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(1S)-2-Ethoxy-1-methyl-2-oxoethyl (1R,5R)-8-(1,1-Dimethylethoxy carbonyl)-5-methyl-8-azabicyclo[3.2.1]octa-2,6-diene-2-carboxylate [20b]. ($\text{Rh}_2(\text{OOct})_4$, 9:1-4:1 petroleum ether/ Et_2O , 0.93 g, 54% yield, 59% de). ^1H NMR (500 MHz, toluene- d_8 , 95 °C) δ 6.58 (t, J = 3.7 Hz, 1H), 6.12 (dd, J = 6.0, 2.6 Hz, 0.2H, minor diastereomer), 6.06 (dd, J = 5.8, 2.8 Hz, 0.8H, major diastereomer), 5.24 (d, J = 6.1 Hz, 1H), 5.17 (br s, 1H), 5.13 (q, J = 6.8 Hz, 1H), 3.94 (q, J = 7.2 Hz, 2H), 2.74 (dd, J = 19.7, 2.9 Hz, 1H), 1.60 (s, 3H), 1.54 (dd, J = 19.7, 3.8 Hz, 1H), 1.38 (s, 9H), 1.32 (d, J = 6.8 Hz, 3H), 0.98 (t, J = 7.2 Hz, 3H); IR (neat) 3084, 2981, 2934, 1760, 1714, 1626, 1367, 1341, 1238 cm^{-1} . Anal. Calcd for $\text{C}_{19}\text{H}_{27}\text{NO}_6$: C, 62.45; H, 7.45; N, 3.83. Found: C, 62.37; H, 7.40; N, 3.76.

(1S)-2-Ethoxy-1-methyl-2-oxoethyl (1R,5R)-5-(tert-Butyldimethylsiloxy-methyl)-8-(1,1-dimethylethoxycarbonyl)-8-azabicyclo[3.2.1]octa-2,6-diene-2-carboxylate [20c]. ($\text{Rh}_2(\text{OOct})_4$, 9:1 pentane/ Et_2O , 0.81 g, 62% yield, 70% de). ^1H NMR (500 MHz, toluene- d_8 , 95 °C) δ 6.61 (t, J = 3.7 Hz, 1H), 6.18 (dd, J = 6.1, 2.6 Hz, 0.15H, minor diastereomer), 6.13 (dd, J = 6.1, 2.6 Hz, 0.85H, major diastereomer), 5.91 (d, J = 6.1 Hz, 1H), 5.20 (br s, 1H), 5.14 (q, J = 7.0 Hz, 1H), 4.47 (d, J = 9.9 Hz, 1H), 4.10 (d, J = 9.9 Hz, 1H), 3.95 (q, J = 7.0 Hz, 2H), 2.72 (br d, J = 19.8 Hz, 1H), 1.92 (dd, J = 19.8, 3.7 Hz, 1H), 1.39 (s, 9H), 1.33 (d, J = 7.0 Hz, 3H), 0.98 (t, J = 7.0 Hz, 3H), 0.93 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); IR (neat) 3090, 2971, 2934, 1760, 1703, 1625, 1476, 1414, 1347 cm^{-1} . Anal. Calcd for $\text{C}_{25}\text{H}_{41}\text{NO}_7\text{Si}$: C, 60.58; H, 8.34; N, 2.83. Found: C, 60.44; H, 8.28; N, 2.90.

(1S)-2-Ethoxy-1-methyl-2-oxoethyl (1R,5R)-8-(1,1-Dimethylethoxycarbonyl)-5-phenyl-8-azabicyclo[3.2.1]octa-2,6-diene-2-carboxylate [20d]. ($\text{Rh}_2(\text{OOct})_4$, 9:1-3:1 pentane/ Et_2O , 1.30 g, 64% yield, 53% de). ^1H NMR (500 MHz, toluene- d_8 , 95 °C) δ 7.33 (d, J = 7.6 Hz, 2H), 7.16 (t, J = 7.6 Hz, 3H), 6.71 (d, J = 3.1 Hz, 1H), 6.21 (dd, J = 6.0, 2.6 Hz, 0.24H, minor diastereomer), 6.14 (dd, J = 5.8, 2.7 Hz, 0.76H, major diastereomer), 5.39 (br s, 1H), 5.27 (d, J = 5.7 Hz, 1H), 5.17 (q, J = 7.0 Hz, 1H), 3.98 (q, J = 7.2 Hz, 2H), 3.23 (dd,

$J = 19.1, 2.6$ Hz, 1H), 2.06 (dd, $J = 19.1, 3.7$ Hz, 1H), 1.34 (d, $J = 7.0$ Hz, 3H), 1.19 (s, 9H), 1.01 (t, $J = 7.2$ Hz, 3H); IR (neat) 3064, 2981, 2934, 1724, 1647, 1450, 1367, 1331, 1248 cm^{-1} . Anal. Calcd for $\text{C}_{24}\text{H}_{29}\text{NO}_6$: C, 67.43; H, 6.84; N, 3.28. Found: C, 67.29; H, 6.85; N, 3.17.

(1S)-2-Ethoxy-1-methyl-2-oxoethyl (1R,5R)-5-Acetyl-8-(1,1-dimethylethoxy carbonyl)-8-azabicyclo[3.2.1]octa-2,6-diene-2-carboxylate [20e]. ($\text{Rh}_2(\text{OOct})_4$, 4:1 hexanes/EtOAc, 0.31 g, 30% yield, 67% de). ^1H NMR (500 MHz, toluene- d_8 , 95 $^\circ\text{C}$) δ 6.53 (t, $J = 3.6$ Hz, 1H), 6.19 (br s, 0.17H, minor diastereomer), 6.14 (br s, 0.83H, major diastereomer), 5.16 (m, 2H), 5.11 (q, $J = 7.0$ Hz, 1H), 3.94 (q, $J = 7.2$ Hz, 2H), 3.05 (br d, $J = 20.8$ Hz, 1H), 2.09 (s, 3H), 1.95 (dd, $J = 20.8, 3.6$ Hz, 1H), 1.31 (s, 9H), 1.31 (d, $J = 7.0$ Hz, 3H), 0.97 (t, $J = 7.2$ Hz, 3H); IR (neat) 3084, 2986, 2934, 1755, 1709, 1626, 1460, 1357, 1274, 1202 cm^{-1} . Anal. Calcd for $\text{C}_{20}\text{H}_{27}\text{NO}_7$: C, 61.06; H, 6.92; N, 3.56. Found: C, 61.00; H, 6.96; N, 3.52.

(1S)-2-Ethoxy-1-methyl-2-oxoethyl (1R,5R)-1,5-Dimethyl-8-(1,1-dimethyl ethoxycarbonyl)-8-azabicyclo[3.2.1]octa-2,6-diene-2-carboxylate [20f]. ($\text{Rh}_2(\text{OOct})_4$, 9:1 pentane/ Et_2O , 0.57 g, 33% yield, 25% de). ^1H NMR (500 MHz, CDCl_3) δ 6.58 (dd, $J = 3.7, 3.3$ Hz, 0.38H, minor diastereomer), 6.55 (dd, $J = 3.9, 3.2$ Hz, 0.62H, major diastereomer), 6.02 (d, $J = 6.1$ Hz, 1H), 5.46 (d, $J = 6.1$ Hz, 1H), 5.11 (q, $J = 7.0$ Hz, 1H), 4.21 (q, $J = 7.2$ Hz, 2H), 2.72 (dd, $J = 19.8, 3.2$ Hz, 1H), 1.93 (dd, $J = 19.8, 3.9$ Hz, 1H), 1.56 (s, 6H), 1.52 (d, $J = 7.0$ Hz, 3H), 1.44 (s, 9H), 1.29 (t, $J = 7.2$ Hz, 3H); IR (neat) 3069, 2981, 2940, 1750, 1724, 1714, 1455, 1372 cm^{-1} . Anal. Calcd for $\text{C}_{20}\text{H}_{29}\text{NO}_6$: C, 63.31; H, 7.70; N, 3.69. Found: C, 63.22; H, 7.74; N, 3.76.

(1S)-2-Ethoxy-1-methyl-2-oxoethyl (1R,5R)-8-(1,1-Dimethylethoxycarbonyl)-6-methyl-8-azabicyclo[3.2.1]octa-2,6-diene-2-carboxylate [20g]. ($\text{Rh}_2(\text{OOct})_4$, 9:1-4:1 pentane/ Et_2O , 0.18 g, 19% yield, 52% de). ^1H NMR (500 MHz, toluene- d_8 , 95 $^\circ\text{C}$) δ 6.49 (br s, 1H), 5.89 (br s, 0.24H, minor diastereomer), 5.83 (br s, 0.76H, major diastereomer), 5.12

(q, $J = 7.1$ Hz, 1H), 5.09 (br s, 1H), 4.27 (br d, $J = 4.1$ Hz, 1H), 3.93 (q, $J = 7.0$ Hz, 2H), 2.60 (br d, $J = 18.2$ Hz, 1H), 2.09 (s, 3H), 1.50 (dd, $J = 18.2, 4.1$ Hz, 1H), 1.42 (s, 9H), 1.30 (d, $J = 7.1$ Hz, 3H), 0.97 (t, $J = 7.0$ Hz, 3H); IR (neat) 2981, 2940, 2914, 1755, 1703, 1625, 1481, 1450, 1367, 1253 cm^{-1} . Anal. Calcd for $\text{C}_{19}\text{H}_{27}\text{NO}_6$: C, 62.45; H, 7.45; N, 3.83. Found: C, 62.63; H, 7.53; N, 3.62.

(1S)-2-Ethoxy-1-methyl-2-oxoethyl (1R,5R)-12-(1,1-Dimethylethoxy carbonyl)-12-azatricyclo[5.4.1^{1.5}.0^{1.7}]dodeca-3,6-diene-4-carboxylate [20h]. ($\text{Rh}_2(\text{OOct})_4$, 4:1 hexanes/EtOAc, 0.46 g, 48% yield, 55% de). ^1H (500 MHz, toluene- d_8 , 95 °C) δ 6.63 (br s, 1H), 5.81 (br s, 0.23H, minor diastereomer), 5.76 (br s, 0.77H, major diastereomer), 5.09 (q, $J = 7.0$ Hz, 1H), 5.04 (br s, 1H), 3.95 (q, $J = 7.0$ Hz, 2H), 2.77-2.63 (m, 1H), 2.60-2.45 (m, 1H), 2.17-2.05 (m, 1H), 1.90-1.70 (m, 3H), 1.60-1.40 (m, 2H), 1.37 (s, 9H), 1.32 (d, $J = 7.0$ Hz, 3H), 1.15-1.05 (m, 2H), 0.99 (t, $J = 7.0$ Hz, 3H); IR (neat) 2975, 2934, 2862, 1749, 1698, 1620, 1449, 1361, 1252, 1201, 1170 cm^{-1} ; MS m/e (relative intensity) 349 ($\text{M}^+ (-t\text{-Bu})$) (4), 321 (13), 305 (35), 304 (25), 232 (16), 231 (44), 204 (61), 187 (99), 186 (75), 160 (33), 159 (100), 130 (12); HRMS Calcd for $\text{C}_{18}\text{H}_{23}\text{NO}_6 (-t\text{-Bu})$ 349.1525; found: 349.1528.

(1S)-2-Ethoxy-1-methyl-2-oxoethyl (1R,5R)-8-(1,1-Dimethylethoxycarbonyl)-3-(1,1-dimethylethoxysiloxy)-5-methyl-8-azabicyclo[3.2.1]octa-2,6-diene-2-carboxylate [21b]. ($\text{Rh}_2(\text{OOct})_4$, 9:1-4:1 petroleum ether/ Et_2O , 1.31 g, 55% yield, 58% de). ^1H NMR (500 MHz, toluene- d_8 , 95 °C) δ 6.29 (dd, $J = 5.8, 2.8$ Hz, 0.21H, minor diastereomer), 6.17 (dd, $J = 5.8, 2.8$ Hz, 0.79H, major diastereomer), 5.36 (d, $J = 2.8$ Hz, 1H), 5.29 (d, $J = 5.8$ Hz, 1H), 5.13 (q, $J = 7.0$ Hz, 1H), 3.96 (q, $J = 7.0$ Hz, 2H), 2.99 (d, $J = 17.7$ Hz, 1H), 1.76 (d, $J = 17.7$ Hz, 1H), 1.66 (s, 3H), 1.45 (s, 9H), 1.33 (d, $J = 7.0$ Hz, 3H), 1.01 (t, $J = 7.0$ Hz, 3H), 0.96 (s, 9H), 0.23 (s, 3H), 0.19 (s, 3H); IR (neat) 2981, 2929, 2893, 2862, 1766, 1703, 1605, 1481, 1445, 1372 cm^{-1} . Anal. Calcd for $\text{C}_{25}\text{H}_{41}\text{NO}_7\text{Si}$: C, 60.58; H, 8.34; N, 2.83. Found: C, 60.31; H, 8.28; N, 2.76.

(1S)-2-Ethoxy-1-methyl-2-oxoethyl (1R,5R)-8-(1,1-Dimethylethoxycarbonyl)-3-(1,1-dimethylethoxysiloxy)-5-phenyl-8-azabicyclo[3.2.1]octa-2,6-diene-2-carboxylate [21d]. ($\text{Rh}_2(\text{OOct})_4$, 9:1-4:1 pentane/ Et_2O , 1.98 g, 74% yield, 52% de). ^1H NMR (500 MHz, toluene- d_8 , 95 °C) δ 7.40 (d, $J = 7.4$ Hz, 2H), 7.16 (t, $J = 7.4$ Hz, 3H), 6.38 (dd, $J = 6.0, 2.6$ Hz, 0.24H, minor diastereomer), 6.26 (dd, $J = 5.8, 2.8$ Hz, 0.76H, major diastereomer), 5.55 (d, $J = 2.8$ Hz, 1H), 5.35 (d, $J = 5.8$ Hz, 1H), 5.18 (q, $J = 7.0$ Hz, 1H), 3.99 (q, $J = 7.0$ Hz, 2H), 3.52 (d, $J = 17.2$ Hz, 1H), 2.34 (d, $J = 17.2$ Hz, 1H), 1.36 (d, $J = 7.0$ Hz, 3H), 1.25 (s, 9H), 1.04 (t, $J = 7.0$ Hz, 3H), 1.00 (s, 9H), 0.30 (s, 3H), 0.26 (s, 3H); IR (neat) 3033, 2986, 2960, 2862, 1755, 1711, 1605, 1476, 1455, 1367 cm^{-1} . Anal. Calcd for $\text{C}_{30}\text{H}_{43}\text{NO}_7\text{Si}$: C, 64.60; H, 7.77; N, 2.51. Found: C, 64.70; H, 7.78; N, 2.41.

(1S)-2-Ethoxy-1-methyl-2-oxoethyl (1R,5R)-5-Acetyl-8-(1,1-dimethylethoxycarbonyl)-3-(1,1-dimethylethoxysiloxy)-8-azabicyclo[3.2.1]octa-2,6-diene-2-carboxylate [21e]. ($\text{Rh}_2(\text{OOct})_4$, 9:1-4:1 pentane/ Et_2O , 1.45 g, 58% yield, 79% de). ^1H NMR (500 MHz, toluene- d_8 , 95 °C) δ 6.40 (br s, 0.1H, minor diastereomer), 6.28 (br d, $J = 3.7$ Hz, 0.9H, major diastereomer), 5.24 (d, $J = 5.8$ Hz, 1H), 5.15 (q, $J = 7.0$ Hz, 1H), 5.18 (s, 1H), 3.97 (q, $J = 7.1$ Hz, 2H), 3.27 (br d, $J = 18.6$ Hz, 1H), 2.16 (d, $J = 18.6$ Hz, 1H), 2.13 (s, 3H), 1.40 (s, 9H), 1.33 (d, $J = 7.0$ Hz, 3H), 1.01 (t, $J = 7.1$ Hz, 3H), 0.94 (s, 9H), 0.22 (s, 3H), 0.18 (s, 3H); IR (neat) 3084, 2986, 2940, 1755, 1714, 1623, 1462, 1357 cm^{-1} . Anal. Calcd for $\text{C}_{26}\text{H}_{41}\text{NO}_8\text{Si}$: C, 59.63; H, 7.89; N, 2.67. Found: C, 59.67; H, 7.93; N, 2.57.

(1S)-2-Ethoxy-1-methyl-2-oxoethyl (1R,5R)-8-(1,1-Dimethylethoxycarbonyl)-3-(1,1-dimethylethoxysiloxy)-8-azabicyclo[3.2.1]octa-2,6-diene-2-carboxylate [21f]. ($\text{Rh}_2(\text{OOct})_4$, 9:1 petroleum ether/ Et_2O , 0.37 g, 30% yield, 52% de). ^1H NMR (500 MHz, toluene- d_8 , 95 °C) δ 6.06 (d, $J = 5.8$ Hz, 0.76H, major diastereomer), 6.01 (d, $J = 5.8$ Hz, 0.24H, minor diastereomer), 5.20 (d, $J = 5.8$ Hz, 1H), 5.17 (q, $J = 7.0$ Hz, 1H), 3.96 (q, $J = 7.0$ Hz, 2H), 3.06 (d, $J = 17.4$ Hz, 1H), 1.97 (s, 3H), 1.70 (d, $J = 17.4$ Hz, 1H), 1.68 (s, 3H), 1.45 (s, 9H), 1.36 (d, $J = 7.0$ Hz, 3H), 1.00 (t, $J = 7.0$ Hz, 3H), 0.93 (s, 9H), 0.21 (s, 3H), 0.16 (s,

3H); IR (neat) 3079, 2960, 2934, 2898, 2862, 1729, 1698, 1631, 1466, 1367, 1259 cm^{-1} . Anal. Calcd for $\text{C}_{26}\text{H}_{43}\text{NO}_7\text{Si}$: C, 61.27; H, 8.50; N, 2.75. Found: C, 61.23; H, 8.52; N, 2.66.

(3*R*)-Tetrahydro-4,4-dimethyl-2-oxo-3-furanyl (1*S*,5*S*)-8-(1,1-Dimethylethoxycarbonyl)-3-(1,1-dimethylethoxysiloxy)-5-phenyl-8-azabicyclo[3.2.1]octa-2,6-diene-2-carboxylate [23d]. ($\text{Rh}_2(\text{OOct})_4$, 9:1-4:1 pentane/ Et_2O , 1.45 g, 56% yield, 52% de). ^1H NMR (500 MHz, toluene- d_8 , 95 $^\circ\text{C}$) δ 7.42 (d, $J = 7.5$ Hz, 2H), 7.18 (t, $J = 7.5$ Hz, 3H), 6.37 (dd, $J = 6.0, 2.6$ Hz, 0.24H, minor diastereomer), 6.21 (dd, $J = 6.1, 2.8$ Hz, 0.76H, major diastereomer), 5.52 (d, $J = 2.4$ Hz, 1H), 5.39 (d, $J = 6.1$ Hz, 1H), 5.18 (s, 1H), 3.59 (d, $J = 17.2$ Hz, 1H), 3.43 (d, $J = 8.9$ Hz, 1H), 3.28 (d, $J = 8.9$ Hz, 1H), 2.36 (d, $J = 17.2$ Hz, 1H), 1.31 (s, 9H), 1.01 (s, 9H), 0.83 (s, 3H), 0.77 (s, 3H), 0.31 (s, 3H), 0.27 (s, 3H); IR (neat) 2971, 2934, 2867, 1802, 1734, 1605, 1476, 1372 cm^{-1} . Anal. Calcd for $\text{C}_{31}\text{H}_{43}\text{NO}_7\text{Si}$: C, 65.35; H, 7.61; N, 2.46. Found: C, 65.45; H, 7.67; N, 2.37.

(3*R*)-Tetrahydro-4,4-dimethyl-2-oxo-3-furanyl (1*S*,5*S*)-5-Acetyl-8-(1,1-dimethylethoxycarbonyl)-3-(1,1-dimethylethoxysiloxy)-8-azabicyclo[3.2.1]octa-2,6-diene-2-carboxylate [23e]. ($\text{Rh}_2(\text{OOct})_4$, 9:1-4:1 petroleum ether/ Et_2O , 2.60 g, 69% yield, 78% de). ^1H NMR (500 MHz, toluene- d_8 , 95 $^\circ\text{C}$) δ 6.41 (dd, $J = 5.8, 2.1$ Hz, 0.11H, minor diastereomer), 6.24 (dd, $J = 5.8, 2.1$ Hz, 0.89H, major diastereomer), 5.33 (d, $J = 1.8$ Hz, 1H), 5.27 (d, $J = 5.8$ Hz, 1H), 5.15 (s, 1H), 3.41 (d, $J = 9.0$ Hz, 1H), 3.27 (d, $J = 9.0$ Hz, 1H), 3.26 (br d, $J = 18.6$ Hz, 1H), 2.19 (d, $J = 18.6$ Hz, 1H), 2.15 (s, 3H), 1.41 (s, 9H), 0.95 (s, 9H), 0.79 (s, 3H), 0.74 (s, 3H), 0.23 (s, 3H), 0.19 (s, 3H); IR (neat) 3079, 2960, 2857, 1791, 1729, 1703, 1636, 1595, 1471, 1398 cm^{-1} . Anal. Calcd for $\text{C}_{27}\text{H}_{41}\text{NO}_8\text{Si}$: C, 60.54; H, 7.71; N, 2.61. Found: C, 60.33; H, 7.76; N, 2.52.

(3*R*)-Tetrahydro-4,4-dimethyl-2-oxo-3-furanyl (1*S*,5*S*)-12-(1,1-Dimethylethoxycarbonyl)-3-(1,1-dimethylethoxysiloxy)-12-azatricyclo[5.4.1^{1.5.0}1.7]dodeca-3,6-diene-4-carboxylate [23h]. ($\text{Rh}_2(\text{OOct})_4$, 9:1 pentane/ Et_2O , 0.45 g, 31% yield, 37% de). ^1H (500 MHz, toluene- d_8 , 95 $^\circ\text{C}$) δ 6.01 (br s, 0.68H, major diastereomer), 5.85

(br s, 0.32H, major diastereomer), 5.19 (br s, 1H), 5.11 (br s, 1H), 3.47 (br d, $J = 8.5$ Hz, 1H), 3.33 (br d, $J = 8.5$ Hz, 1H), 2.85-2.65 (m, 2H), 2.17-2.07 (m, 3H), 1.90-1.75 (m, 2H), 1.63-1.50 (m, 1H), 1.38 (s, 9H), 1.15-1.05 (m, 2H), 0.98 (s, 9H), 0.92 (s, 3H), 0.83 (s, 3H), 0.26 (s, 3H), 0.22 (s, 3H); IR (neat) 2966, 2929, 2862, 1786, 1724, 1693, 1600, 1471, 1367, 1259, 1171; MS m/e (relative intensity) 490 (M^+ (-*t*-Bu)) (21), 447 (13), 434 (17), 390 (21), 334 (27), 290 (55), 289 (100), 278 (31), 260 (32), 187 (25). HRMS Calcd for $C_{25}H_{36}NO_7Si$ (M^+ (-*t*-Bu)) 490.2261; found 490.2245.

(1*S*)-2-Ethoxy-1-methyl-2-oxoethyl (1*R*,5*S*)-8-(1,1-Dimethylethoxycarbonyl)-5-phenyl-8-azabicyclo[3.2.1]octa-2-ene-2-carboxylate [24d]. (4:1-1:1 pentane/Et₂O, 2.35 g, 83%). ¹H NMR (500 MHz, toluene-*d*₈, 95 °C) δ 7.24 (d, $J = 7.8$ Hz, 2H), 7.13 (t, $J = 7.8$ Hz, 3H), 6.86 (t, $J = 2.3$ Hz, 1H), 5.28 (d, $J = 6.1$ Hz, 1H), 5.15 (q, $J = 6.7$ Hz, 1H), 3.95 (q, $J = 7.2$ Hz, 2H), 3.19 (br d, $J = 18.6$ Hz, 1H), 2.21 (dd $J = 18.6, 4.6$ Hz, 1H), 1.74-1.95 (m, 3H), 1.33 (m, 1H), 1.32 (d, $J = 6.7$ Hz, 3H), 1.14 (s, 9H), 1.00 (t, $J = 7.0$ Hz, 3H). Anal. Calcd for $C_{24}H_{31}NO_6$: C, 67.11; H, 7.27; N, 3.26. Found: C, 67.16; H, 7.34; N, 3.18.

1*S*-(2-Ethoxy-1-methyl-2-oxoethyl (1*R*,5*R*,7*R*)-12-(1,1-Dimethylethoxy-carbonyl)-12-azatricyclo[5.4.1^{1.5.0}1.7]dodeca-3-ene-4-carboxylate [24h]. Palladium on activated carbon (10%) (0.274 g, 0.26 mmol) was added to a solution of **20h** (1.37 g, 3.4 mmol) in absolute ethanol (100 mL) in a ParrTM hydrogenation flask. The flask was installed in a ParrTM hydrogenator, and the flask was flushed with H₂ four times. This solution was pressurized with H₂ (45 psi) and the flask was agitated for 4.5 hours. The crude reaction mixture was filtered through Celite and the solvent removed under reduced pressure to yield the crude material as a yellow oil. The residue was purified by silica gel column chromatography (4:1 hexanes/EtOAc) to yield the title compound as a pale yellow oil in quantitative yield (1.37 g). ¹H (500 MHz, toluene-*d*₈, 95 °C) δ 6.54 (dd, $J = 3.7, 3.4$ Hz, 1H), 5.07 (q, $J = 7.0$ Hz, 1H), 4.86 (d, $J = 7.6$ Hz, 1H), 3.87 (q, $J = 7.0$ Hz, 2H), 2.59 (m, 1H), 2.28 (dd, $J = 20.1, 4.3$ Hz, 1H), 2.12 (dd, $J = 20.1, 3.4$ Hz, 1H), 1.69-0.95 (m, 10H), 1.32 (s, 9H), 1.26 (d, $J = 6.7$ Hz, 3H),

0.90 (t, $J = 7.0$ Hz, 3H); IR (neat) 2971, 2929, 2872, 1755, 1742, 1698, 1647, 1367, 1248, 1170, 1103 cm^{-1} ; MS m/e (relative intensity) 407 (M⁺) (2), 351 (3), 307 (58), 234 (6), 206 (31), 190 (12), 163 (13), 162 (11), 161 (28), 145 (4), 117 (2), 57 (100). Anal. Calcd for $\text{C}_{22}\text{H}_{33}\text{NO}_6$: C, 64.84; H, 8.16; N, 3.44. Found: C, 64.72; H, 8.10; N, 3.35.

Methyl (1*R*,5*S*)-8-(1,1-Dimethylethoxycarbonyl)-5-methyl-8-azabicyclo[3.2.1]octa-2-ene-2-carboxylate [25b]. (No further purification necessary, 0.44 g, 80%). ^1H NMR (200 MHz, CDCl_3) δ 6.74 (dd, $J = 4.4, 2.8$ Hz, 1H), 4.85 (d, $J = 5.7$ Hz, 1H), 3.73 (s, 3H), 2.84 (br d, $J = 19.1$ Hz, 1H), 1.99 (dd, $J = 19.1, 4.4$ Hz, 1H), 1.60-2.00 (m, 4H), 1.59 (s, 3H), 1.38 (s, 9H). Anal. Calcd for $\text{C}_{15}\text{H}_{23}\text{NO}_4$: C, 64.02; H, 8.24; N, 4.98. Found: C, 64.12; H, 8.27; N, 4.92.

Methyl (1*R*,5*R*,6*R*)-8-(1,1-Dimethylethoxycarbonyl)-6-methyl-8-azabicyclo[3.2.1]octa-2-ene-2-carboxylate [25g]. (9:1-4:1 petroleum ether/ Et_2O , 1.51 g, 74%). ^1H NMR (500 MHz, toluene- d_8 , 95 $^\circ\text{C}$) δ 6.64 (m, 1H), 4.99 (d, $J = 6.1$ Hz, 1H), 4.20 (br s, 1H), 3.51 (s, 3H), 2.66 (d, $J = 19.4$ Hz, 1H), 2.25-2.37 (m, 2H), 1.93 (dd, $J = 19.4, 4.1$ Hz, 1H), 1.49 (s, 9H), 1.31 (dd, $J = 11.8, 4.1$ Hz, 1H), 0.82 (d, $J = 7.0$ Hz, 3H). Anal. Calcd for $\text{C}_{15}\text{H}_{23}\text{NO}_4$: C, 64.04; H, 8.24; N, 4.98. Found: C, 64.08; H, 8.28; N, 4.91.

Methyl (1*R*,5*R*,7*R*)-12-(1,1-Dimethylethoxycarbonyl)-12-azatricyclo[5.4.1^{1.5}.0^{1.7}]dodeca-3-ene-4-carboxylate [25h]. (4:1 hexanes/ EtOAc , 0.84 g, 81%). ^1H NMR (500 MHz, toluene- d_8 , 95 $^\circ\text{C}$) δ 6.53 (br s, 1H), 4.94 (d, $J = 7.6$ Hz, 1H), 3.51 (s, 3H), 2.69 (m, 1H), 2.36 (d, $J = 20.1$ Hz, 1H), 2.23 (d, $J = 20.1$ Hz, 1H), 2.12-2.06 (m, 1H), 1.79-0.85 (m, 9H), 1.40 (s, 9H); IR (neat) 2976, 2934, 2877, 1703, 1647, 1449, 1367, 1253, 1170 cm^{-1} ; MS m/e (relative intensity) 321 (M⁺) (7), 265 (16), 264 (3), 248 (5), 222 (17), 221 (100), 220 (10), 219 (5), 206 (13), 162 (8), 161 (10), 57 (2). Anal. Calcd for $\text{C}_{18}\text{H}_{27}\text{NO}_4$: C, 67.26; H, 8.47; N, 4.36. Found: C, 67.02; H, 8.55; N, 4.17.

















