Intramolecular Titanium-mediated Aminocyclopropanation of Terminal Alkenes – An Easy Access to Various Substituted Azabicyclo[*n*.1.0]alkanes

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Supporting Information

(*E*)-*N*-Benzyl-*N*-hexa-3,5-dienylformamide (**8a**): A solution of 4.21 g (16.7 mmol) of (*E*)-hexa-3,5-dienyl *p*-toluenesulfonate in 10 mL of acetonitrile was added to a solution of 4.0 mL (37 mmol) of benzylamine in 17 mL of acetonitrile at 25 °C. The reaction mixture was stirred at 60 °C for 1 h, then at 25 °C for 2 h. The resulting precipitate was filtered off and washed with acetonitrile (20 mL). The solvent was removed under reduced pressure to give 3.08 g of a mixture of benzylamine und (*E*)-*N*-benzyl-*N*-hexa-3,5-dienylamine. This mixture was dissolved in 25 mL of ethyl formate and the solution heated under reflux for 24 h. After removal of the excess ester under reduced pressure, chromatography on silica gel, eluting with ethyl acetate/petroleum ether (1:1) yielded 1.86 g (52%, based on the tosylate) of **8a** (R_f = 0.4) as a colorless oil. – IR (film): ν = 3086 cm^{-1} (Aryl-H), 3031, 3009, 2931 (CH_2), 2862, 2772, 1671 (CO), 1603 (C=C), 1496, 1425, 1398, 1368, 1305, 1262, 1200, 1166, 1151, 1078, 1006,

955, 903, 839, 821, 740, 703, 646, 592, 528, 462. – ^{1}HNMR (250 MHz, $CDCl_3$): Rotamer A: δ = 2.28 (q, ^3J = 7.2 Hz, 2 H, 2-H), 3.21 (t, ^3J = 7.2 Hz, 2 H, 1-H), 4.39 (s, 2 H, CH_2-Ph), 5.01 (dd, ^2J = 9.9 Hz, ^3J = 9.9 Hz, 1 H, 6-H_{trans}), 5.11 (dd, ^2J = 9.9 Hz, ^3J = 16.8 Hz, 1 H, 6-H_{cis}), 5.55 (m_c, 1 H, 3-H), 6.04 (m_c, 1 H, 4-H), 6.27 (ddt, ^3J = 1.9 Hz, ^3J = 9.9 Hz, ^3J = 16.8 Hz, 1 H, 5-H), 7.16–7.44 (m, 5 H, Aryl-H), 8.18 (s, 1 H, CHO); rotamer B: δ = 2.28 (q, ^3J = 7.2 Hz, 2 H, 2-H), 3.30 (t, ^3J = 7.2 Hz, 2 H, 1-H), 4.55 (s, 2 H, CH_2-Ph), 5.01 (dd, ^2J = 9.9 Hz, ^3J = 9.9 Hz, 1 H, 6-H_{trans}), 5.11 (dd, ^2J = 9.9 Hz, ^3J = 16.8 Hz, 1 H, 6-H_{cis}), 5.55 (m_c, 1 H, 3-H), 6.04 (m_c, 1 H, 4-H), 6.27 (ddt, ^3J = 1.9 Hz, ^3J = 9.9 Hz, ^3J = 16.8 Hz, 1 H, 5-H), 7.16–7.44 (m, 5 H, Aryl-H), 8.27 (s, 1 H, CHO). – ^{13}CNMR (62.9 MHz, $CDCl_3$, DEPT): Rotamer A: δ = 30.29 (–, C-2), 41.56 (–, C-1), 46.53 (–, *C*H_2Ph), 115.94 (–, C-6), 127.48 (+, 2 C, C-Aryl), 127.60 (+, C-Aryl), 128.62 (+, 2 C, C-Aryl), 129.37 (+, C-3), 133.12 (+, C-4), 136.03 (C_{quat}, C-Aryl), 136.39 (+, C-5), 162.83 (+, CHO); rotamer B: δ = 31.54 (–, C-2), 45.39 (–, C-1), 51.48 (–, *C*H_2Ph), 116.62 (–, C-6), 127.60 (+, 2 C, C-Aryl), 128.09 (+, C-Aryl), 128.87 (+, 2 C, C-Aryl), 130.68 (+, C-3), 134.01 (+, C-4), 136.03 (C_{quat}, C-Aryl), 136.72 (+, C-5), 162.86 (+, CHO). – MS (EI, 70 eV), *m/z* (%): 215 (12) [M^+], 148 (26) [M^+ – Ph], 91 (100) [CH_2Ph^+], 80 (8), 65 (5), 41 (4). – Anal. calcd for $C_{14}H_{17}NO$ (215.3): C, 78.10; H, 7.96; N, 6.51. Found: C, 77.93; H, 8.22; N, 6.38.

(*Z*)-*N*-Benzyl-*N*-hexa-3,5-dienylformamide (**8b**): **8b** was prepared analogously to **8a**. Starting from 2.04 g (8.12 mmol) of (*Z*)-hexa-3,5-dienyl *p*-toluenesulfonate the reaction sequence yielded 1.09 g (62%, based on the tosylate) of **8b** (R_f = 0.36) as a colorless oil. – IR (film): ν = 3085 cm^{-1} (Aryl-H), 3028, 2932 (CH_2), 2863, 2771, 1675 (CO), 1496, 1424, 1398, 1362, 1306, 1258, 1196, 1078, 1002, 965, 911, 741, 703, 650, 617, 591. – ^{1}HNMR (250 MHz, $CDCl_3$): Rotamer A: δ = 2.38 (q, ^3J = 7.3 Hz, 2 H, 2-H), 3.20 (t, ^3J = 7.3 Hz, 2 H, 1-H), 4.40 (s, 2 H, CH_2-Ph), 5.10–5.42 (m, 3 H, 6-H_{trans}, 6-H_{cis}, 3-H), 6.08 (d, ^3J = 10.8 Hz, 1 H, 4-H), 6.38–6.60 (m_c, 1 H, 5-H), 7.19–7.41 (m, 5 H, Aryl-H), 8.18 (s, 1 H, CHO); rotamer B: δ = 2.38 (q, ^3J = 7.3 Hz, 2 H, 2-H), 3.29 (t, ^3J = 7.3 Hz, 2 H, 1-H), 4.55 (s, 2 H, CH_2-Ph), 5.10–5.42 (m, 3 H, 6-H_{trans}, 6-H_{cis}, 3-H), 6.08 (d, ^3J = 10.8 Hz, 1 H, 4-H), 6.38–6.60 (m_c, 1 H, 5-H), 7.19–7.41 (m, 5 H, Aryl-H), 8.28 (s, 1 H, CHO). – ^{13}CNMR (62.9 MHz, $CDCl_3$, DEPT): Rotamer A: δ = 25.57 (–, C-2), 41.70 (–, C-1), 46.33 (–, *C*H_2Ph), 118.03 (–, C-6), 126.67 (+, C-Aryl), 127.45 (+, 2 C, C-Aryl), 127.93 (+, C-3), 128.64 (+, 2 C, C-Aryl), 131.16 (+, C-4'),

131.61 (+, C-5), 135.99 (C_{quat}, C-Aryl), 162.75 (+, CHO); rotamer B: δ = 26.70 (–, C-2), 45.32 (–, C-1), 51.62 (–, *C*H_2Ph), 118.79 (–, C-6), 127.56 (+, C-Aryl'), 128.03 (+, 2 C, C-Aryl), 128.13 (+, C-3), 128.83 (+, 2 C, C-Aryl), 131.40 (+, C-4), 132.04 (+, C-5), 136.31 (C_{quat}, C-Aryl), 162.83 (+, CHO). – MS (EI, 70 eV), *m/z* (%): 215 (18) [M^+], 148 (37) [M^+ – Ph], 91 (100) [CH_2Ph^+], 80 (7), 65 (5), 41 (2). – Anal. calcd for $C_{14}H_{17}NO$ (215.3): C, 78.10; H, 7.96. Found: C, 78.33; H, 8.28.

***N*-Benzyl-*N*-hepta-4,6-dienylformamide** (**10**): A solution of 2.70 g (19.4 mmol) of *N*-hepta-4,6-dienylformamide in 8 mL of DMF was added to a solution of 0.975 g (24.4 mmol, 60% dispersion in mineral oil) of sodium hydride in 40 mL of DMF at 25 °C. After stirring at 25 °C for 30 min and at 50 °C for 90 min, 2.54 mL (21.4 mmol) of benzyl bromide in 6 mL of DMF was added, and stirring was continued for 24 h at 25 °C. After addition of 200 mL of water to the reaction mixture, the aqueous phase was extracted with diethyl ether (4 × 50 mL), and the organic phases were washed with 20 mL of brine. After drying over Na_2SO_4 and removal of the solvent under reduced pressure, column chromatography on silica gel, eluting with ethyl acetate/petroleum ether (1:1) afforded 3.63 g (81%) of **10** (**R_f** = 0.35). – IR (film): ν = 3064 cm^{-1} (Aryl-CH), 3029 (Aryl-CH), 2931, 2860, 1673 (CO), 1496, 1428, 1398, 1357, 1204, 1078, 1006, 969, 907, 821, 738, 703, 592. – ^{1}HNMR (250 MHz, $CDCl_3$): Rotamer A: δ = 1.59 (quint, ^3J = 7.2 Hz, 2 H, 2-H), 2.04 (q, ^3J = 7.2 Hz, 2 H, 3-H), 3.13 (t, ^3J = 7.2 Hz, 2 H, 1-H), 4.38 (s, 2 H, C*H*$_2$Ph), 4.97 (dd, ^2J = 7.0 Hz, ^3J = 10.3 Hz, 1 H, 7-H), 5.09 (dd, ^2J = 7.0 Hz, ^3J = 16.9 Hz, 1 H, 7-H), 5.61 (dt, ^3J = 7.2 Hz, ^3J = 16.5 Hz, 1 H, 4-H), 6.01 (dd, ^3J = 10 Hz, ^3J = 16.5 Hz, 1 H, 5-H), 6.27 (dt, ^3J = 10.3 Hz, ^3J = 16.9 Hz, 1 H, 6-H), 7.17–7.39 (m, 5 H, Aryl-H), 8.17 (s, 1 H, CHO); rotamer B: δ = 1.59 (quint, ^3J = 7.2 Hz, 2 H, 2-H), 2.04 (q, ^3J = 7.2 Hz, 2 H, 3-H), 3.22 (t, ^3J = 7.2 Hz, 2 H, 1-H), 4.53 (s, 2 H, C*H*$_2$Ph), 4.97 (dd, ^2J = 7.0 Hz, ^3J = 10.3 Hz, 1 H, 7-H), 5.09 (dd, ^2J = 7.0 Hz, ^3J = 16.9 Hz, 1 H, 7-H), 5.61 (dt, ^3J = 7.2 Hz, ^3J = 16.5 Hz, 1 H, 4-H), 6.01 (dd, ^3J = 10 Hz, ^3J = 16.5 Hz, 1 H, 5-H), 6.27 (dt, ^3J = 10.3 Hz, ^3J = 16.9 Hz, 1 H, 6-H), 7.17–7.39 (m, 5 H, Aryl-H), 8.27 (s, 1 H, CHO). – ^{13}CNMR (62.9 MHz, $CDCl_3$, DEPT): Rotamer A: δ = 26.34 (–, C-2), 29.09 (–, C-3), 41.61 (–, C-1), 46.00 (–, *C*H_2Ph), 115.26 (–, C-7), 127.46 [+, 2 C, C-2'(6')], 128.07 (+, C-5), 128.65 [+, 2 C, C-3'(5')], 131.59 (+, C-4'), 132.84 (+, C-4), 136.11 (C_{quat}, C-1'), 136.69 (+, C-6), 162.83 (+, CHO); rotamer B: δ = 27.31 (–, C-2), 29.76 (–, C-3), 45.14 (–, C-1), 51.30 (–, CH_2Ph),

115.76 (–, C-7), 127.57 [+, 2 C, C-2'(6')], 128.16 (+, C-5), 128.86 [+, 2 C, C-3'(5')], 132.20 (+, C-4), 133.65 (+, C-4), 136.42 (C_{quat}, C-1'), 136.97 (+, C-6), 162.89 (+, CHO). – MS (EI, 70 eV), *m/z* (%): 229 (10) [M^+], 202 (2) [$M^+ - CH{=}CH_2$], 181 (4), 174 (2), 148 (15) [$M^+ - C_6H_9$], 134 (10) [$M^+ - C_7H_{11}$], 106 (5), 95 (9), 92 (14), 91 (100) [CH_2Ph^+], 79 (7), 58 (11), 41 (6). – Anal. calcd for $C_{15}H_{19}NO$ (229.3): C, 78.55; H, 8.36; N, 6.11. Found: C, 78.86; H, 8.45; N, 5.98.

General procedure for the intramolecular cyclopropanation (GP1):

***exo*-2-Benzyl-6-vinyl-2-azabicyclo[3.1.0]hexane** (**9**): 6.5 mL (14 mmol) of cyclohexylmagnesium bromide (2.1 N solution in Et_2O) was slowly (during 90 min) added by syringe into a solution of 0.835 g (3.88 mmol) of *N*-benzyl-*N*-hexa-3,5-dienylformamide (**8**) and 1.21 g (4.27 mmol) of titanium(IV) tetraisopropoxide in 60 mL of THF at 0 °C. After stirring at 25 °C for 24 h, 5 mL of water was added. The resulting colorless precipitate was filtered off and washed with diethyl ether (2 × 30 mL). The combined organic phases were washed with 10 mL of brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (2:1) afforded 180 mg (23%) of **9** (R_f = 0.30) as a colorless oil. – IR (film): ν = 3083 cm^{-1}, 3062 (Aryl-CH), 3028 (Aryl-CH), 2930, 2868, 2813, 1633, 1491, 1453, 1377, 1358, 1282, 1251, 1203, 1142, 1075, 1046, 1029, 982, 890, 861, 841, 743, 699, 650. – ^{1}HNMR (250 MHz, $CDCl_3$): δ = 1.53 (ddd, ^3J = 3.7 Hz, ^3J = 4.2 Hz, ^3J = 6.2 Hz, 1 H, 5-H), 1.75 (ddd, ^3J = 2.0 Hz, ^3J = 3.7 Hz, ^3J = 8.2 Hz, 1 H, 6-H), 1.90–2.10 (m, 3 H, 3-H, 4-H), 2.58 (dd, ^3J = 2.0 Hz, ^3J = 6.2 Hz, 1 H, 1-H), 2.90–2.97 (m, 1 H, 3-H), 3.64 (AB, d, J = 10.3 Hz, 1 H, CH_2Ph), 3.70 (AB, d, ^2J = 10.3 Hz, 1 H, CH_2Ph), 4.82 (dd, ^2J = 1.8 Hz, ^3J = 10.3 Hz, 1 H, CH=CH_2), 4.93 (dd, ^2J = 1.8 Hz, ^3J = 17.1 Hz, 1 H, CH=CH_2), 5.40 (ddd, ^3J = 8.2 Hz, ^3J = 10.3 Hz, ^3J = 17.1 Hz, 1 H, CH=CH_2), 7.22–7.36 (m, 5 H, Aryl-H). – ^{13}CNMR (62.9 MHz, $CDCl_3$, DEPT): δ = 18.32 (+, C-5), 24.07 (+, C-6), 26.74 (–, C-4), 49.06 (–, C-3), 50.05 (+, C-1), 58.74 (–, *C*H_2Ph), 110.80 (–, CH=*C*H_2), 126.99 (+, 2 C, C-Aryl), 128.23 (+, C-Aryl), 129.12 (+, 2 C, C-Aryl), 138.36 (–, *C*H=CH_2), 138.89 (C_{quat}, C-Aryl). – MS (EI, 70 eV), *m/z* (%): 199 (4) [M^+], 172 (21) [$M^+ - CH{=}CH_2$], 159 (43) [$M^+ - C_3H_4$], 133 (13), 124 (12), 110 (7), 104 (3), 91 (100) [CH_2Ph^+], 68 (5), 65 (10), 55 (4), 42 (33).

2-Benzyl-6-propenyl-2-azabicyclo[3.1.0]hexane (11): According to GP1 a solution of 1.05 g (4.58 mmol) of *N*-hepta-4,6-dienyl-*N*-benzylformamide (**10**), 1.43 g (5.03 mmol) of titanium(IV) tetraisopropoxide in 100 mL of THF and 8.70 mL (16.1 mmol) of cyclohexylmagnesium bromide (1.85 N solution in Et_2O) afforded 151 mg (15%) of **11** (R_f = 0.30) as a colorless oil. – ^{1}HNMR (250 MHz, $CDCl_3$): δ = 1.45 (dt, ^3J = 3.6 Hz, ^3J = 6.5 Hz, 1 H, 5-H), 1.63 (dd, ^4J = 1.5 Hz, ^3J = 6.4 Hz, 3 H, CH=CHCH_3), 1.70 (m, 1 H, 6-H), 1.85–2.09 (m, 3 H, 3-H, 4-H), 2.55 (dd, ^3J = 2.1 Hz, ^3J = 6.3 Hz, 1 H, 1-H), 2.93 (m_c, 1 H, 3-H), 3.65 (AB, d, ^2J = 12.6 Hz, 1 H, CH_2Ph), 3.72 (AB, d, ^2J = 12.6 Hz, 1 H, CH_2Ph), 5.01 (ddq, ^4J = 1.5 Hz, ^3J = 6.3 Hz, ^3J = 15.3 Hz, 1 H, CH=CHCH$_3$), 5.38 (dq, ^3J = 6.4 Hz, ^3J = 15.3 Hz, 1 H, CH=CHCH$_3$), 7.24–7.38 (m, 5 H, Aryl-H). – ^{13}CNMR (62.9 MHz, $CDCl_3$, DEPT): δ = 17.06 (+, C-5), 17.91 (+, CH=CH*C*H$_3$), 23.57 (+, C-6), 26.77 (–, C-4), 49.14 (–, C-3), 49.40 (+, C-1), 58.81 (–, *C*H$_2$Ph), 122.07 (+, CH=*C*HCH$_3$), 126.91 (+, C-Aryl), 128.19 (+, 2 C, C-Aryl), 129.07 (+, 2 C, C-Aryl), 130.79 (+, *C*H=CHCH$_3$), 139.01 (C_{quat}, C-Aryl). – MS (EI, 70 eV), *m/z* (%): 213 (60) [M^+], 198 (26) [M^+ – CH_3], 184 (4), 172 (8) [M^+ – CH=CHCH$_3$], 159 (13), 136 (5), 122 (7), 106 (3), 95 (11), 91 (100) [CH_2Ph^+], 77 (6) [$C_6H_5^+$], 67 (8), 65 (10), 55 (7), 41 (7).

***N*-Benzyl-*N*-but-3-enylformamide** (**3**): A solution of 8.12 g (36.0 mmol) of but-3-enyl toluene-4-sulfonate in 20 mL of acetonitrile was slowly (15 min) added by syringe to a solution of 9.47 g (88.4 mmol) of benzylamine in 40 mL of acetonitrile at 25 °C. After stirring at 60 °C for 24 h, the resulting precipitate was filtered off and washed with 20 mL of acetonitrile. The solvent was removed under reduced pressure, the crude product was dissolved in 100 mL of diethyl ether and washed with 50 mL of 10% aqueous $NaHCO_3$ solution and 10 mL of brine. Drying of the organic phase with Na_2SO_4 and removal of the solvent under reduced pressure afforded 6.14 g of a mixture of benzylamine and *N*-benzyl-*N*-but-3-enylamine. This mixture was dissolved in 60 mL of ethyl formate and heated under reflux for 48 h. After removal of the excess ester under reduced pressure, column chromatography on silica gel, eluting with diethyl ether afforded 4.71 g (69%) of **3** (R_f = 0.4). – IR (film): ν = 3065 cm^{-1} (Aryl-CH), 3030 (Aryl-CH), 3004 (Aryl-CH), 2978, 2931, 2864, 2772, 1671, 1496, 1426, 1398, 1304, 1268, 1205, 1114, 1078, 1029, 1002, 973, 918, 741, 703, 607. – ^{1}HNMR (250 MHz, $CDCl_3$): Rotamer A: δ = 2.21 (q, ^3J = 6.9 Hz, 2 H, 2-H), 3.18 (t,

^3J = 6.9 Hz, 2 H, 1-H), 4.36 (s, 2 H, CH_2Ph), 4.95–5.09 (m, 4-H, 2 H), 5.66 (m_c, 1 H, 3-H), 7.15–7.40 (m, 5 H, Aryl-H), 8.15 (s, 1 H, CHO); rotamer B: δ = 2.21 (q, ^3J = 6.9 Hz, 2 H, 2-H), 3.28 (t, ^3J = 6.9 Hz, 2 H, 1-H), 4.52 (s, 2 H, CH_2Ph), 4.95–5.09 (m, 2 H, 4-H), 5.66 (m_c, 1 H, 3-H), 7.15–7.40 (m, 5 H, Aryl-H), 8.24 (s, 1 H, CHO). – ^{13}CNMR (62.9 MHz, $CDCl_3$, DEPT): Rotamer A: δ = 31.42 (–, C-2), 41.33 (–, C-1), 46.27 (–, CH_2Ph), 116.91 (–, C-4), 127.46 (+, C-4'), 128.04 [+, 2 C, C-2'(6')], 128.64 [+, 2 C, C-3'(5')], 133.94 (+, C-3), 136.08 (C_{quat}, C-1'), 162.83 (+, CHO); rotamer B: δ = 32.60 (–, C-2), 45.28 (–, C-1), 51.36 (–, *C*H_2Ph), 118.03 (–, C-4), 127.57 (+, C-4'), 128.16 [+, 2 C, C-2'(6')], 128.85 [+, 2 C, C-3'(5')], 134.94 (+, C-3), 136.40 (C_{quat}, C-1'), 162.91 (+, CHO). – MS (EI, 70 eV), *m/z* (%): 189 (4) [M^+], 148 (18) [$M^+ - C_3H_5$], 130 (1), 92 (6), 91 (100) [CH_2Ph^+], 73 (3), 65 (10), 60 (6), 51 (3), 41 (3) [$C_3H_5^+$]. – Anal. calcd for $C_{12}H_{15}NO$ (189.3): C, 76.16; H, 7.99; N, 7.40. Found: C, 75.89; H, 7.70; N, 7.35.

***N*-Pent-4-enylformamide**: A solution of 3.16 g (39.0 mmol) of pent-4-enenitrile (**4**) in 10 mL of diethyl ether was added to a suspension of 1.74 g (45.9 mmol) of lithium aluminum hydride in 50 mL of diethyl ether at 0 °C. After stirring for 36 h at 25 °C, 3 mL of water and then 50 mL of 15% aqueous sodium hydroxide were added. The aqueous phase was extracted with diethyl ether (4 × 50 mL). After drying the combined organic phases over Na_2SO_4, the solvent was removed by distillation through a Vigreux column (20 cm). The crude product was added to 50 mL of ethyl formate and the mixture stirred at 60 °C for 24 h. Removal of the excess ester under reduced pressure and purification by column chromatography on silica gel with diethyl ether afforded 3.49 g (79%) of *N*-pent-4-enylformamide (R_f = 0.15) as a colorless oil. – IR (film): ν = 3064 cm^{-1}, 2934, 2864, 1663 (CO), 1540, 1442, 1384, 1239, 1150, 994, 914, 869, 776. – ^{1}HNMR (250 MHz, $CDCl_3$): Rotamer A: δ = 1.59 (quint, ^3J = 7.2 Hz, 2 H, 2-H), 2.07 (q, ^3J = 7.2 Hz, 2 H, 3-H), 3.24 (t, ^3J = 7.2 Hz, 2 H, 1-H), 4.92–5.05 (m, 2 H, 5-H), 5.75 (ddt, ^3J = 7.2 Hz, $^3J_{cis}$ = 10.3 Hz, $^3J_{trans}$ = 17.0 Hz, 1 H, 4-H), 6.00 (br. s, 1 H, NH), 8.01 (s, 1 H, CHO); rotamer B: δ = 1.59 (quint, ^3J = 7.2 Hz, 2 H, 2-H), 2.07 (q, ^3J = 7.2 Hz, 2 H, 3-H), 3.27 (t, ^3J = 7.2 Hz, 1 H, 1-H), 4.92–5.05 (m, 2 H, 5-H), 5.75 (ddt, ^3J = 7.2 Hz, $^3J_{cis}$ = 10.3 Hz, $^3J_{trans}$ = 17.0 Hz, 1 H, 4-H), 6.00 (br. s, 1 H, NH), 8.11 (s, 1 H, CHO). – ^{13}CNMR (62.9 MHz, $CDCl_3$, DEPT): Rotamer A: δ = 28.50 (–, C-2), 30.90 (–, C-3), 37.56

(–, C-1), 115.32 (–, C-5), 137.43 (+, C-4), 161.26 (+, CHO); rotamer B: δ = 30.02 (–, C-2), 30.29 (–, C-3), 40.95 (–, C-1), 115.79 (–, C-5), 136.98 (+, C-4), 164.69 (+, CHO). – MS (DCI, 70 eV), *m/z* (%): 244 (46) [2M + NH_4^+], 148 (50) [M + NH_4^+ + NH_3], 131 (100) [M + NH_4^+].

***N*-Benzyl-*N*-pent-4-enylformamide** (**5**): A solution of 1.00 g (8.86 mmol) of *N*-pent-4-enylformamide in 4 mL of DMF was added to a suspension of 0.511 g (12.8 mmol, 60% dispersion in mineral oil) of sodium hydride in 20 mL of DMF. After stirring for 1 h at 60 °C, 1.90 g (11.1 mmol) of benzyl bromide in 3 mL of DMF was added slowly at 25 °C. Stirring was continued for 24 h at 25 °C, and then 150 mL of water was added. The aqueous phase was extracted with diethyl ether (4 × 50 mL), the combined organic phases were washed with brine (30 mL) and dried with Na_2SO_4. After removal of the solvent under reduced pressure, column chromatography on silica gel, eluting with diethyl ether afforded 1.14 g (63%) of **5** (R_f = 0.4) as a colorless oil. – IR (film): ν = 3065 cm^{-1} (Aryl-CH), 3031 (Aryl-CH), 2975, 2931, 2865, 2773, 1674 (CO), 1496, 1428, 1399, 1305, 1261, 1203, 1116, 1078, 1029, 996, 969, 914, 739, 703, 606. – ^{1}HNMR (250 MHz, $CDCl_3$): Rotamer A: δ = 1.57 (quint, ^3J = 7.5 Hz, 2 H, 2-H), 2.01 (q, ^3J = 7.5 Hz, 2 H, 3-H), 3.23 (t, ^3J = 7.5 Hz, 2 H, 1-H), 4.38 (s, 2 H, CH_2Ph), 4.90–5.05 (m, 2 H, 5-H), 5.73 (m_c, 1 H, 4-H), 7.16–7.40 (m, 5 H, Aryl-H), 8.18 (s, 1 H, CHO); rotamer B: δ = 1.60 (quint, ^3J = 7.5 Hz, 2 H, 2-H), 2.01 (q, ^3J = 7.5 Hz, 2 H, 3-H), 3.14 (t, ^3J = 7.5 Hz, 2 H, 1-H), 4.53 (s, 2 H, CH_2Ph), 4.90–5.05 (m, 2 H, 5-H), 5.73 (m_c, 1 H, 4-H), 7.16–7.40 (m, 5 H, Aryl-H), 8.28 (s, 1 H, CHO). – ^{13}CNMR (62.9 MHz, $CDCl_3$, DEPT): Rotamer A: δ = 26.03 (–, C-2), 30.29 (–, C-3), 41.57 (–, C-1), 45.95 (–, *C*H_2Ph), 115.12 (–, C-5), 127.43 (+, C-4'), 128.05 [+, 2 C, C-2'(6')], 128.64 [+, 2 C, C-3'(5')], 136.15 (C_{quat}, C-1'), 136.95 (+, C-4), 162.84 (+, CHO); rotamer B: δ = 26.98 (–, C-2), 30.93 (–, C-3), 45.12 (–, C-1), 51.28 (–, *C*H_2Ph), 115.83 (–, C-5), 127.56 (+, C-4'), 128.14 [+, 2 C, C-2'(6')], 128.85 [+, 2 C, C-3'(5')], 136.44 (C_{quat}, C-1'), 137.53 (+, C-4), 162.91 (+, CHO). – MS (EI, 70 eV), *m/z* (%): 203 (15) [M^+], 202 (56) [M^+ – H], 174 (2) [M^+ – CHO], 158 (12), 148 (37), 134 (18), 106 (12), 91 (100) [CH_2Ph^+], 79 (7), 77 (6), 65 (19), 58 (10), 51 (3), 41 (9).

General procedure for the intramolecular cyclopropanation (GP2):

2-Benzyl-2-azabicyclo[3.1.0]hexane (**6**): 14.2 mL (26.3 mmol) of cyclohexylmagnesium bromide (1.85 N solution in Et_2O) was slowly (90 min) added to a solution of 1.50 g (7.93 mmol) of *N*-benzyl-*N*-but-3-enylformamide (**3**) and 2.70 g (9.50 mmol) of titanium(IV) tetraisopropoxide in 120 mL of THF at 0 °C. After stirring for 24 h at 25 °C, 6 mL of water was added. The resulting colorless precipitate was filtered off, washed with THF (3 × 30 mL) and the organic phase was washed with 10 mL of brine. The solvent was removed under reduced pressure, and the crude product dissolved in 30 mL of 1 N sulfuric acid. After extraction of the acidic phase with pentane (5 × 20 mL), 1 N NaOH was added to get to pH = 13, and the basic phase was extracted with Et_2O (3 × 30 mL). Drying the organic phases over Na_2SO_4 and removal of the solvent under reduced pressure afforded 1.16 g (84%) of **6** as a colorless oil. For an analytical sample a fraction of the product was subjected to kugelrohr distillation (1 mbar, 140 °C). – IR (film): ν = 3064 cm^{-1} (Aryl-CH), 3028 (Aryl-CH), 2998, 2929, 2866, 2810, 1494, 1453, 1347, 1288, 1253, 1157, 1135, 1075, 1008, 963, 907, 816, 751, 698, 645. – ^{1}HNMR (250 MHz, $CDCl_3$): δ = 0.09 (dt, ^3J = 5.8 Hz, ^2J = 8.2 Hz, 1 H, 6-H), 0.73 (ddd, ^3J = 2.8 Hz, ^3J = 4.2 Hz, ^2J = 8.2 Hz, 1 H, 6-H), 1.40 (m_c, 1 H, 5-H), 1.80–2.10 (m, 3 H, 3-H, 4-H), 2.65 (dt, ^3J = 2.8 Hz, ^3J = 5.8 Hz, 1 H, 1-H), 2.89 (t, ^3J = 7.8 Hz, 1 H, 3-H), 3.60 (AB, d, ^2J = 12.5 Hz, 1 H, C*H*$_2$Ph), 3.66 (AB, d, ^2J = 12.5 Hz, 1 H, C*H*$_2$Ph), 7.20–7.42 (m, 5 H, Aryl-H). – ^{13}CNMR (62.9 MHz, $CDCl_3$, DEPT): δ = 1.44 (–, C-6), 14.92 (+, C-5), 26.74 (–, C-4), 40.78 (+, C-1), 48.22 (–, C-3), 59.00 (–, *C*H_2Ph), 126.79 (+, C-Aryl), 128.12 (+, 2 C, C-Aryl), 128.91 (+, 2 C, C-Aryl), 139.37 (C_{quat}, C-Aryl). – MS (EI, 70 eV), *m/z* (%): 173 (59) [M^+], 158 (6), 144 (3), 120 (2), 104 (4), 96 (13) [$M^+ - C_6H_5^+$], 91 (100) [CH_2Ph^+], 82 (14) [$M^+ - CH_2Ph^+$], 65 (12), 55 (13), 41 (6). – Anal. calcd for $C_{12}H_{15}N$ (173.3): C, 83.19; H, 8.73; N, 8.08. Found: C, 83.12; H, 8.43; N, 8.13.

2-Benzyl-2-azabicyclo[4.1.0]heptane (7): According to GP2, a solution of 0.518 g (2.55 mmol) of *N*-benzyl-*N*-pent-3-enylformamide (**5**), 0.847 g (2.98 mmol) of titanium(IV) tetraisopropoxide in 40 mL of THF and 5.51 mL (10.2 mmol) of cyclohexylmagnesium bromide (1.85 N solution in Et_2O) afforded 0.321 g (67%) of **7** as a colorless oil. – IR (film): ν = 3064 cm^{-1} (Aryl-CH), 3027 (Aryl-CH), 2931, 2855, 2810, 1495, 1453, 1353, 1320, 1281, 1206, 1166, 1138, 1074, 1026, 890, 830, 739, 697. – ^{1}HNMR (250 MHz, $CDCl_3$):

δ = 0.28–0.36 (m, 2 H, 7-H), 1.02 (m_c, 1 H, 6-H), 1.34–1.61 [m, 3 H, 4(5)-H], 1.93–2.13 [m, 2 H, 3(5)-H], 2.23 (m_c, 1 H, 1-H), 2.50–2.57 (m, 1 H, 3-H), 3.62 (AB, d, ^3J = 12.8 Hz, 1 H, CH_2Ph), 3.69 (AB, d, ^3J = 12.8 Hz, 1 H, CH_2Ph), 7.21–7.41 (m, 5 H, Aryl-H). – ^{13}CNMR (62.9 MHz, $CDCl_3$, DEPT): δ = 6.79 (–, C-7), 9.68 (+, C-6), 22.16 (–, C-4), 22.23 (–, C-5), 35.52 (+, C-1), 47.45 (–, C-3), 62.06 (–, CH_2Ph), 126.78 (+, C-Aryl), 128.09 (+, 2 C, C-Aryl), 129.19 (+, 2 C, C-Aryl), 139.01 (C_{quat}, C-Aryl). – MS (EI, 70 eV), *m/z* (%): 187 (59) [M^+], 172 (23), 148 (4), 120 (2), 110 (13), 96 (13) [$M^+ - CH_2Ph$], 91 (100) [CH_2Ph^+], 68 (12), 65 (8), 55 (6), 41 (15). – 187.1360 (correct HRMS).

General procedure for the synthesis of homoallyl formamides (GP3):

***N*-Benzyl-*N*-(2-ethylbut-3-enyl)formamide (13a)**: 7.65 mL (17.2 mmol) of ethylmagnesium chloride (2.25 N in Et_2O) was slowly (15 min) added to a solution of 1.24 mL (6.89 mmol) of *N*-benzylpyrroline (**12**) and 2.44 mL (8.27 mmol) of titanium(IV) tetraisopropoxide in 40 mL of diethyl ether at –40 °C. Stirring was continued for 3 h at –40 °C, and 10 mL of 1 N HCl was added. After the precipitate had become colorless, the aqueous phase was made basic (pH = 9) by addition of 1 N NaOH and extracted with diethyl ether (3 × 20 mL). The organic phases were dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was dissolved in 30 mL of ethyl formate and stirred for 2 d at 60 °C. The ester was removed under reduced pressure. Purification by column chromatography on silica gel with pentane/diethyl ether (2:1) afforded 613 mg (41%) of **13a** (R_f = 0.30) as a colorless oil. – IR (film): ν = 3067 cm^{-1}, 3030, 2963, 2930, 2874, 2772, 1675, 1497, 1456, 1430, 1399, 1363, 1270, 1214, 1155, 1115, 1078, 1029, 996, 973, 918, 822, 742, 703, 679, 608, 592. – ^{1}HNMR (250 MHz, $CDCl_3$): Rotamer A: δ = 0.82 (t, ^3J = 7.3 Hz, 3 H, CH_3), 1.19 (m_c, 2 H, CH_2CH_3), 2.15 (m_c, 1 H, 2-H), 3.03 (AB, d, ^3J = 8.2 Hz, 1 H, 1-H), 3.18 (AB, d, ^3J = 8.2 Hz, 1 H, 1-H), 4.34 (AB, d, ^2J = 14.6 Hz, 1 H, NCH_2), 4.69 (AB, d, ^2J = 14.6 Hz, 1 H, NCH_2), 4.95–5.12 (m, 2 H, 4-H), 5.35–5.60 (m, 1 H, 3-H), 7.15–7.39 (m, 5 H, Aryl-H), 8.11 (s, 1 H, CHO); rotamer B: δ = 0.82 (t, ^3J = 7.3 Hz, 3 H, CH_3), 1.34 (m_c, 2 H, CH_2CH_3), 2.27 (m_c, 1 H, 2-H), 3.04 (AB, d, ^3J = 6.4 Hz, 1 H, 1-H), 3.17 (AB, d, ^3J = 6.4 Hz, 1 H, 1-H), 4.37 (s, 2 H, NCH_2), 4.95–5.12 (m, 2 H, 4-H), 5.35–5.60 (m, 1 H, 3-H), 7.15–7.39 (m, 5 H, Aryl-H), 8.28 (s, 1 H, CHO). – ^{13}CNMR (62.9 MHz, $CDCl_3$, DEPT): Rotamer A: δ = 11.42 (+, CH_3), 24.78 (–, CH_2CH_3), 44.19 (+, $CHCH_2CH_3$), 45.69 (–, NCH_2CH), 51.10 (–, CH_2Ph), 116.67 (–, C-4), 127.49 (+,

2 C, C-Aryl), 127.57 (+, C-Aryl), 128.63 (+, 2 C, C-Aryl), 136.02 (C_{quat}, C-Aryl), 138.74 (+, C-3), 163.12 (+, CHO); rotamer B: δ = 11.45 (+, CH_3), 25.11 (–, *C*H_2CH_3), 44.22 (+, *C*HCH_2CH_3), 45.83 (–, N*C*H_2CH), 51.67 (–, *C*H_2Ph), 117.81 (–, C-4), 128.29 (+, 2 C, C-Aryl), 128.02 (+, C-Aryl), 128.84 (+, 2 C, C-Aryl), 136.37 (C_{quat}, C-Aryl), 139.90 (+, C-3), 163.23 (+, CHO). – MS (EI, 70 eV), *m/z* (%): 217 (16) [M^+], 202 (1) [$M^+ - CH_3$], 188 (1) [$M^+ - C_2H_5$], 173 (4), 148 (45), 136 (4), 91 (100) [CH_2Ph^+], 65 (6), 41 (4). – Anal. calcd for $C_{14}H_{19}NO$ (217.3): C, 77.38; H, 8.81; N, 6.45. Found: C, 77.12; H, 8.66; N, 6.22. – 217.1467 (correct HRMS).

***N*-Benzyl-*N*-(2-isopropylbut-3-enyl)formamide (13b)**: According to GP3, 6.70 mL (17.2 mmol) of isopropylmagnesium chloride (2.57 N in Et_2O), 1.24 mL (6.89 mmol) *N*-benzylpyrroline (**12**) and 2.44 mL (8.27 mmol) of titanium(IV) tetraisopropoxide in 40 mL of diethyl ether afforded 621 mg (39%) of **13b** (R_f = 0.30) as a colorless oil. – IR (film): ν = 3067 cm^{-1}, 3030, 2959, 2873, 1674, 1496, 1429, 1399, 1369, 1270, 1215, 1164, 1121, 1078, 1029, 1001, 918, 821, 743, 702, 607. – ^{1}HNMR (250 MHz, $CDCl_3$): Rotamer A: δ = 0.81 (d, ^3J = 6.7 Hz, 3 H, CH_3), 0.83 (d, ^3J = 6.7 Hz, 3 H, CH_3), 1.55 [sept, ^3J = 6.7 Hz, 1 H, C*H*$(CH_3)_2$], 2.07 (m_c, 1 H, 2-H), 3.02 (ABM, dd, ^3J = 10.0 Hz, ^2J = 14.0 Hz, 1 H, 1-H), 3.33 (ABM, dd, ^3J = 10.0 Hz, ^2J = 14.0 Hz, 1 H, 1-H), 4.19 (AB, d, ^2J = 14.8 Hz, 1 H, NCH_2), 4.79 (AB, d, ^2J = 14.8 Hz, 1 H, NCH_2), 4.96 (dd, ^2J = 1.8 Hz, ^3J = 17.1 Hz, 1 H, 4-H), 5.07 (dd, ^2J = 1.8 Hz, ^3J = 10.0 Hz, 1 H, 4-H), 5.47 (dt, ^3J = 10.0 Hz, ^3J = 17.1 Hz, 1 H, 3-H), 7.17 (m, 5 H, Aryl-H), 8.08 (s, 1 H, CHO); rotamer B: δ = 0.82 (d, ^3J = 6.7 Hz, 3 H, CH_3), 0.84 (d, ^3J = 6.7 Hz, 3 H, CH_3), 1.55 [sept, ^3J = 6.7 Hz, 1 H, C*H*$(CH_3)_2$], 2.19 (m_c, 1 H, 2-H), 3.12 (ABM, d, ^2J = 14.0 Hz, 1 H, 1-H), 3.17 (ABM, d, ^2J = 14.0 Hz, 1 H, 1-H), 4.30 (AB, d, ^2J = 15.6 Hz, 1 H, NCH_2), 4.38 (AB, d, ^2J = 15.6 Hz, 1 H, NCH_2), 4.98 (dd, ^2J = 1.8 Hz, ^3J = 17.1 Hz, 1 H, 4-H), 5.12 (dd, ^2J = 1.8 Hz, ^3J = 10.0 Hz, 1 H, 4-H), 5.47 (dt, ^3J = 10.0 Hz, ^3J = 17.1 Hz, 1 H, 3-H), 7.17 (m, 5 H, Aryl-H), 8.26 (s, 1 H, CHO). – ^{13}CNMR (62.9 MHz, $CDCl_3$): Rotamer A: δ = 18.53 (CH_3), 20.70 (CH_3), 29.27 [*C*$H_2(CH_3)_2$], 43.93 (N*C*H_2CH), 48.43 [*C*H$CH_2(CH_3)_2$], 49.08 (*C*H_2Ph), 117.44 (C-4), 127.55 (2 C, C-Aryl), 127.59 (C-Aryl), 128.64 (2 C, C-Aryl), 135.99 (C-Aryl), 136.54 (C-3), 163.09 (CHO); rotamer B: δ = 18.69 (CH_3), 20.70 (CH_3), 29.77 [*C*$H_2(CH_3)_2$], 45.55 (N*C*H_2CH), 48.62 [*C*H$CH_2(CH_3)_2$], 51.51 (*C*H_2Ph), 118.78 (C-4), 128.03 (C-Aryl), 128.38 (2 C, C-Aryl), 128.84 (2 C, C-Aryl), 136.37

(C-Aryl), 137.79 (C-3), 163.23 (CHO). – MS (DCI, 70 eV), *m/z* (%): 463 (21) [2M + H^+], 249 (100) [M + NH_4^+], 232 (70) [M + H^+]. – Anal. calcd for $C_{15}H_{21}NO$ (231.3): C, 77.88; H, 9.15; N, 6.05. Found: C, 78.25; H, 8.99; N, 5.97. – 231.1623 (correct HRMS).

***N*-Benzyl-*N*-(2-*sec*-butylbut-3-enyl)formamide (13c)**: According to GP3, 23.5 mL (40.0 mmol) of *n*-butylmagnesium chloride (1.7 N in Et_2O), 2.70 mL (14.2 mmol) of *N*-benzylpyrroline (**12**) and 6.00 mL (20.2 mmol) of titanium(IV) tetraisopropoxide in 90 mL of diethyl ether afforded 1.59 g (46%) of **13c** (R_f = 0.26) as a colorless oil. – IR (film): ν = 3066 cm^{-1}, 3029, 2962, 2930, 2875, 1675 (C=O), 1496, 1455, 1429, 1381, 1271, 1213, 1163, 1119, 1077, 1000, 970, 917, 741, 701, 607. – ^{1}HNMR (250 MHz, $CDCl_3$): Rotamers A+B: δ = 0.78–0.86 (m, 6 H, CH_3, 1'-H, 4'-H), 1.01–1.11 (m, 1 H, 2'-H), 1.08–1.20 (m, 2 H, 3'-H), 2.09–2.42 (m, 1 H, 2-H), 2.99–3.39 (m, 2 H, 1-H), 4.25–4.76 (m, 2 H, C*H*$_2$Ph), 4.91–5.17 (m, 2 H, 4-H), 5.34–5.68 (m, 1 H, 3-H), 7.17–7.38 (m, 5 H, Aryl-H), 8.08+8.24 (s, 1 H, CHO). – ^{13}CNMR (50.3 MHz, $CDCl_3$, APT): Rotamer A: δ = 11.39 (+, C-3'), 14.68 (+, C-4'), 28.94 (–, C-2'), 35.63 (+, C-1'), 44.01 (–, C-1), 45.64 (+, C-2), 49.95 (–, *C*H_2Ph), 117.49 (–, C-4), 127.44 (+, 2 C, C-Aryl), 127.49 (+, C-Aryl), 128.27 (+, 2 C, C-Aryl), 135.75 (+, C-3), 135.87 (–, C-Aryl), 163.01 (+, CHO); rotamer B: δ = 11.39 (+, C-3'), 14.93 (+, C-4'), 29.01 (–, C-2'), 36.13 (+, C-1'), 45.49 (–, C-1), 45.79 (+, C-2), 51.41 (–, *C*H_2Ph), 118.66 (–, C-4), 128.20 (+, 2 C, C-Aryl), 128.53 (+, C-Aryl), 128.74 (+, 2 C, C-Aryl), 136.26 (–, C-Aryl), 137.15 (+, C-3), 163.18 (+, CHO). – MS (EI, 70 eV), *m/z* (%): 245 (10) [M^+], 201 (3), 188 (4), 148 (53), 136 (3), 110 (4), 91 (100), 65 (1). – Anal. calcd for $C_{16}H_{23}NO$ (245.4): C, 78.32; H, 9.45; N, 5.71. Found: C, 78.35; H, 9.22; N, 5.76. – 245.1780 (correct HRMS).

***N*-Benzyl-*N*-(2-cyclopentylbut-3-enyl)formamide (13d)**: According to GP3, 2.70 mL (14.2 mmol) of *N*-benzylpyrroline (**12**), 6.00 mL (20.2 mmol) of titanium(IV) tetraisopropoxide and 33.3 mL (40.0 mmol) of cyclopentylmagnesium bromide (1.2 N in THF) afforded 1.14 g (31%) of **13d** (R_f = 0.12) as a colorless oil. – IR (film): ν = 3065 cm^{-1}, 3028, 2952, 2866, 2784, 1674 (C=O), 1495, 1430, 1398, 1350, 1269, 1205, 1155, 1077, 996, 972, 916, 742, 701, 609, 592. – ^{1}HNMR (250 MHz, $CDCl_3$): Rotamers A+B: δ = 0.99–1.23 (m, 2 H, *c*pent-H), 1.35–1.77 (m, 7 H, *c*pent-H), 2.03–2.31 (m, 1 H, 2-H), 2.93–3.38 (m, 2 H,

1-H), 4.11–4.39 (m, 2 H, C*H*$_2$Ph), 4.79–5.12 (m, 2 H, 4-H), 5.40–5.69 (m, 1 H, 3-H), 7.16–7.39 (m, 5 H, Aryl-H), 8.07+8.25 (s, 1 H, CHO). – ^{13}CNMR (50.3 MHz, $CDCl_3$, DEPT): Rotamer A: δ = 24.94 (–, C-2'), 25.20 (–, C-5'), 30.15 (+, C-1'), 30.40 (–, C-4'), 41.64 (–, C-3'), 45.04 (–, C-1), 47.95 (+, C-2), 50.24 (–, *C*H$_2$Ph), 116.58 (–, C-4), 127.57 (+, 2 C, C-Aryl), 128.00 (+, C-Aryl), 128.82 (+, 2 C, C-Aryl), 136.01 (C_{quat}, C-Aryl), 138.05 (+, C-3), 162.99 (+, CHO); rotamer B: δ = 24.97 (–, C-2'), 25.26 (–, C-5'), 30.31 (+, C-1'), 30.55 (–, C-4'), 42.16 (–, C-3'), 45.62 (–, C-1), 48.15 (+, C-2), 51.61 (–, *C*H$_2$Ph), 118.06 (–, C-4), 128.42 (+, 2 C, C-Aryl), 128.62 (+, C-Aryl), 131.88 (+, 2 C, C-Aryl), 136.38 (C_{quat}, C-Aryl), 139.38 (+, C-3), 163.23 (+, CHO). – MS (EI, 70 eV), *m/z* (%): 257 (25) [M^+], 213 (13), 188 (4), 148 (65), 136 (5), 122 (9), 91 (100), 65 (3). – Anal. calcd for $C_{17}H_{23}NO$ (257.4): C, 79.33; H, 9.01; N, 5.44. Found: C, 79.94; H, 8.93; N, 5.29. – 257.1780 (correct HRMS).

2-Benzyl-4-ethyl-2-azabicyclo[3.1.0]hexane (14a): According to GP1, 613 mg (2.82 mmol) of *N*-benzyl-*N*-(2-ethylbut-3-enyl)formamide (**13a**), 1.00 mL (3.38 mmol) of titanium(IV) tetraisopropoxide in 50 mL of THF and 5.72 mL (9.32 mmol) of cyclohexylmagnesium bromide (1.63 N in diethyl ether), and column chromatography on silica gel, eluting with pentane/diethyl ether (20:1) afforded 463 mg (82%) of **14a** (R_f = 0.25) as a colorless oil. – *exo*-**14a**: IR (film): ν = 3064 cm^{-1}, 3028, 2960, 2925, 2809, 1678, 1650, 1604, 1494, 1454, 1378, 1351, 1137, 1075, 1029, 908, 838, 740, 698, 646, 527. – ^{1}HNMR (250 MHz, $CDCl_3$): δ = 0.12 (dt, ^2J = 5.8 Hz, ^3J = 5.8 Hz, ^3J = 8.6 Hz, 1 H, 6-H), 0.69 (ddd, ^3J = 2.7 Hz, ^3J = 4.3 Hz, ^2J = 5.8 Hz, 1 H, 6-H), 0.94 (t, ^3J = 7.3 Hz, 3 H, CH_3), 1.25 (ddd, ^3J = 4.3 Hz, ^3J = 5.8 Hz, ^3J = 8.6 Hz, 1 H, 5-H), 1.47 (q, ^3J = 7.3 Hz, 2 H, CH_3CH_2), 1.94–2.05 (m, 2 H, 3-H, 4-H), 2.66 (dt, ^3J = 2.7 Hz, ^3J = 5.8 Hz, 1 H, 1-H), 2.68 (d, ^2J = 8.6 Hz, 1 H, 3-H), 3.55 (AB, d, ^2J = 13.0 Hz, C*H*$_2$Ph), 3.70 (AB, d, ^2J = 13.0 Hz, C*H*$_2$Ph), 7.22–7.41 (m, 5 H, Aryl-H).). – ^{13}CNMR (62.9 MHz, $CDCl_3$, DEPT): δ = 2.14 (–, C-6), 12.32 (+, C-5), 19.84 (+, CH_3), 28.01 (–, *C*H$_2$CH$_3$), 40.51 (+, C-1), 41.95 (+, C-4), 53.69 (–, C-3), 58.95 (–, *C*H$_2$Ph), 126.68 (+, C-Aryl), 128.09 (+, 2 C, C-Aryl), 128.77 (+, 2 C, C-Aryl), 139.73 (C_{quat}, C-Aryl). – MS (EI, 70 eV), *m/z* (%): 201 (31) [M^+], 186 (5) [$M^+ - CH_3$], 172 (74) [$M^+ - C_2H_5$], 158 (5), 124 (1), 110 (3), 91 (100) [CH_2Ph^+], 65 (8), 55 (3), 41 (5). – Anal. calcd for $C_{14}H_{19}N$ (201.3): C, 83.53; H 9.51; N, 6.96. Found: C, 83.80; H, 9.52; N, 7.12. – 201.1517 (correct HRMS).

2-Benzyl-4-isopropyl-2-azabicyclo[3.1.0]hexane (14b): According to GP1, 621 mg (2.68 mmol) of *N*-benzyl-*N*-(2-isopropylbut-3-enyl)formamide (**13b**), 0.95 mL (3.2 mmol) of titanium(IV) tetraisopropoxide in 50 mL of THF and 5.4 mL (8.8 mmol) of cyclohexylmagnesium bromide (1.63 N in diethyl ether), and column chromatography on silica gel, eluting with pentane/diethyl ether (20:1) afforded 445 mg (77%) of **14b** (R_f = 0.25) as a colorless oil. – *exo*-**14b**: IR (film): ν = 3064 cm^{-1}, 3028, 2997, 2956, 2927, 2806, 1495, 1453, 1386, 1368, 1350, 1162, 1142, 1029, 1003, 907, 856, 823, 740, 698. – ^{1}HNMR (250 MHz, $CDCl_3$): δ = 0.13 (dt, ^2J = 5.8 Hz, ^3J = 5.8 Hz, ^2J = 8.5 Hz, 1 H, 6-H), 0.64 (ddd, ^3J = 2.7 Hz, ^3J = 4.3 Hz, ^2J = 5.8 Hz, 1 H, 6-H), 0.94 (d, ^3J = 6.7 Hz, 3 H, CH_3), 0.97 (d, ^3J = 6.7 Hz, 3 H, CH_3), 1.29 (ddd, ^3J = 4.3 Hz, ^3J = 5.8 Hz, ^3J = 8.5 Hz, 1 H, 5-H), 1.69 [sep, ^3J = 6.7 Hz, 1 H, C*H*$(CH_3)_2$], 1.89–2.02 (m, 2 H, 3-H, 4-H), 2.67 (dt, ^3J = 2.7 Hz, ^3J = 5.8 Hz, 1 H, 1-H), 2.78 (d, ^2J = 9.8 Hz, 1 H, 3-H), 3.52 (AB, d, ^2J = 13.1 Hz, 1 H, CH_2Ph), 3.72 (AB, d, ^2J = 13.1 Hz, 1 H, CH_2Ph), 7.21–7.40 (m, 5 H, Aryl-H). – ^{13}CNMR (62.9 MHz, $CDCl_3$, DEPT): δ = 2.66 (–, C-6), 17.78 (+, C-5), 20.38 (+, CH_3), 20.54 (+, CH_3), 31.72 [+, *C*H$(CH_3)_2$], 41.39 (+, C-1), 47.12 (+, C-4), 52.34 (–, C-3), 59.05 (–, *C*H_2Ph), 126.60 (+, C-Aryl), 128.08 (+, 2 C, C-Aryl), 128.55 (+, 2 C, C-Aryl), 140.03 (C_{quat}, C-Aryl). – MS (EI, 70 eV), *m/z* (%): 215 (29) [M^+], 200 (21) [$M^+ - CH_3$], 186 (5), 172 (95) [$M^+ - C_3H_7$], 146 (5), 120 (4), 91 (100) [CH_2Ph^+], 65 (4), 41 (3). – Anal. calcd for $C_{15}H_{21}N$ (215.3): C, 83.67; H, 9.83; N, 6.50. Found: C, 83.39; H, 10.10; N, 6.39. – 215.1674 (correct HRMS).

2-Benzyl-4-*sec*-butyl-2-azabicyclo[3.1.0]hexane (14c): According to GP1, 1.25 g (5.09 mmol) of *N*-benzyl-*N*-(2-*sec*-butylbut-3-enyl)formamide (**13c**), 1.83 mL (6.20 mmol) of titanium(IV) tetraisopropoxide in 50 mL of THF and 7.67 mL (16.8 mmol) of cyclohexylmagnesium bromide (2.19 N in diethyl ether), and column chromatography on silica gel, eluting with pentane/diethyl ether (20:1) afforded 871 mg (74%) of **14c** (R_f = 0.24) as a colorless oil. – *exo*-**14c**: IR (film): ν = 3064 cm^{-1}, 3028, 2959, 2906, 2809, 1495, 1453, 1380, 1352, 1256, 1161, 1143, 1073, 1028, 1003, 978, 904, 852, 738, 697, 650. – ^{1}HNMR (300 MHz, C_6D_6): δ = –0.08 (m_c, 1 H, 6-H), 0.53 (m_c, 1 H, 6-H), 0.87 (t, ^3J = 7.2 Hz, 3 H, 4'-H), 0.99 (d, ^3J = 6.7 Hz, 3 H, 1'-H), 1.01 (m_c, 1 H, 5-H), 1.19 (m_c, 1 H, 3'-H), 1.36 (m_c, 1 H, 2'-H), 1.44 (m_c, 1 H, 3'-H), 1.87 (dd, ^2J = 10.1 Hz, ^3J = 8.0 Hz, 1 H, 3-H), 1.97 (m_c, 1 H, 4-H), 2.56

(m_c, 1 H, 1-H), 2.67 (d, ^2J = 10.1 Hz, 1 H, 3-H), 3.44 (d, ^2J = 12.8 Hz, 1 H, CH_2Ph), 3.63 (d, ^2J = 12.8 Hz, 1 H, CH_2Ph), 7.11–7.46 (m, 5 H, Aryl-H). – ^{13}CNMR (62.9 MHz, $CDCl_3$, DEPT): δ = 2.82 (–, C-6), 11.94 (+, C-4'), 16.41 (+, C-1'), 17.11 (+, C-5), 27.31 (–, C-3'), 38.76 (+, C-2'), 41.75 (+, C-1), 45.40 (+, C-4), 53.22 (–, C-3), 59.01 (–, *C*H_2Ph), 126.59 (+, C-Aryl), 128.09 (+, 2 C, C-Aryl), 128.56 (+, 2 C, C-Aryl), 140.03 (C_{quat}, C-Aryl). – MS (EI, 70 eV), *m/z* (%): 229 (18) [M^+], 214 (17) [$M^+ - CH_3$], 200 (11), 172 (99) [M^+ – *sec*-butyl], 146 (3), 91 (100) [CH_2Ph^+], 65 (4), 41 (6). – Anal. calcd for $C_{16}H_{23}N$ (229.4): C, 83.79; H, 10.11; N, 6.11. Found: C, 83.68; H, 9.98; N, 5.79. – 229.1830 (correct HRMS).

2-Benzyl-4-cyclopentyl-2-azabicyclo[3.1.0]hexane (14d): According to GP1, 1.10 g (4.27 mmol) of *N*-benzyl-*N*-(2-cyclopentylbut-3-enyl)formamide (**13d**), 1.54 mL (5.22 mmol) of titanium(IV) tetraisopropoxide in 50 mL of THF and 6.45 mL (14.2 mmol) of cyclohexylmagnesium bromide (2.19 N in diethyl ether), and column chromatography on silica gel, eluting with pentane/diethyl ether (20:1) afforded 882 mg (85%) of **14d** (R_f = 0.14) as a colorless oil. – *exo*-**14d**: IR (film): ν = 3027 cm^{-1}, 2929, 2852, 1495, 1451, 1349, 1256, 1205, 1137, 1073, 1028, 970, 846, 739, 698, 556. – ^{1}HNMR (250 MHz, $CDCl_3$): δ = 0.07 (m_c, 1 H, 6-H), 0.64 (m_c, 1 H, 6-H), 1.19 (m_c, 2 H, *c*pent-H), 1.15 (m_c, 1 H, 5-H), 1.55 (m_c, 4 H, *c*pent-H), 1.65–2.04 (m, 5 H, 3-H, 4-H, *c*pent-H), 2.64 (m_c, 1 H, 1-H), 2.79 (d, ^2J = 9.3 Hz, 1 H, 3-H), 3.52 (d, ^2J = 12.0 Hz, 1 H, CH_2Ph), 3.70 (d, ^2J = 12.0 Hz, 1 H, CH_2Ph), 7.20–7.38 (m, 5 H, Aryl-H). – ^{13}CNMR (62.9 MHz, $CDCl_3$, zusätzl. DEPT): δ = 2.18 (–, C-6), 19.12 (+, C-5), 25.25 (–, C-2'), 25.49 (–, C-5'), 31.12 (–, C-3'), 31.48 (–, C-4'), 40.81 (+, C-1'), 43.96 (+, C-4), 46.27 (+, C-1), 53.33 (–, C-3), 59.03 (–, *C*H_2Ph), 126.68 (+, C-Aryl), 128.10 (+, 2 C, C-Aryl), 128.77 (+, 2 C, C-Aryl), 139.69 ($C_{quat.}$, C-Aryl). – MS (EI, 70 eV), *m/z* (%): 241 (25) [M^+], 212 (8), 172 (100) [M^+ – *c*pent], 158 (9), 134 (3), 91 (80), 82 (7), 41 (4). – Anal. calcd for $C_{17}H_{23}N$ (241.4): C, 84.59; H, 9.60; N, 5.80. Found: C, 84.63; H, 9.56; N, 5.67. – 241.1830 (correct HRMS).

***N*-Benzyl-*N*-(3-methylenepent-4-enyl)formamide**: The title compound was prepared analogous to **8**. Starting from 2.32 g (13.2 mmol) of crude 3-methylenepent-4-enyl methanesulfonate the reaction sequence yielded 2.08 g (73%, based on the mesylate) of the

title compound (R_f = 0.36, silica gel, dichloromethane/diethyl ether/pentane 1:1:1) as a colorless oil. – IR (film): ν = 3087 cm^{-1} (Aryl-H), 3030, 3004, 2935 (CH_2), 2865, 1675 (CO), 1594 (C=C), 1496, 1429, 1398, 1368, 1303, 1204, 1180, 1078, 995, 969, 904, 821, 740, 703, 607, 590. – ^{1}HNMR (250 MHz, $CDCl_3$): Rotamer A: δ = 2.40 (t, ^3J = 7.2 Hz, 2 H, 2-H), 3.28 (t, ^3J = 7.2 Hz, 2 H, 1-H), 4.38 (s, 2 H, CH_2Ph), 4.94–5.28 [m, 4 H, 5-H, CH_2C(vin)CH_2], 6.32 (dd, ^3J = 10.8 Hz, ^3J = 17.7 Hz, 1 H, 4-H), 7.19–7.38 (m, 5 H, Aryl-H), 8.11 (s, 1 H, CHO); rotamer B: δ = 2.40 (t, ^3J = 7.2 Hz, 2 H, 2-H), 3.35 (t, ^3J = 7.2 Hz, 2 H, 1-H), 4.55 (s, 2 H, CH_2-Ph), 4.94–5.28 [m, 4 H, 5-H, CH_2C(vin)CH_2], 6.32 (dd, ^3J = 10.8 Hz, ^3J = 17.7 Hz, 1 H, 4-H), 7.19–7.38 (m, 5 H, Aryl-H), 8.28 (s, 1 H, CHO). – ^{13}CNMR (62.9 MHz, $CDCl_3$, DEPT): Rotamer A: δ = 29.04 (–, C-2), 41.68 (–, C-1), 45.40 (–, *C*H_2Ph), 113.92 (–, C-5), 117.60 [(–, CH_2C(vin)CH_2)], 127.50 (+, 2 C, C-Aryl), 127.59 (+, C-Aryl), 128.64 (+, 2 C, C-Aryl), 136.09 (C_{quat}, C-Aryl), 137.74 (+, C-4), 142.01 (C_{quat}, C-3), 162.68 (+, CHO); rotamer B: δ = 30.76 (–, C-2), 45.27 (–, C-1), 51.77 (–, *C*H_2Ph), 114.00 (–, C-5), 118.74 [(–, CH_2C(vin)CH_2)], 128.05 (+, C-Aryl), 128.20 (+, 2 C, C-Aryl), 128.81 (+, 2 C, C-Aryl), 136.38 (C_{quat}, C-Aryl), 137.96 (+, C-4), 143.09 (C_{quat}, C-3), 162.95 (+, CHO). – MS (EI, 70 eV), *m/z* (%): 215 (18) [M^+], 148 (17), 124 (7), 91 (100) [CH_2Ph^+], 65 (7), 41 (3). – Anal. calcd for $C_{14}H_{17}NO$ (215.3): C, 78.10; H, 7.96. Found: C, 77.93; H, 8.11.

2-Benzyl-5-methylene-2-azabicyclo[4.1.0]heptane: According to GP1 with 0.78 g (3.62 mmol) of *N*-benzyl-*N*-(3-methylenepent-4-enyl)formamide, 1.19 mL (4.03 mmol) of titanium(IV) tetraisopropoxide in 55 mL of THF and 14.0 mL (11.2 mmol) of cyclohexylmagnesium bromide (0.80 N in diethyl ether), column chromatography on silica gel, eluting with pentane/diethyl ether (8:1 with 0.7% of NEt_3) afforded 66.4 mg (9%) of the title compound (R_f = 0.34) as a colorless oil. – IR (film): ν = 3073 cm^{-1}, 3027, 2922, 2849, 2806, 1704, 1639, 1601, 1494, 1453, 1365, 1352, 1316, 1270, 1203, 1159, 1120, 1073, 1028, 878, 820, 758, 736, 698. – ^{1}HNMR (250 MHz, $CDCl_3$): δ = 0.59 (ddd, ^3J = 1.2 Hz, ^3J = 3.4 Hz, ^3J = 5.4 Hz, 1 H, 7-H), 0.73 (dt, ^3J = 4.5 Hz, ^2J = 5.4 Hz, ^3J = 5.4 Hz, 1 H, 7-H), 1.70 (ddd, ^3J = 2.3 Hz, ^3J = 3.4 Hz, ^3J = 5.4 Hz, 1 H, 6-H), 2.13–2.35 (m, 3 H, 3-H, 4-H), 2.51 (ddd, ^3J = 1.2 Hz, ^3J = 2.3 Hz, ^3J = 4.5 Hz, 1 H, 1-H), 2.58–2.64 (m, 1 H, 3-H), 3.65 (AB, d, ^2J = 13.1 Hz, 1 H, CH_2Ph), 3.77 (AB, d, ^2J = 13.1 Hz, 1 H, CH_2Ph), 4.83 (s, 1 H, C=CH_2), 4.95 (s, 1 H, C=CH_2), 7.23–7.41 (m, 5 H, Aryl-H). – ^{13}CNMR (62.9 MHz, $CDCl_3$, zusätzl.

DEPT): δ = 8.31 (–, C-7), 17.12 (+, C-6), 30.66 (–, C-4), 37.57 (+, C-1), 47.22 (–, *C*H_2Ph), 61.47 (–, C-3), 109.84 (–, C=*C*H_2), 126.91 (+, C-Aryl), 128.18 (+, 2 C, C-Aryl), 129.04 (+, 2 C, C-Aryl), 138.86 ($C_{quat.}$, C-Aryl), 143.90 (C_{quat}, C-5). – MS (EI, 70 eV), *m/z* (%): 199 (25) [M^+], 184 (8), 122 (5) [M^+ – Ph], 108 (9) [M^+ – CH_2Ph], 91 (100) [CH_2Ph^+], 79 (12), 65 (15). – 199.1361 (correct HRMS).