) and H(6), H(6) and H(7), H(7) and H(8), H(9) and H(10), H(10) and H(5).

1-(Toluene-4-sulfonyl)-2-vinyl-2,3,3a,4,5,7a-hexahydro-1*H*-indole-3-carboxylic acid ethyl ester (**16Ts**). To a solution of amine **16H** (3.7 mg, 0.016 mmol) in CH_2Cl_2 (1 mL) at rt was added triethyl amine (0.030 mL, 0.22 mmol) and TsCl (30.5 mg, 0.16 mmol). The reaction mixture was stirred at room temperature for 3 hr and then diluted with brine (2 mL). The aqueous phase was extracted with CH_2Cl_2 , the extracts were dried (Na_2SO_4), and concentrated. Flash chromatography (10:1 hexanes:ethyl acetate) gave 5.0 mg (79%) of tosyl amine **16Ts** as a white solid.

16Ts: mp = 80-81 $^\circ\text{C}$; ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, $J = 8.3$ Hz, 2 H), 7.31 (d, $J = 7.8$ Hz, 2 H), 5.86 (ddd, $J = 17.2, 10.2, 7.3$ Hz, 1 H), 5.76-5.68 (m, 2 H), 5.26 (d, $J = 17.1$ Hz, 1 H), 5.12 (d, $J = 10.3$ Hz, 1 H), 4.32-4.28 (m, 2 H), 4.20 (q, $J = 7.1$ Hz, 2 H), 2.79 (dd, $J = 11.4, 9.0$ Hz, 1 H), 2.44 (s, 3 H), 2.07-1.92 (m, 3 H), 1.67-1.63 (m, 2 H), 1.21 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.9, 143.8, 139.0, 135.4, 129.9, 128.1, 127.9, 127.9, 116.4, 65.5, 61.2, 59.4, 51.2, 39.7, 21.8, 21.3, 19.6, 14.5; IR

(neat) 2918, 2850, 1731, 1348, 1162 cm^{-1} ; LRMS (CI) calc'd for $\text{C}_{20}\text{H}_{26}\text{NO}_4\text{S}$ $[\text{M}+\text{H}]^+$ 376.2, found, 376.1.

COSY summary: the following crossing peaks are observed: terminal alkene (H(1)) and H(2), H(2) and H(3), H(3) and H(4), H(4) and H(5), H(5) and H(6), H(6) and H(7), H(7) and H(8), H(9) and H(10), H(10) and H(5).

2-Vinyl-2,3,3a,4,5,7a-hexahydro-indole-1,3-dicarboxylic acid 1-*tert*-butyl ester 3-ethyl ester (**17**). To a solution of **17** (7.0 mg, 0.0218 mmol) and ethylene (1 atm) in 5 mL CH_2Cl_2 at rt was added a solution of catalyst **9** (6.0 mg, 0.0078 mmol) in CH_2Cl_2 (3 mL) in 3 portions. After stirring for 60 h the reaction was concentrated. Flash chromatography (solvent) gave 5.9 mg (84%) of **17** as a colorless oil. Indoline **17** was characterized as the corresponding *N*-tosyl derivative.

1-(Toluene-4-sulfonyl)-2-vinyl-2,3,3a,4,5,7a-hexahydro-1*H*-indole-3-carboxylic acid ethyl ester (**17Ts**). To a solution of **17** (4.0 mg, 0.012 mmol) in CH_2Cl_2 (1 mL) at rt was added TFA (0.2 mL). After stirring for 3 h, the mixture was neutralized with saturated Na_2CO_3 (3 mL). The aqueous phase was extracted with CH_2Cl_2 (3 X 5 mL), the extracts were dried (Na_2SO_4) and concentrated. The resulting residue was used directly in the next step without purification.

To a solution of amine in CH_2Cl_2 (1 mL) at 0 °C was added NaOH (5.0 mg, 1.25 mmol) followed by TsCl (18.2 mg, 0.096 mmol). The resulting mixture was stirred for 3

h and then concentrated. Flash chromatography gave 3.0 mg (64%) of **17Ts** as a colorless oil.

17Ts: ^1H NMR (500 MHz, CDCl_3) δ 7.75 (d, $J = 8.3$ Hz, 2 H), 7.33 (d, $J = 7.7$ Hz, 2 H), 6.17-6.14 (m, 1 H), 6.12 (dd, $J = 10.6, 5.1$ Hz, 1 H), 5.99-5.94 (m, 1 H), 5.48 (ddd, $J = 17.0, 1.8, 1.8$ Hz, 1 H), 5.19 (ddd, $J = 10.3, 1.7, 1.7$ Hz, 1 H), 4.57-4.54 (m, 1 H), 4.12 (q, $J = 7.2$ Hz, 2 H), 3.91-3.86 (m, 1 H), 2.68 (dd, $J = 8.5, 6.7$ Hz, 1 H), 2.51-2.39 (m, 1 H), 2.44 (s, 3 H), 2.07-2.01 (m, 1 H), 1.92-1.86 (m, 1 H), 1.85-1.77 (m, 1 H), 1.66-1.58 (m, 1 H), 1.24 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.4, 143.9, 136.3, 134.7, 130.7, 130.0, 127.9, 127.1, 118.2, 62.4, 60.9, 57.7, 50.3, 39.5, 24.1, 21.8, 21.2, 14.4; IR: 2924, 2851, 2361, 2338, 1736, 1348, 1161 cm^{-1} ; LRMS (CI) calc'd for $\text{C}_{20}\text{H}_{26}\text{NO}_4\text{S}$ $[\text{M}+1]^+$ 376.2, found, 376.2.

COSY summary: the following crossing peaks are observed: terminal alkene (H(1)) and H(2), H(2) and H(3), H(3) and H(4), H(4) and H(5), H(5) and H(6), H(6) and H(7), H(7) and H(8), H(9) and H(10), H(10) and H(5).

7-Aza-bicyclo[2.2.1]hept-5-ene-2,7-dicarboxylic acid 7-*tert*-butyl ester 2-ethyl ester (**18**). To a solution of **12** (0.400 g, 0.95 mmol) in THF (4 mL) at rt was added tributyltin hydride (1.02 mL, 3.82 mmol). After 1 h, the reaction mixture was cooled to 0 $^\circ\text{C}$ and 3 mL MeOH was added. To the resulting mixture was added NaBH_4 (318 mg, 7.6 mmol) portionwise. After an additional 2 h, the reaction was quenched with 1 M HCl until gas evolution ceased. The mixture was extracted with ether (3 X 20 mL). The extracts were

dried (Na₂SO₄) and concentrated. Flash chromatography (15:1 hexanes:ethyl acetate) gave 140 mg (55%) of **18** as pale yellow oil.

18: ¹H NMR (500 MHz, CDCl₃) δ 6.39 (bs, 1 H), 6.19 (bs, 1 H), 4.90 (bs, 1 H), 4.68 (bs, 1 H), 4.09 (m, 2 H), 3.14 (bs, 1 H), 2.17 (bs, 1 H), 1.55 (bs, 1 H), 1.42 (s, 9 H), 1.24 (t, *J* = 7.1 Hz, 3 H); IR (neat) 2980, 1738, 1708, 1346, 1321, 1168 cm⁻¹; LRMS (CI) calc'd for C₁₄H₂₂NO₄ [M+H]⁺ 268.2, found, 268.1.

5-(1-Hydroxy-but-3-enyl)-7-aza-bicyclo[2.2.1]hept-2-ene-7-carboxylic acid *tert*-butyl ester (**19**) and 5-(1-Hydroxy-but-3-enyl)-7-aza-bicyclo[2.2.1]hept-2-ene-7-carboxylic acid *tert*-butyl ester (**20**). To a solution of **18** (1.40 g, 5.2 mmol) in toluene (20 mL) at -90 °C was slowly added diisobutyl aluminum hydride (15.7 mL of a 1.0 M solution in toluene, 15.7 mmol). After stirring for 0.5 h, propenylmagnesium bromide (15 mL of a 1.0 M solution in diethyl ether, 15 mmol) was added to the reaction mixture. The reaction was warmed to rt, quenched with Rochelle's salt (20 mL), and stirred for 12 h. The aqueous phase was extracted with diethyl ether. The extracts were dried (Na₂SO₄) and concentrated. Flash chromatography (10:1 to 3:1 hexanes:ethyl acetate) gave 500 mg (36%) of **19** and 541 mg (39%) of **20** both as colorless oils.

19: ¹H NMR (500 MHz, CDCl₃) δ 6.40 (broad s, 1 H), 6.16 (broad, 1 H), 5.88-5.79 (m, 1 H), 5.20 (broad s, 1 H), 5.18 (broad s, 1 H), 4.61 (broad s, 2 H), 3.11- 3.05 (m, 1 H), 2.40-2.36 (m, 1 H), 2.29 (broad s, 1 H), 2.21-2.13 (m, 2 H), 1.66-1.53 (m, 1 H), 1.41

(s, 9 H), 1.10 (broad d, $J = 8.8$ Hz, 1 H); IR (neat) 3430 (broad) 3075, 2975, 2927, 1703, 1368, 1170 cm^{-1} ; LRMS (CI) calc'd for $\text{C}_{15}\text{H}_{24}\text{NO}_3$ $[\text{M}+\text{H}]^+$ 266.2, found, 266.2.

20: ^1H NMR (500 MHz, CDCl_3) δ 6.35 (broad s, 1 H), 6.30 (broad s, 1 H), 5.76 (ddd, $J = 17.5, 10.0, 7.1$ Hz, 1 H), 5.13-5.12 (m, 2 H), 4.81 (broad s, 1 H), 4.62 (broad s, 1 H), 3.02-2.94 (m, 1 H), 2.35-2.10 (m, 2 H), 2.08-2.00 (m, 3 H), 1.42 (s, 9 H), 0.65 (dd, $J = 11.2, 3.6$ Hz, 1 H); IR (neat) 3431 (broad), 3075, 2976, 2930, 1703, 1368, 1170 cm^{-1} ; LRMS (CI) calc'd for $\text{C}_{15}\text{H}_{24}\text{NO}_4$ $[\text{M}+1]^+$ 266.2, found, 266.2.

5-(1-Acetoxy-but-3-enyl)-7-aza-bicyclo[2.2.1]hept-2-ene-7-carboxylic acid *tert*-butyl ester (**21**). To a solution of **19** (27.8 mg, 0.105 mmol) in CH_2Cl_2 (3 mL) was added Hünig's base (0.365 mL, 2.1 mmol), acetic anhydride (0.100 mL, 1.05 mmol) and catalytic DMAP. After stirring at rt for 3 h, the reaction mixture was quenched with saturated NaHCO_3 (3 mL). The organic extracts were extracted with CH_2Cl_2 (3 X 10 mL), dried (Na_2SO_4), and concentrated. Flash chromatography (5:1 hexanes:ethyl acetate) gave 30.0 mg (93%) of acetate **21** as colorless oil.

21: ^1H NMR (500 MHz, CDCl_3): δ 6.41 (broad s, 1 H), 6.17 (broad s, 1 H), 5.75 (dddd, $J = 17.0, 10.2, 8.1, 8.1$ Hz, 1 H), 5.14-5.08 (m, 2 H), 4.58 (broad s, 2 H), 4.45 (ddd, $J = 10.2, 6.4, 3.9$ Hz, 1 H), 2.48-2.40 (m, 2 H), 2.24 (ddd, $J = 14.7, 7.3, 7.3$ Hz, 1

H), 2.04 (ddd, $J = 12.2, 8.8, 4.4$ Hz, 1 H), 1.98 (s, 3 H), 1.42 (s, 9 H), 0.89 (dd, $J = 3.9, 11.9$ Hz, 1 H); IR: 3077, 2977, 1737, 1706, 1368, 1238 cm^{-1} ; LRMS (CI) calc'd for $\text{C}_{17}\text{H}_{26}\text{NO}_4$ $[\text{M}+1]^+$ 308.2, found, 308.1.

5-(1-Acetoxy-but-3-enyl)-7-aza-bicyclo[2.2.1]hept-2-ene-7-carboxylic acid *tert*-butyl ester (**22**). To a solution of **20** (0.029 g, 0.11 mol) in CH_2Cl_2 (3 mL) at rt was added Hünig's base (0.384 mL, 2.2 mmol), acetic anhydride (0.100 mL, 1.05 mmol), and catalytic DMAP. After stirring for 8 h, the reaction was quenched with saturated NaHCO_3 (3 mL). The aqueous phase was extracted with CH_2Cl_2 (3 X 10 mL). The extracts were dried (Na_2SO_4) and concentrated. Flash chromatography (5:1 hexanes:ethyl acetate) gave 30.7 mg (91%) of **22** as a colorless oil.

22: ^1H NMR (500 MHz, CDCl_3) δ 6.38 (broad s, 1 H), 6.16 (broad s, 1 H), 5.75 (dddd, $J = 17.6, 8.8, 8.8, 6.4$, 1 H), 5.06-5.02 (m, 2 H), 4.59 (broad s, 2 H), 4.45 (ddd, $J = 10.7, 6.8, 3.9$ Hz, 1 H), 2.51-2.45 (m, 1 H), 2.38-2.34 (m, 1 H), 2.15 (ddd, $J = 14.6, 6.8, 6.8$ Hz, 1 H), 2.09-2.04 (partially obscured m, 1 H), 2.07 (s, 3 H), 1.41 (s, 9H), 0.73 (dd, $J = 11.5, 4.1$ Hz, 1 H); IR (neat) 2918, 2850, 1736, 1706, 1367, 1238 cm^{-1} ; LRMS (CI) calc'd for $\text{C}_{17}\text{H}_{26}\text{NO}_4$ $[\text{M}+1]^+$ 308.2, found, 308.1.

5-[1-(*tert*-Butyl-dimethyl-silanyloxy)-but-3-enyl]-7-aza-bicyclo[2.2.1]hept-2-ene-7-carboxylic acid *tert*-butyl ester (**23**). To a solution of **19** (100 mg, 0.377 mol) in DMF (2 mL) at rt was added imidazole (0.154 g, 2.64 mmol) and TBSCl (0.154 g, 1.02 mmol). The reaction mixture was stirred at rt for 8 h and then quenched with saturated NaHCO₃ (5 mL). The aqueous phase was extracted with ether (3 X 20 mL), dried (Na₂SO₄), and concentrated. Flash chromatography (25:1 hexanes:ethyl acetate) gave 140 mg (98%) of **23** as a colorless oil.

23: ¹H NMR (500 MHz, CDCl₃) 6.36 (broad s, 1 H), 6.10 (broad s, 1 H), 5.97-5.87 (m, 1 H), 5.14 (d, *J* = 17.2 Hz, 1 H), 5.12 (d, *J* = 7.6 Hz, 1 H), 4.59 (broad s, 1 H), 4.54 (broad s, 1 H), 3.15 (ddd, *J* = 10.2, 5.1, 5.1 Hz, 1 H), 2.38-2.31 (m, 2 H), 2.21-2.16 (m, 1 H), 2.10-2.05 (m, 1 H), 1.40 (s, 9 H), 0.94 (dd, *J* = 10.9, 4.1 Hz, 1 H), 0.85 (s, 9 H), 0.0 (s, 3 H), -0.03 (s, 3 H); IR (neat) 2925, 2854, 1708, 1364, 1255, 1081 cm⁻¹; LRMS (CI) calc'd for C₂₁H₃₈NO₃Si [M+H]⁺ 380.3, found, 380.2.

5-[1-(*tert*-Butyl-dimethyl-silanyloxy)-but-3-enyl]-7-aza-bicyclo[2.2.1]hept-2-ene-7-carboxylic acid *tert*-butyl ester (**24**). To a solution of **20** (0.090 g, 0.34 mol) in DMF (2 mL) at rt was added imidazole (0.139 g, 2.03 mmol) and TBSCl (153.5, 1.02 mmol). The reaction mixture was stirred at rt for 8 h and then diluted with saturated NaHCO₃ (5 mL). The aqueous phase was extracted with ether (3 X 20 mL), dried (Na₂SO₄), and concentrated. Flash chromatography (25:1 hexanes:ethyl acetate) gave 128 mg (100%) of **24** as colorless oil.

24: ¹H NMR (300 MHz, CDCl₃): δ 6.36 (dd, *J* = 5.9, 2.1 Hz, 1 H), 6.22 (dd, *J* = 5.8, 1.9 Hz, 1 H), 5.87 (dddd, *J* = 16.5, 10.4, 8.6, 5.9 Hz, 1 H), 5.06-4.98 (m, 2 H), 4.69 (bs, 1 H), 4.56 (bs, 1 H), 3.19 (ddd, *J* = 10.2, 5.0, 5.0 Hz, 1 H), 2.40 (ddd, *J* = 13.6, 8.8, 4.4 Hz,

1 H), 2.34-2.24 (m, 1 H), 2.13-2.03 (m, 1 H), 1.97 (ddd, $J = 11.4, 9.1, 4.5$ Hz, 1 H), 1.41 (s, 9 H), 0.92 (s, 9 H), 0.62 (dd, $J = 4.1, 10.9$ Hz, 1 H), 0.06 (s, 3 H), 0.06 (s, 3 H); IR (neat) 2956, 2929, 2857, 1710, 1365, 1072 cm^{-1} ; LRMS (CI) calc'd for $\text{C}_{21}\text{H}_{38}\text{NO}_3\text{Si}$ $[\text{M}+\text{H}]^+$ 380.3, found, 380.2.

4-Acetoxy-2-vinyl-2,3,3a,4,5,7a-hexahydro-indole-1-carboxylic acid *tert*-butyl ester (**25**). To a solution of **21** (8.0 mg, 0.026 mmol) and ethylene (1 atm) in benzene (3 mL) was added **9** (4.0 mg, 0.0047 mmol). The reaction mixture was heated to reflux for 20 h and then concentrated. Flash chromatography gave 7.8 mg (98%) of indoline **25** as a colorless oil.

25: ^1H NMR (500 MHz, CDCl_3) δ 5.82 (bd, $J = 10.2$ Hz, 1 H), 5.68 (ddd, $J = 17.6, 8.8, 8.8$ Hz, 1 H), 5.56 (d, $J = 9.7$ Hz, 1 H), 5.15-5.08 (m, 2 H), 5.02 (d, $J = 9.8$ Hz, 1 H), 4.47 (bs, 1 H), 4.21 (bs, 1 H), 2.51-2.46 (m, 1 H), 2.37-2.33 (m, 1 H), 2.17-2.13 (m, 2 H), 2.05 (s, 3 H), 1.58-1.45 (partially obscured m, 1 H), 1.42 (s, 9 H); IR (neat) 2921, 2851, 1732, 1691, 1389, 1242 cm^{-1} ; LRMS (CI) calc'd for $\text{C}_{17}\text{H}_{26}\text{NO}_4$ $[\text{M}+1]^+$ 308.2, found, 308.1.

Acetic acid 2-vinyl-2,3,3a,4,5,7a-hexahydro-1*H*-indol-4-yl ester (**25H**). To a solution of **25** (7.8 mg, 0.025 mmol) in CH₂Cl₂ (1 mL) at rt was added TFA (0.06 mL). After stirring for 3 h, the reaction was neutralized with saturated Na₂CO₃ (2 mL). The aqueous phase was extracted with CH₂Cl₂ (3 X 5 mL). The extracts were dried (Na₂SO₄) and concentrated. Flash chromatography gave 5.1 mg (97%) of amine **25H** as a colorless oil.

25H: ¹H NMR (500 MHz, C₆D₆) δ 5.80 (ddd, *J* = 17.1, 10.3, 6.8 Hz, 1 H), 5.68 (d, *J* = 10.2 Hz, 1 H), 5.44-5.40 (m, 1 H), 5.10 (d, *J* = 16.9 Hz, 1 H), 4.98 (ddd, *J* = 8.8, 8.8, 4.4 Hz, 1 H), 4.92 (d, *J* = 10.3 Hz, 1 H), 3.37-3.32 (m, 2 H), 2.33 (ddd, *J* = 16.6, 5.4, 5.4 Hz, 1 H), 2.08 (ddd, *J* = 15.6, 6.4, 6.4 Hz, 1 H), 1.94-1.85 (m, 2 H), 1.68 (s, 3 H), 1.44 (bs, 1 H), 1.36 (ddd, *J* = 12.7, 8.8, 5.9 Hz, 1 H); ¹³C NMR (125 MHz, C₆D₆) δ 170.4, 141.8, 129.0, 125.2, 114.7, 73.1, 61.7, 58.7, 42.6, 36.9, 30.4, 21.2; IR (neat) 3381 (broad), 2921, 2853, 1736, 1446, 12439 cm⁻¹; LRMS (CI) calc'd for C₁₂H₁₈NO₂ [M+1]⁺ 208.1, found 208.2.

COSY summary: the following crossing peaks are observed: terminal alkene (H(1)) and H(2), H(2) and H(3), H(3) and H(4), H(4) and H(5), H(5) and H(6), H(6) and H(7), H(7) and H(8), H(9) and H(10), H(10) and H(5).

Acetic acid 1-(toluene-4-sulfonyl)-2-vinyl-2,3,3a,4,5,7a-hexahydro-1*H*-indol-4-yl ester (**25Ts**). To a solution of amine **25H** (5.4 mg, 0.026 mmol) in CH₂Cl₂ (1 mL) at rt was added triethyl amine (0.01 mL, 0.08 mmol) and TsCl (0.008 g, 0.04 mmol). The reaction mixture was stirred for 12 h and then quenched with brine (2 mL). The aqueous phase was extracted with CH₂Cl₂ (3 X 5 mL). The extracts were dried (Na₂SO₄) and concentrated. Flash chromatography (8:1 hexanes:ethyl acetate) gave 7.3 mg (77%) of tosyl amine **25Ts** as white solid.

25Ts: m.p. = 126 °C; ^1H NMR (500 MHz, C_6D_6) δ 7.76 (d, J = 7.8 Hz, 2 H), 6.77 (d, J = 7.8 Hz, 2 H), 5.99 (dd, J = 10.3, 2.5 Hz, 1 H), 5.88 (ddd, J = 17.1, 10.3, 6.8 Hz, 1 H), 5.24-5.20 (m, 1 H), 5.19 (ddd, J = 17.0, 1.1, 1.1 Hz, 1 H), 5.00 (d, J = 10.2 Hz, 1 H), 4.83 (dd, J = 7.3, 3.4 Hz, 1 H), 4.59 (dd, J = 5.1, 2.2 Hz, 1 H), 3.99 (ddd, J = 7.3, 7.3, 7.3 Hz, 1 H), 1.88 (s, 3 H), 1.82-1.77 (m, 3 H), 1.58 (s, 3 H), 1.36 (ddd, J = 12.2, 6.9, 6.9 Hz, 1 H), 1.23 (ddd, J = 11.7, 11.7, 8.8 Hz, 1 H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.6, 143.8, 139.9, 135.8, 129.9, 128.2, 127.8, 123.1, 115.9, 69.0, 62.3, 57.7, 39.6, 34.5, 26.2, 21.8, 21.5; IR (neat) 2928, 1733, 1346, 1241, 1161 cm^{-1} ; LRMS (CI) calc'd for $\text{C}_{19}\text{H}_{24}\text{NO}_4\text{S}$ $[\text{M}+1]^+$ 362.1, found, 362.1.

COSY summary: the following crossing peaks are observed: terminal alkenes and H(2), H(2) and H(3), H(3) and H(4), H(4) and H(5), H(5) and H(6), H(6) and H(7), H(7) and H(8), H(9) and H(10), H(10) and H(5).

X-ray (**25Ts**)

4-Acetoxy-2-vinyl-2,3,3a,4,5,7a-hexahydro-indole-1-carboxylic acid *tert*-butyl ester (**26**). To a solution of **22** (12.2 mg, 0.040 mmol) and ethylene (1 atm) in benzene (4 mL) at rt was added **9** (4.5 mg, 0.0053 mmol). The reaction mixture was heated to reflux for 20 h and then concentrated. Flash chromatography (5:1 hexanes:ethyl acetate) gave 11.8 mg (97%) of **26** as colorless oil.

26: ^1H NMR (500 MHz, CDCl_3): δ 5.72-5.52 (m, 3 H), 5.20-4.96 (m, 3 H), 4.59 (broad s, 0.5 H), 4.50 (broad s, 0.5 H), 4.22 (broad s, 0.5 H), 4.12 (broad s, 0.5 H), 2.66-2.59 (m, 1 H), 2.42-2.35 (m, 1 H), 2.11 (ddd, $J = 12.7, 7.3, 7.3$ Hz, 2 H), 2.05 (s, 3H), 1.72-1.62 (m, 1 H), 1.45 (s, 4.5 H), 1.43 (s, 4.5 H); IR (neat) 2919, 2851, 1731, 1240, 1031 cm^{-1} ; LRMS (CI) calc'd for $\text{C}_{17}\text{H}_{26}\text{NO}_4$ $[\text{M}+1]^+$ 308.2, found, 308.1.

Acetic acid 2-vinyl-2,3,3a,4,5,7a-hexahydro-1*H*-indol-4-yl ester (**26H**). To a solution of **27** (7.0 mg, 0.025 mmol) in CH_2Cl_2 (1 mL) at rt was added TFA (0.1 mL). After stirring for 3 h, the reaction was neutralized with saturated Na_2CO_3 (2 mL). The aqueous phase was extracted with CH_2Cl_2 (3 X 5 mL). The extracts were dried (Na_2SO_4) and concentrated. Flash chromatography (gradient of ethyl acetate (neat) to 10:1 ethyl acetate: methanol) gave 4.3 mg (91%) of amine **26H** as a colorless oil.

26H: ^1H NMR (500 MHz, C_6D_6) δ 5.82 (ddd, $J = 17.1, 10.2, 6.8$ Hz, 1 H), 5.62 (ddd, $J = 10.0, 2.2, 2.2$ Hz, 1 H), 5.29-5.25 (m, 1 H), 5.17-5.10 (m, 2 H), 4.93 (ddd, $J = 10.2, 1.5, 1.5$ Hz, 1 H), 3.47-3.39 (m, 2 H), 2.26 (dddd, $J = 9.8, 7.3, 7.3, 4.4$ Hz, 1 H), 2.06-2.03 (m, 2 H), 1.78 (ddd, $J = 12.2, 7.5, 7.5$ Hz, 1 H), 1.66 (s, 3 H), 1.39 (ddd, $J = 12.7, 9.7, 9.7$ Hz, 1 H); ^{13}C NMR (125 MHz, C_6D_6): δ 170.0, 140.8, 129.3, 124.0, 115.3, 69.9, 61.2, 57.6, 41.4, 33.1, 27.6, 21.2. IR (neat) 3358 (broad), 2920, 2851, 1731, 1240 cm^{-1} ; LRMS (CI) calc'd for $\text{C}_{12}\text{H}_{18}\text{NO}_2$ $[\text{M}+1]^+$ 208.1, found, 208.2.

COSY summary: the following crossing peaks are observed: terminal alkenes and H(2), H(2) and H(3), H(3) and H(4), H(4) and H(5), H(6) and H(7), H(7) and H(8), H(9) and H(10), H(10) and H(5).

Acetic acid 1-(toluene-4-sulfonyl)-2-vinyl-2,3,3a,4,5,7a-hexahydro-1*H*-indol-4-yl ester (**26Ts**). To a solution of amine **26H** (4.0 mg, 0.019 mmol) in CH_2Cl_2 (1 mL) at rt was added triethyl amine (40 μL , 0.293 mmol) and TsCl (4.8 mg, 0.025 mmol). The reaction mixture was stirred for 12 h and then quenched with brine (2 mL). The aqueous phase was extracted with CH_2Cl_2 (3 X 5 mL). The extracts were dried (Na_2SO_4) and concentrated. Flash chromatography (10:1, hexanes:ethyl acetate) gave 5.2 mg (75%) of tosyl amine **26Ts** as viscous oil.

26Ts: ^1H NMR (500 MHz, CDCl_3) δ 7.72 (d, $J = 8.3$ Hz, 2 H), 7.33 (d, $J = 7.8$ Hz, 2 H), 5.87 (ddd, $J = 17.3, 10.2, 7.8$ Hz, 1 H), 5.70 (d, $J = 10.3$ Hz, 1 H), 5.58-5.55 (m, 1 H), 5.19 (d, $J = 17.1$ Hz, 1 H), 5.09 (d, $J = 10.3$ Hz, 1 H), 5.04 (ddd, $J = 10.7, 5.8, 5.8$ Hz, 1 H), 4.41 (d, $J = 7.3$ Hz, 1 H), 3.91 (ddd, $J = 9.8, 7.4, 7.4$ Hz, 1 H), 2.44 (s, 3 H), 2.35 (ddd, $J = 17.6, 5.7, 5.7$ Hz, 1 H), 2.13 (ddd, $J = 12.5, 12.5, 6.2$ Hz, 1 H), 2.06-1.96 (m, 2 H), 1.98 (s, 3 H), 1.75 (ddd, $J = 12.7, 12.7, 10.2$ Hz, 1 H); ^{13}C (125 MHz, CDCl_3) δ

170.4, 143.8, 140.2, 135.4, 130.0, 128.7, 127.8, 123.3, 115.5, 68.9, 62.9, 60.9, 39.2, 32.2, 25.7, 21.8, 21.3; IR (neat) 3035, 2927, 1731, 1347, 1240, 1162 cm^{-1} ; LRMS (CI) calc'd for $\text{C}_{19}\text{H}_{24}\text{NO}_4\text{S}$ $[\text{M}+\text{H}]^+$ 362.1, found, 362.1.

COSY summary: the following crossing peaks are observed: terminal alkenes and H(2), H(2) and H(3), H(3) and H(4), H(4) and H(5), H(6) and H(7), H(7) and H(8), H(9) and H(10), H(10) and H(5).

4-(*tert*-Butyl-dimethyl-silanyloxy)-2-vinyl-2,3,3a,4,5,7a-hexahydro-indole-1-carboxylic acid *tert*-butyl ester (**27**) To a solution of **23** (15.0 mg, 0.040 mmol) and ethylene (1 atm) in toluene (5 mL) was added a solution of **9** (5.0 mg, 0.006 mmol) in toluene (1 mL). The reaction mixture was heated to reflux for 20 h and then concentrated. Flash chromatography (15:1, hexanes:ethyl acetate) gave 13.8 mg (92%) of indoline **27** as a colorless oil.

27: ^1H NMR (500 MHz, CDCl_3) δ 5.85 (broad d, $J = 9.3$ Hz, 1 H), 5.71 (ddd, $J = 16.6, 7.3, 7.3$ Hz, 1 H), 5.54 (broad d, $J = 9.8$ Hz, 1 H), 5.06 (d, $J = 16.6$ Hz, 1 H), 4.98 (d, $J = 10.3$ Hz, 1 H), 4.40 (broad s, 1 H), 4.23 (broad s, 1 H), 3.95 (broad s, 1 H), 2.35-2.27 (m, 1 H), 2.22 (broad d, $J = 17.6$ Hz, 1 H), 2.11-2.04 (m, 1 H), 1.97 (broad d, $J = 18.1$ Hz, 1 H), 1.61-1.49 (m, 1 H), 1.44 (s, 9 H), 0.87 (s, 9 H), 0.05 (s, 3 H), 0.04 (s, 3 H); IR (neat) 2931, 2859, 1695, 1387, 1176, 1092 cm^{-1} ; LRMS (CI) calc'd for $\text{C}_{21}\text{H}_{38}\text{NO}_3\text{Si}$ $[\text{M}+1]^+$ 380.3, found, 380.1.

4-(*tert*-Butyl-dimethyl-silanyloxy)-2-vinyl-2,3,3a,4,5,7a-hexahydro-1*H*-indole (**27H**).

To a solution of **27** (4.2 mg, 0.011 mmol) in CH₂Cl₂ (1 mL) at rt was added TFA (0.06 mL). After stirring for 3 h, the reaction was neutralized with saturated Na₂CO₃ (2 mL). The aqueous phase was extracted with CH₂Cl₂ (3 X 5 mL). The extracts were dried (Na₂SO₄) and concentrated. Flash chromatography (gradient of ethyl acetate (neat) to methanol (neat)) gave 2.8 mg (90%) of amine **27H** as a colorless oil.

27H: ¹H NMR (500 MHz, C₆D₆): δ 5.95 (ddd, *J* = 17.5, 10.2, 7.3 Hz, 1 H), 5.75 (ddd, *J* = 9.8, 2.6, 2.6 Hz, 1 H), 5.57 (dddd, *J* = 9.8, 5.8, 2.0, 2.0 Hz, 1 H), 5.17 (ddd, *J* = 17.1, 1.7, 1.7 Hz, 1 H), 4.99 (dd, *J* = 10.3, 1.5 Hz, 1 H), 3.70 (ddd, *J* = 9.2, 9.2, 4.9 Hz, 1 H), 3.39-3.34 (m, 2 H), 2.14 (ddd, *J* = 16.6, 4.9, 4.9 Hz, 1 H), 2.07-1.92 (m, 3 H), 1.61-1.56 (m, 1 H), 0.98 (s, 9 H), 0.07 (s, 3 H), 0.03 (s, 3 H); ¹³C NMR (125 MHz, CDCl₃) δ 133.1, 131.7, 121.4, 120.5, 68.8, 61.4, 58.4, 43.1, 34.5, 33.3, 25.9, 18.1, -4.1, -4.8; IR(neat) 3398 (broad), 2919, 2851, 1070 cm⁻¹; LRMS (CI) calc'd for C₁₆H₃₀NOSi [M+1]⁺ 280.2, found, 280.2.

COSY summary: the following crossing peaks are observed: terminal alkenes (H(1)) and H(2), H(2) and H(3), H(3) and H(4), H(4) and H(5), H(5) and H(6), H(6) and H(7), H(7) and H(8), H(9) and H(10), H(10) and H(5).

4-(*tert*-Butyl-dimethyl-silanyloxy)-2-vinyl-2,3,3a,4,5,7a-hexahydro-indole-1-carboxylic acid *tert*-butyl ester (**28**). To a solution of **24** (10.0 mg, 0.026 mmol) and

ethylene (1 atm) in toluene (5 mL) was added **9** (3.4 mg, 0.004 mmol). The reaction mixture was heated to reflux for 12 h and then concentrated. Flash chromatography gave 8.8 mg (88%) of indoline **28** as a white solid.

28: m.p. = 53-55 °C; ¹H NMR (500 MHz, CDCl₃) δ 5.71-5.61 (m, 2 H), 5.52-5.46 (m, 1 H), 5.17-4.94 (m, 2 H), 4.50 (broad s, 0.5 H), 4.40 (broad s, 0.5 H), 4.22-4.06 (m, 2 H), 2.45 (broad s, 1 H), 2.21-2.10 (m, 2 H), 2.06-2.01 (m, 1 H), 1.68-1.58 (m, 1 H), 1.44 (s, 4.5 H), 1.42 (s, 4.5 H), 0.88 (s, 9 H), 0.05 (s, 3 H), 0.04 (s, 3 H); IR (neat) 2928, 2856, 1676, 1089 cm⁻¹; LRMS (CI) calc'd for C₂₁H₃₈NO₃Si [M+H]⁺ 380.3, found, 380.2.

4-(*tert*-Butyl-dimethyl-silanyloxy)-2-vinyl-2,3,3a,4,5,7a-hexahydro-1*H*-indole (**28H**).

To a solution of **28** (5.0 mg, 0.013 mmol) in CH₂Cl₂ (1 mL) at rt was added TFA (0.08 mL). After stirring for 3 h, the reaction was neutralized with saturated Na₂CO₃ (2 mL). The aqueous phase was extracted with CH₂Cl₂ (3 X 5 mL). The extracts were dried (Na₂SO₄) and concentrated. Flash chromatography (gradient of ethyl acetate (neat) to methanol (neat)) gave 3.3 mg (90%) of amine **28H** as a colorless oil.

28H: ¹H NMR (500 MHz, C₆D₆) δ 5.90 (ddd, *J* = 17.1, 9.8, 6.8 Hz, 1 H), 5.73 (d, *J* = 9.8 Hz, 1 H), 5.38-5.36 (m, 1 H), 5.15 (d, *J* = 17.1 Hz, 1 H), 4.96 (d, *J* = 10.2 Hz, 1 H), 3.80-3.67 (m, 3 H), 2.36-2.29 (m, 1 H), 1.99-1.86 (m, 3 H), 1.57 (ddd, *J* = 10.5, 10.5, 10.5 Hz, 1 H), 1.36-1.18 (m, 2 H), 0.92 (s, 9 H), -0.01 (s, 3 H), -0.03 (s, 3 H); ¹³C NMR (125 MHz, CDCl₃) δ 140.4, 128.9, 124.4, 115.3, 68.2, 61.4, 57.8, 44.2, 33.1, 31.3, 26.1, 18.3, -4.3, -4.5; IR (neat) 3400 (broad), 2928, 2856 1693, 1386, 1096 cm⁻¹; LRMS (CI) calc'd for C₁₆H₃₀NOSi [M+H]⁺ 280.2, found, 280.2.

COSY summary: the following crossing peaks are observed: terminal alkene (H(1)) and H(2), H(2) and H(3), H(3) and H(4), H(4) and H(5), H(5) and H(6), H(6) and H(7), H(7) and H(8), H(8) and H(9), H(9) and H(10), H(10) and H(5).

Acetic acid 1-bromomethyl-3-oxo-4a,7,8,8a,9,9a-hexahydro-1*H*-oxazolo[3,4-*a*]indol-8-yl ester (**29**). To a mixture of **26** (15.0 mg, 0.049 mmol), THF (1.0 mL), and H₂O (0.6 mL) at 0°C was added NBS (10.8 mg, 0.060 mmol). After stirring for 6 h, the reaction mixture was diluted with brine. The aqueous phase was extracted with CH₂Cl₂ (3 X 5 mL). The extracts were dried (Na₂SO₄) and concentrated. Flash chromatography (solvent) gave 15.0 mg (93%) of **29** as a colorless oil.

29: ¹H NMR (500 MHz, CDCl₃) δ 6.29 (ddd, *J* = 10.3, 4.9, 2.4 Hz, 1 H), 5.75 (dddd, *J* = 9.4, 4.7, 3.3, 1.5 Hz, 1 H), 5.10 (ddd, *J* = 7.5, 4.9, 4.9 Hz, 1 H), 4.41 (ddd, *J* = 9.0, 6.7, 4.2 Hz, 1 H), 4.21-4.19 (m, 1 H), 3.94 (ddd, *J* = 8.8, 6.7, 6.7 Hz, 1 H), 3.62 (ddd, *J* = 10.2, 4.3, 1.1 Hz, 1 H), 3.43 (dd, *J* = 10.2, 9.0 Hz, 1 H), 2.85-2.80 (m, 1 H), 2.39-2.33 (m, 1 H), 2.31-2.22 (m, 2 H), 2.07 (s, 3 H), 1.69 (ddd, *J* = 12.4, 9.1, 9.1 Hz, 1 H); ¹³C NMR (125 MHz, CDCl₃) δ 170.7, 156.2, 125.5, 122.8, 80.1, 69.0, 64.3, 55.5, 42.8, 32.1, 31.5, 27.3, 21.3; IR (neat) 2920, 2851, 1754, 1241 cm⁻¹; LRMS (CI) calc'd for C₁₃H₁₇BrNO₄ [M+H]⁺ 330.0, found, 330.2, also found [M+H+2]⁺ 332.1

COSY summary: the following crossing peaks are observed: H(1) and H(2), H(2) and H(3), H(3) and H(4), H(4) and H(5), H(5) and H(6), H(6) and H(7), H(7) and H(8), H(8) and H(9), H(9) and H(10), H(10) and H(5).

1-Bromomethyl-8-(*tert*-butyl-dimethyl-silanyloxy)-4a,7,8,8a,9,9a-hexahydro-1*H*-oxazolo[3,4-*a*]indol-3-one (**30**). To a mixture of **28** (10.0 mg, 0.026 mmol), THF (1.0 mL), and H₂O (0.3 mL) at 0°C was added NBS (5.9 mg, 0.032 mmol). After stirring for 6 h, the reaction mixture was diluted with brine. The aqueous phase was extracted with CH₂Cl₂ (3 X 5 mL). The extracts were dried (Na₂SO₄) and concentrated. Flash chromatography (6:1 hexanes:ethyl acetate) gave 7.4 mg (70%) of **30** as a colorless oil.

30: ¹H NMR (500 MHz, CDCl₃) δ 6.21 (d, *J* = 10.3 Hz, 1 H), 5.69-5.65 (m, 1 H), 4.44 (ddd, *J* = 8.1, 8.1, 4.4 Hz, 1 H), 4.26-4.24 (m, 1 H), 4.03 (ddd, *J* = 9.8, 5.2, 5.2 Hz, 1 H), 3.93 (ddd, *J* = 10.7, 7.8, 5.4 Hz, 1 H), 3.60 (dd, *J* = 10.2, 3.9 Hz, 1 H), 3.44 (dd, *J* = 10.2, 8.3 Hz, 1 H), 2.77 (ddd, *J* = 12.7, 12.7, 5.4 Hz, 1 H), 2.23 (ddd, *J* = 17.6, 5.9, 5.9 Hz, 1 H), 2.14-2.04 (m, 2 H), 1.65 (dd, *J* = 11.7, 11.7 Hz, 1 H), 0.89 (s, 9 H), 0.07 (s, 3 H), 0.07 (s, 3 H); ¹³C NMR (125 MHz, CDCl₃) δ 155.9, 126.4, 126.2, 122.9, 80.3, 67.1, 64.9, 55.7, 48.0, 31.9, 30.2, 30.1, 26.0, 18.2, -4.4, -4.6; IR (neat) 2926, 2855, 1761, 1098 cm⁻¹; LRMS (CI) calc'd for C₁₇H₂₉BrNO₃Si [M+1]⁺ 402.1, found, 402.1, [M+2+H] 404.1

COSY summary: the following crossing peaks are observed: H(1) and H(2), H(2) and H(3), H(3) and H(4), H(4) and H(5), H(6) and H(7), H(7) and H(8), H(8) and H(9), H(9) and H(10), H(10) and H(5).

4-(*tert*-Butyl-dimethyl-silanyloxy)-2-(2-oxo-ethyl)-2,3,3a,4,5,7a-hexahydro-indole-1-carboxylic acid *tert*-butyl ester (**31**). To a solution of **30** (0.045 g, 0.11 mmol) in MeOH (3 mL) at rt was added K₂CO₃ (0.46 g, 3.36 mmol). The reaction mixture was stirred at rt for 12 h, diluted with brine (5 mL), and extracted with ethyl acetate (3 X 10 mL). The organic phase was dried (Na₂SO₄) and concentrated. Flash chromatography (5:1 hexanes:ethyl acetate) gave 25.3 mg (64%) of epoxide **31** as a white solid.

31: mp 78-80 °C; ¹H NMR (500 MHz, CDCl₃): δ 5.61-5.54 (m, 2 H), 4.59-4.44 (m, 1 H), 4.05-3.96 (m, 2 H), 3.74 (broad s, 3 H), 3.16 (broad s, 0.5 H), 3.01 (broad s, 0.5 H), 2.71 (dd, *J* = 4.6, 4.6 Hz, 1 H), 2.49-2.40 (m, 2 H), 2.26-2.14 (m, 1 H), 2.10-2.00 (m, 2 H), 1.75-1.71 (m, 1 H), 0.87 (s, 9H), 0.04 (s, 3 H), 0.04 (s, 3H); IR (neat) 2953, 2930, 2857, 1702, 1450, 1374, 1254, 1190, 1099 cm⁻¹; LRMS (CI) calc'd for C₁₈H₃₂NO₄Si [M+1]⁺ 354.2, found, 354.3.

5-Bromo-7-(*tert*-butyl-dimethyl-silanyloxy)-2-oxo-3-oxa-10-azatricyclo[6.2.1.00,0]undecane-10-carboxylic acid methyl ester (**33**). To a solution of **31** (25.0 mg, 0.071 mmol) in diethyl ether (3 mL) at rt was added a solution of periodic acid (64.3 mg, 0.28 mmol) in THF (0.4 mL). After stirring for 4 h an additional portion of

periodic acid (12 mg, 0.05 mmol) was added. After stirring an additional 0.5 h, the reaction mixture was diluted with brine (3 mL). The aqueous phase was extracted with ether (3 X 6 mL). The organic phase was dried (Na₂SO₄) and concentrated. Flash chromatography (6:1 hexanes:ethyl acetate) gave 15 mg (62%) of aldehyde **31a** as a colorless oil.

31a: ¹H NMR (500 MHz, CDCl₃) δ 9.37 (d, *J* = 3.3 Hz, 0.5 H), 9.27 (d, *J* = 3.6 Hz, 0.5 H), 5.74 (d, *J* = 10.5 Hz, 0.5 H), 5.64-5.58 (m, 1.5 H), 4.62 (broad d, *J* = 6.6 Hz, 0.5 H), 4.49 (broad d, *J* = 5.9 Hz, 0.5 H) 4.18 (ddd, *J* = 10.8, 7.9, 3.5 Hz, 0.5 H), 4.12-4.04 (m, 1.5 H), 3.75 (s, 1.5 H), 3.68 (s, 1.5 H), 2.61-2.53 (m, 1 H), 2.27-2.14 (m, 2 H), 2.05-2.00 (m, 1 H), 1.83-1.71 (m, 1 H), 0.88 (s, 9 H), 0.06 (s, 3H), 0.05 (s, 3 H); ¹³C NMR (125 MHz, CDCl₃) δ 168.0, 154.4, 77.2, 64.5, 56.4, 52.9, 45.4, 41.7, 30.1, 29.4, 25.9, 18.2, -4.9, -4.6; IR (neat) 2929, 2856, 1737, 1702, 1659, 1453, 1374, 1098 cm⁻¹; LRMS (CI) calc'd for C₁₇H₃₀NO₄Si [M+H]⁺ 340.2, found, 340.2.

To a solution of aldehyde **31a** (13 mg, 0.0383 mmol) and 2-methyl-2-butene (0.2 mL, 2.22 mmol) in *t*-butyl alcohol (0.5 mL) at rt was slowly added a solution of NaClO₂ (35 mg, 0.31 mmol) and NaH₂PO₄ (39 mg, 0.33 mol) in H₂O (0.4 mL). The reaction mixture was stirred for 2 h and then diluted with saturated NH₄Cl (3 mL). The aqueous phase was extracted with CH₂Cl₂ (3 X 5 mL). The extracts were dried and concentrated. Flash chromatography gave acid 13.6 mg (100%) of acid **32** as white solid. The acid was taken directly into the bromolactonization reaction.

To a mixture of acid **32** (13.6 mg, 0.0383 mmol), THF (1.5 mL), and H₂O (0.5 mL) at 0 °C was added NBS (12.6 mg, 0.07 mmol). The reaction mixture was stirred for 5 h, diluted with brine (2 mL), and extracted with CH₂Cl₂ (3 X 5 mL). The extracts were dried

(Na₂SO₄) and concentrated. Flash chromatography (5:1 hexanes:ethyl acetate) gave lactone 7.0 mg (42%) of lactone **33** as a colorless oil.

33: ¹H NMR (500 MHz, CDCl₃) δ 4.80 (broad s, 1 H), 4.77 (broad s, 1 H), 4.66 (broad s, 1 H), 4.44 (ddd, *J* = 11.0, 5.5, 5.5 Hz, 1 H), 4.33 (dd, *J* = 6.4, 2.9 Hz, 1 H), 3.76 (s, 3 H), 2.72 (dddd, *J* = 12.2, 5.9, 5.9, 5.9 Hz, 1 H), 2.30 (ddd, *J* = 14.7, 11.8, 8.4 Hz, 1 H), 2.04-1.90 (m, 3 H), 0.087 (s, 9 H), 0.08 (s, 3H), 0.08 (s, 3 H); ¹³C NMR (125 MHz, CDCl₃) δ 168.0, 154.4, 77.2, 64.5, 56.4, 53.5, 52.9, 45.4, 41.7, 30.1, 29.4, 25.9, 18.2, -4.9, -4.6; IR (neat) 3159, 2923, 1773, 1694, 1372, 1191 cm⁻¹; LRMS (CI) calc'd for C₁₇H₂₉BrNO₅Si [M+H]⁺ 434.1, found, 433.9, [M+H+2]⁺ 436.0

COSY summary: the following crossing peaks are observed: H(2) and H(3), (3'); H(3), (3') and H(4), H(4) and H(5), H(5) and H(6),(6'); H(6) (6') and H(7), H(7) and H(8), H(8) and H(9), H(9) and H(5).