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Supporting Information for the Paper

Additions of Allenyl/Propargyl Organometallic Reagents to 4-Oxoazetidine-2-carbaldehydes. Novel Palladium-Catalyzed Domino Reactions in Allenynes

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Boron Trifluoride Diethyl Etherate Promoted Reaction between Propargyltrimethylsilane and 4-Oxoazetidine-2-carbaldehyde (+)-1a. Synthesis of α-Allenic Alcohol (+)-2. A solution of the aldehyde (+)-**1a** (56 mg, 0.33 mmol) in dichloromethane (1 mL) was added dropwise to a stirred solution of boron trifluoride diethyl etherate (71 mg, 0.50 mmol) in dichloromethane (1 mL) at –78 ºC. After 5 min, propargyltrimethylsilane (75 mg, 0.66 mmol) was added and the mixture was stirred for 12 h at –78 ºC. Saturated aqueous sodium hydrogen carbonate (5 mL) was added, and the mixture was allowed to warm to room temperature, before being partitioned between dichloromethane and water. The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes (3:1) gave 29 mg (42%) of the less polar compound (+)-*syn*-**2** and 3 mg (4%) of the more polar compound, its (+)-*anti* -**2** epimer.

(3*R*,4*S*)-4-[(*R*)-1-Hydroxy-2,3-butadienyl)]-3-methoxy-1-(3-propenyl)-2-azetidinone, (+)-*syn*-2. $[\alpha]_D$ = +34.7 (*c* = 0.8 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 5.79 (m, 1H), 5.36 (m,

1H), 5.23 (m, 2 H), 4.93 (dd, *J* = 6.7, 3.0 Hz, 1H), 4.51 (d, *J* = 4.7 Hz, 1H), 4.48 (m, 1H), 4.15 (dd, *J* = 15.4, 5.2 Hz, 1H), 3.80 (dd, *J* = 5.0 Hz, 1H), 3.78 (m, 1H), 3.62 (s, 3H), 2.51 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 207.1, 167.3, 131.8, 118.3, 91.9, 83.4, 78.4, 67.9, 60.8, 59.5, 43.9; IR ($CHCl_3$): ν = 3422, 2990, 1938, 1751 cm^{-1}; MS (CI): *m/z* (%): 210 (100) [*M* + H]$^+$, 209 (22) [*M*]$^+$; elemental analysis calcd (%) for $C_{11}H_{15}NO_3$ (209.2): C 63.14, H 7.23, N 6.69; found C 63.21, H 7.20, N 6.67.

(3*R*,4*S*)-4-[(*S*)-1-Hydroxy-2,3-butadienyl)]-3-methoxy-1-(3-propenyl)-2-azetidinone, (+)-*anti*-2. $[\alpha]_D$ = +88.6 (*c* = 0.3 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 5.76 (m, 1H), 5.32 (q, *J* = 6.8 Hz, 1H), 5.23 (m, 2 H), 4.89 (m, 2H), 4.59 (d, *J* = 4.9 Hz, 1H), 4.44 (m, 1H), 4.09 (ddt, *J* = 15.6, 5.4, 1.5 Hz, 1H), 3.78 (t, *J* = 4.9 Hz, 1H), 3.69 (m, 1H), 3.64 (s, 3H), 2.99 (brs, 1H); IR ($CHCl_3$): ν = 3420, 2992, 1940, 1749 cm^{-1}; MS (CI): *m/z* (%): 210 (100) [*M* + H]$^+$, 209 (15) [*M*]$^+$; elemental analysis calcd (%) for $C_{11}H_{15}NO_3$ (209.2): C 63.14, H 7.23, N 6.69; found C 63.08, H 7.21, N 6.71.

Spectroscopic and analytical data for some representative pure forms of **3** follow.

(3*R*,4*S*)-4-[(*R*)-1-Hydroxy-3-chloro-4-trimethylsilyl-2-butenyl]-3-phenoxy-1-(2-propenyl)-2-azetidinone, (+)-3b. From 87.4 mg (0.188 mmol) of 4-oxoazetidine-2-carbaldehyde (+)-**1b**, and after chromatography of the residue using hexanes/ethyl acetate (1:2) as eluent gave two fractions. The less polar fraction contained the allylic alcohol (+)-**3b** (72 mg, 50%) as a colorless oil; $[\alpha]_D$ = +11.8 (*c* = 1.2 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.31 (m, 2H), 7.09 (m, 3H), 5.82 (m, 1H), 5.43 (d, *J* = 7.8 Hz, 1H), 4.96 (dd, *J* = 7.8, 3.7 Hz, 1H), 4.21 (dd, *J* = 15.6, 5.1 Hz, 1H),

4.08 (dd, *J* = 4.8, 3.8 Hz, 1H), 3.79 (dd, *J* = 15.8, 6.8 Hz, 1H), 2.38 (brs, 1H), 1.88 (s, 2H), 0.09 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 165.8, 157.3, 136.5, 131.5, 129.6, 122.6, 121.8, 118.7, 115.8, 80.6, 68.4, 60.4, 59.6, 44.3, 30.9, –1.4; IR ($CHCl_3$): ν = 3421, 1750 cm^{-1}; MS (CI): *m/z* (%): 382 (10) [*M* + 3]$^+$, 380 (100) [*M* + H]$^+$; elemental analysis calcd (%) for $C_{19}H_{26}NO_3SiCl$ (379.9): C 60.06, H 6.90, N 3.69, Cl 9.33; found C 60.14, H 6.92, N 3.68, Cl 9.31. The more polar fraction contained the chlorodiene (+)-**4b** (20 mg, 18%).

(3*R*,4*S*)-1-(3-Butenyl)-4-[(*R*)-1-hydroxy-3-chloro-4-trimethylsilyl-2-butenyl]-3-methoxy-2-azetidinone, (+)-3c. From 60 mg (0.327 mmol) of 4-oxoazetidine-2-carbaldehyde (+)-**1c**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave two fractions. The less polar fraction contained the allylic alcohol (+)-**3c** (46 mg, 42%) as a colorless oil; $[\alpha]_D$ = +23.6 (*c* 1.5 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 5.74 (m, 1H), 5.42 (d, *J* = 7.6 Hz, 1H), 5.08 (m, 2 H), 4.82 (dd, *J* = 7.6, 2.7 Hz, 1H), 4.49 (d, *J* = 4.9 Hz, 1H), 3.92 (dd, *J* = 4.9, 2.9 Hz, 1H), 3.61 (s, 3 H), 3.58 (m, 1H), 3.08 (dt, *J* = 13.7, 7.1 Hz, 1H), 2.72 (brs, 1H), 2.32 (m, 2H), 1.93 (s, 2H), 0.10 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 167.4, 135.8, 134.8, 122.1, 117.1, 83.5, 68.3, 59.9, 59.5, 40.6, 31.6, 30.9, –1.4; IR ($CHCl_3$): ν = 3428, 1750 cm^{-1}; MS (CI): *m/z* (%): 334 (48) [*M* + 3]$^+$, 331 (100) [*M* + H]$^+$; elemental analysis calcd (%) for $C_{15}H_{26}NO_3SiCl$ (331.9): C 54.28, H 7.90, N 4.22, Cl 10.68; found C 54.36, H 7.92, N 4.21, Cl 10.65. The more polar fraction contained the chlorodiene (+)-**4c** (4 mg, 5%).

(3*RS*,4*SR*)-4-[(*R*)-1-Hydroxy-3-chloro-4-trimethylsilyl-2-butenyl]-1-(*p*-methoxyphenyl)-3-(2-propenyl)-2-azetidinone, (±)-3f.

From 63 mg (0.257 mmol) of 4-oxoazetidine-2-carbaldehyde (±)-**1f**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave two fractions. The less polar fraction contained the allylic alcohol (±)-**3f** (54 mg, 53%) as a colorless oil; $[\alpha]_D$ = +67.7 (*c* = 1.4 in $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, 25 ^oC): δ = 7.43 and 6.85 (d, *J* = 9.0 Hz, each 2H), 5.99 (m, 1H), 5.36 (d, *J* = 8.3 Hz, 1H), 5.15 (m, 2H), 4.89 (dd, *J* = 8.0, 5.4 Hz, 1H), 4.29 (t, *J* = 5.4 Hz, 1H), 3.79 (s, 3H), 3.44 (dd, *J* = 7.8, 5.4 Hz, 1H), 2.62 (m, 2H), 1.92 (s, 3H), 0.11 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$, 25 ^oC): δ = 167.8, 156.4, 137.1, 135.5, 131.3, 123.0, 120.5, 114.0, 69.1, 58.7, 55.5, 50.6, 30.9, 29.1, –1.4; IR ($CHCl_3$): ν = 3422, 1747 cm^{-1}; MS (CI): *m/z* (%): 396 (44) $[M + 3]^+$, 394 (100) $[M + H]^+$; elemental analysis calcd (%) for $C_{20}H_{28}NO_3SiCl$ (393.9): C 60.97, H 7.16, N 3.56, Cl 8.00, found C 61.05, H 7.14, N 3.55, Cl 8.02. The more polar fraction contained the chlorodiene (±)-**4f** (3 mg, 4%).

Spectroscopic and analytical data for some representative pure forms of **4** follow.

(3*R*,4*S*)-4-[(1*E*)-3-Chloro-1,3-butadienyl]-3-phenoxy-1-(2-propenyl)-2-azetidinone, (+)-4b. Method A. From 36 mg (0.095 mmol) of 2-chloro-3-silapropenyl alcohol (+)-**3b**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave the chlorodiene (+)-**4b** (15 mg, 55%) as a colorless oil.

Method B. From 36 mg (0.095 mmol) of 2-chloro-3-silapropenyl alcohol (+)-**3b**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave the chlorodiene (+)-**4b** (22 mg, 81%) as a colorless oil; $[\alpha]_D$ = +17.2 (*c* = 0.7, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.28 (m, 2H), 6.99 (m, 3H),

6.38 (d, *J* = 15.0 Hz, 1H), 6.14 (dd, *J* = 15.0, 8.5 Hz, 1H), 5.77 (m, 1H), 5.40 (m, 2H), 5.36 (d, *J* = 4.6 Hz, 1H), 5.21 (m, 2H), 4.49 (dd, *J* = 8.5, 4.6 Hz, 1H), 4.14 (ddt, *J* = 15.6, 5.4, 1.5 Hz, 1H), 3.62 (ddt, *J* = 15.4, 6.8, 0.9 Hz, 1H); IR ($CHCl_3$): ν 1750 cm^{-1}; MS (CI): *m/z* (%): 292 (42) $[M + 3]^+$, 289 (100) $[M + H]^+$; elemental analysis calcd (%) for $C_{16}H_{16}NO_2Cl$ (289.8): C 66.32, H 5.57, N 4.83, Cl 12.24; found C 66.40, H 5.60, N 4.81, Cl 12.27.

(3*R*,4*S*)-1-(3-Butenyl)-4-[(1*E*)-3-chloro-1,3-butadienyl]-3-methoxy-2-azetidinone, (+)-4c. Method A. From 36 mg (0.108 mmol) of 2-chloro-3-silapropenyl alcohol (+)-**3c**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave the chlorodiene (+)-**4c** (16 mg, 60%) as a colorless oil.

Method B. From 36 mg (0.108 mmol) of 2-chloro-3-silapropenyl alcohol (+)-**3c**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave the chlorodiene (+)-**4c** (21 mg, 80%) as a colorless oil; $[\alpha]_D$ = +43.7 (*c* = 0.4, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 6.43 (d, *J* = 15.0 Hz, 1H), 6.16 (dd, *J* = 15.0, 8.8 Hz, 1H), 5.74 (m, 1H), 5.46 (m, 2H), 5.11 (m, 2H), 4.58 (d, *J* = 4.4 Hz, 1H), 4.27 (dd, *J* = 8.8, 4.4 Hz, 1H), 3.44 (s, 3H), 3.37 (m, 1H), 3.11 (dt, *J* = 13.9, 6.6 Hz, 1H), 2.28 (m, 2H); IR ($CHCl_3$): ν 1751 cm^{-1}; MS (CI): *m/z* (%): 244 (43) $[M + 3]^+$, 242 (100) $[M + H]^+$; elemental analysis calcd (%) for $C_{12}H_{16}NO_2Cl$ (241.8): C 59.63, H 6.67, N 5.79, Cl 14.67; found C 59.71, H 6.65, N 5.81, Cl 14.70.

(3*R*,4*S*)-4-[(1*E*)-3-Chloro-1,3-butadienyl]-1-(*p*-methoxyphenyl)-3-(2-propenyl)-2-azetidinone, (±)-4f. Method A. From 34 mg (0.086 mmol) of 2-chloro-3-silapropenyl alcohol (±)-**3f**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as

eluent gave the chlorodiene (±)-**4f** (13 mg, 49%) as a colorless oil.

Method B. From 34 mg (0.086 mmol) of 2-chloro-3-silapropenyl alcohol (±)-**3f**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave the chlorodiene (±)-**4f** (23 mg, 88%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.33 and 6.86 (dd, *J* = 6.8, 2.4 Hz, each 2H), 6.38 (d, *J* = 15.0 Hz, 1H), 6.21 (dd, *J* = 15.0, 6.6 Hz, 1H), 5.85 (m, 1H), 5.43 (d, *J* = 1.0 Hz, 1H), 5.37 (s, 1H), 5.12 (m, 2H), 4.72 (t, *J* = 5.9 Hz, 1H), 3.79 (s, 3H), 3.58 (dt, *J* = 9.5, 5.9 Hz, 1H), 2.60 and 2.35 (m, each 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 166.2, 156.0, 137.2, 134.6, 131.4, 131.3, 129.4, 118.1, 117.1, 117.0, 114.4, 55.7, 55.5, 53.6, 29.4; IR ($CHCl_3$): ν 1749 cm^{-1}; MS (CI): *m/z* (%): 306 (42) $[M + 3]^+$, 304 (100) $[M + H]^+$; elemental analysis calcd (%) for $C_{17}H_{18}NO_2Cl$ (303.8): C 67.21, H 5.97, N 4.61, Cl 11.67; found C 67.29, H 5.95, N 4.62, Cl 11.65.

Spectroscopic and analytical data for some representative pure forms of **7** follow.

(3*R*,4*S*)-4-[(*R*)-1-Hydroxy-3-butynyl]-3-methoxy-1-(2-propenyl)-2-azetidinone, (+)-7a. From 112 mg (0.665 mmol) of aldehyde (+)-**1a**, and after chromatography of the residue using hexanes/ethyl acetate (1:2) as eluent gave compound (+)-**7a** (76 mg, 55%) as a colorless oil; $[\alpha]_D$ = +49.5 (*c* = 1.3 in $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$, 25 ^{o}C): δ = 5.79 (m, 1H), 5.26 (m, 2H), 4.50 (d, *J* = 4.9 Hz, 1H), 4.11 (ddt, *J* = 15.6, 5.4, 1.5 Hz, 1H), 3.99 (m, 1H), 3.94 (d, *J* = 4.9 Hz, 1H), 3.83 (ddt, *J* = 15.6, 6.6, 1.5 Hz, 1H), 3.61 (s, 3H), 2.68 (s, 1H), 2.52 (dd, *J* = 6.4, 2.7 Hz, 2H), 2.09 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$, 25 ^{o}C): δ = 167.4, 131.9, 118.6, 83.1, 79.8, 71.4, 69.1, 59.4, 59.3, 44.2, 24.0; IR ($CHCl_3$):

ν = 3424, 1749•cm^{-1}; MS (CI): *m/z* (%): 210 (100) [*M* + H]$^{+}$, 209 (21) [*M*]$^{+}$; elemental analysis calcd (%) for $C_{11}H_{15}NO_3$ (209.2): C 63.14, H 7.23, N 6.69; found C 63.07, H 7.21, N 6.71.

(3*R*,4*S*)-4-[(*R*)-1-Hydroxy-3-butynyl]-3-phenoxy-1-(2-propynyl)-2-azetidinone, (+)-7d. From 60 mg (0.264 mmol) of aldehyde (+)-**1h**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound (+)-**7d** (40 mg, 57%) as a colorless oil; $[\alpha]_D$ = +140.3 (*c* = 1.1 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.33 (m, 2H), 7.09 (m, 3H), 5.27 (d, *J* = 4.9 Hz, 1H), 4.44 (dd, *J* = 17.6, 2.4 Hz, 2H), 4.23 (d, *J* = 4.9 Hz, 1H), 4.22 (m, 1H), 4.09 (dd, *J* = 17.6, 2.4 Hz, 2H), 2.62 (m, 2H), 2.36 and 2.15 (t, *J* = 2.7 Hz, each 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 165.3, 157.2, 129.7, 122.8, 115.9, 80.4, 79.3, 76.7, 73.1, 71.8, 69.1, 59.4, 31.4, 24.4; IR ($CHCl_3$): ν = 3427, 1748•cm^{-1}; MS (CI): *m/z* (%): 270 (100) [*M* + H]$^{+}$, 269 (22) [*M*]$^{+}$; elemental analysis calcd (%) for $C_{16}H_{15}NO_3$ (269.3): C 71.36, H 5.61, N 5.20; found C 71.43, H 5.63, N 5.18.

Preparation of homopropargylic alcohols (+)-7f and (+)-8f. From 54 mg (0.229 mmol) of aldehyde (+)-**1j**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent, 37 mg (59%) of the less polar compound (+)-**7f** and 4 mg (6%) of the more polar compound (+)-**8f** were obtained.

(3*R*,4*S*)-4-[(*R*)-1-Hydroxy-3-butynyl]-3-methoxy-1-(*p*-methoxyphenyl)-2-azetidinone, (+)-7f. Colorless solid; m. p. 121–123 ^{o}C; $[\alpha]_D$ = +66.6 (*c* = 0.9 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.48 and 6.87 (dd, *J* = 6.8, 2.2 Hz, each 2H), 4.66 (d, *J* = 5.2 Hz, 1H), 4.59 (dd, *J* = 5.2, 3.4 Hz, 1H), 4.16 (m, 1H), 3.79 and 3.69 (s, each 3H), 2.84 (d, *J* = 3.4 Hz, 1H), 2.59 (ddd, *J* = 16.9, 6.6, 2.7 Hz, 1H), 2.41 (ddd, *J* = 16.9, 8.0, 2.7 Hz, 2H),

2.15 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 164.8, 156.8, 130.7, 120.1, 114.2, 82.6, 80.1, 71.3, 69.1, 59.7, 58.7, 55.4, 23.9; IR ($CHCl_3$): ν = 3425, 1748•cm^{-1}; MS (CI): *m/z* (%): 276 (100) $[M + H]^+$, 275 (20) $[M]^+$; elemental analysis calcd (%) for $C_{15}H_{17}NO_4$ (275.3): C 65.44, H 6.22, N 5.09; found C 65.51, H 6.20, N 5.08.

(3*R*,4*S*)-4-[(*S*)-1-Hydroxy-3-butynyl]-3-methoxy-1-(*p*-methoxyphenyl)-2-azetidinone, (+)-8f. Colorless oil; $[\alpha]_D$ = +138.9 (*c* = 0.6 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.27 and 6.87 (d, *J* = 9.0 Hz, each 2H), 4.73 (d, *J* = 5.4 Hz, 1H), 4.53 (dd, *J* = 5.4, 3.9 Hz, 1H), 3.79 and 3.56 (s, each 3H), 3.10 (d, *J* = 8.1 Hz, 1H), 2.56 (td, *J* = 5.9, 2.7 Hz, 2H), 2.14 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 164.2, 157.0, 130.0, 119.4, 114.5, 83.2, 80.0, 71.2, 68.4, 59.7, 58.4, 55.5, 24.3; IR ($CHCl_3$): ν = 3423, 1747•cm^{-1}; MS (CI): *m/z* (%): 276 (100) $[M + H]^+$, 275 (15) $[M]^+$; elemental analysis calcd (%) for $C_{15}H_{17}NO_4$ (275.3): C 65.44, H 6.22, N 5.09; found C 65.37, H 6.20, N 5.07.

Indium Promoted Reaction between Propargyl Bromide and 4-Oxoazetidine-2-carbaldehydes 1 in an Aqueous Medium Containing NH_4Cl. Propargyl bromide (59 mg, 0.53 mmol, 57 ml of a 80% solution in toluene) was added to a well stirred suspension of the corresponding aldehyde **1** (0.35 mmol) and indium powder (48 mg, 0.42 mmol) in THF/NH_4Cl (aq. sat.) (1:5, 2.5 mL) at 0 ^{o}C. After 2 h the mixture was extracted with ethyl acetate (3 x 5 mL). The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes mixtures gave compounds **7**.

From 56 mg (0.333 mmol) of aldehyde (+)-**1a**, 49 mg (72%) of compound (+)-**7a**, containing ca. 45% of its isomer (+)-**9a** was obtained.

From 68 mg (0.407 mmol) of aldehyde (+)-**1g**, 55 mg (65%) of compound (+)-**7c**, containing ca. 43% of its isomer (+)-**9c** was obtained.

From 62 mg (0.315 mmol) of aldehyde (+)-**1i**, 49 mg (66%) of compound (+)-**7e**, containing ca. 45% of its isomer (+)-**9e** was obtained.

From 54 mg (0.229 mmol) of aldehyde (+)-**1j**, 47 mg (74%) of compound (+)-**7f**, containing ca. 20% of its isomer (+)-**9f** was obtained.

Indium Promoted Reaction between Propargyl Bromide and 4-Oxoazetidine-2-carbaldehydes 1. Propargyl bromide (49 mg, 0.41 mmol, 46 ml of a 80% solution in toluene) was added to a well stirred suspension of the corresponding aldehyde **1** (0.205 mmol) and indium powder (47 mg, 0.411 mmol) in THF/H_2O (1:1, 2 mL) at room temperature. After 16 h saturated aqueous sodium hydrogen carbonate (3 mL) was added at 0 ºC, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 5 mL). The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes mixtures gave compounds **7**.

From 54 mg (0.229 mmol) of aldehyde (+)-**1j**, 44 mg (69%) of compound (+)-**7f**, containing ca. 35% of its isomer (+)-**9f** was obtained.

Tin Promoted Reaction between Propargyl Bromide and 4-Oxoazetidine-2-carbaldehydes 1 in an Aqueous Medium Containing

NH_4Cl. Propargyl bromide (57 mg, 0.482 mmol, 54 ml of a 80% solution in toluene) was added to a well stirred suspension of the corresponding aldehyde **1** (0.16 mmol) and tin powder (114 mg, 0.96 mmol) in THF/NH_4Cl (aq. sat.) (1:5, 2.5 mL) at 0 ºC. After 2 h at room temperature the mixture was extracted with ethyl acetate (3 x 5 mL). The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes mixtures gave compounds **7**.

From 54 mg (0.229 mmol) of aldehyde (+)-**1j**, 41 mg (65%) of compound (+)-**7f**, containing ca. 43% of its isomer (+)-**9f** was obtained.

Tin Promoted Reaction between Propargyl Bromide and 4-Oxoazetidine-2-carbaldehydes 1. Propargyl bromide (49 mg, 0.41 mmol, 46 ml of a 80% solution in toluene) was added to a well stirred suspension of the corresponding aldehyde **1** (0.205 mmol) and tin powder (49 mg, 0.411 mmol) in THF/H_2O (1:1, 2 mL) at room temperature. After 16 h saturated aqueous sodium hydrogen carbonate (3 mL) was added at 0 ºC, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate (3 x 5 mL). The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes mixtures gave compounds **7**.

From 54 mg (0.229 mmol) of aldehyde (+)-**1j**, 37 mg (59%) of compound (+)-**7f**, containing ca. 46% of its isomer (+)-**9f** was obtained.

Spectroscopic and analytical data for some representative pure forms of **13** follow.

(3*R*,4*S*)-1-(3-Butenyl)-4-[(*R*)-1-hydroxy-2-methyl-2,3-butadienyl]-3-methoxy-2-azetidinone, (+)-13b. From 95 mg (0.52 mmol) of aldehyde (+)-**1c**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound (+)-**13b** (95 mg, 77%) as a colorless oil; $[\alpha]_D$ = +46.1 (*c* = 0.7 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 5.73 (m, 1H), 5.06 (m, 2H), 4.81 (q, *J* = 3.0 Hz, 1H), 4.42 (d, *J* = 4.8 Hz, 1H), 4.23 (m, 1H), 3.94 (t, *J* = 4.6 Hz, 1H), 3.55 (s, 3H), 3.50 (m, 1H), 3.20 (ddd, *J* = 13.6, 7.0, 6.0 Hz, 1H), 2.67 (brs, 1H), 2.31 (m, 2H), 1.79 (t, *J* = 3.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 205.4, 167.7, 135.0, 116.8, 99.8, 83.3, 77.2, 70.3, 59.5, 59.3, 40.7, 31.9, 16.0; IR ($CHCl_3$): ν = 3421, 2992, 1942, 1747•cm^{-1}; MS (CI): *m/z* (%): 238 (100) $[M + H]^+$, 237 (19) $[M]^+$; elemental analysis calcd (%) for $C_{13}H_{19}NO_3$ (237.3): C 65.80, H 8.07, N 5.90; found C 65.87, H 8.09, N 5.88.

Preparation of α-allenic alcohols (+)-13c and (+)-14c. From 90 mg (0.367 mmol) of aldehyde (+)-**1d**, and after chromatography of the residue using dichloromethane/ethyl acetate (9:1) as eluent, 10 mg (9%) of the less polar compound (+)-**14c** and 91 mg (83%) of the more polar compound (+)-**13c** were obtained.

(3*R*,4*S*)-1-(3-Butenyl)-4-[(*R*)-1-hydroxy-2-methyl-2,3-butadienyl]-3-phenoxy-2-azetidinone, (+)-13c. Colorless oil; $[\alpha]_D$ = +160.1 (*c* = 0.8 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 7.29 (m, 2H), 7.04 (m, 3H), 5.79 (m, 1H), 5.18 (d, *J* = 4.9 Hz, 1H), 5.11 (m, 2H), 4.72 (m, 2H), 4.39 (m, 1H), 4.11 (t, *J* = 4.9 Hz, 1H), 3.63 (dt, *J* = 15.1, 7.8 Hz, 1H), 3.34 (dt, *J* = 13.7, 6.0 Hz, 1H), 2.41 (m, 3H), 1.81 (t, *J* = 3.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 205.7, 166.4, 157.6, 135.0, 129.5, 122.4, 117.0, 115.9, 99.6, 80.2, 77.2, 71.1, 59.7, 41.1, 31.9, 15.9; IR ($CHCl_3$):

ν = 3420, 2990, 1941, 1746•cm^{-1}; MS (CI): *m/z* (%): 300 (100) [*M* + H]$^+$, 299 (27) [*M*]$^+$; elemental analysis calcd (%) for $C_{18}H_{21}NO_3$ (299.4): C 72.22, H 7.07, N 4.68; found C 72.30, H 7.04, N 4.66.

(3*R*,4*S*)-1-(3-Butenyl)-4-[(*S*)-1-hydroxy-2-methyl-2,3-butadienyl]-3-methoxy-2-azetidinone, (+)-14c. Colorless oil; $[\alpha]_D$ = +135.9 (*c* = 0.5 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.23 (m, 2H), 7.07 (m, 2H), 6.97 (m, 1H), 5.69 (m, 1H), 5.21 (d, *J* = 4.9 Hz, 1H), 5.06 (m, 2H), 4.64 (m, 2H), 4.36 (m, 1H), 4.00 (t, *J* = 4.9 Hz, 1H), 3.51 (dt, *J* = 14.2, 7.3 Hz, 1H), 3.09 (dt, *J* = 13.2, 5.9 Hz, 1H), 2.71 (d, *J* = 7.8 Hz, 1H), 2.29 (m, 2H), 1.81 (t, *J* = 3.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 206.1, 166.1, 157.3, 134.7, 129.6, 122.8, 117.4, 116.2, 98.5, 81.9, 76.5, 70.9, 58.8, 39.8, 32.1, 15.5; IR ($CHCl_3$): ν = 3423, 2991, 1940, 1747•cm^{-1}; MS (CI): *m/z* (%): 300 (100) [*M* + H]$^+$, 299 (31) [*M*]$^+$; elemental analysis calcd (%) for $C_{18}H_{21}NO_3$ (299.4): C 72.22, H 7.07, N 4.68; found C 72.15, H 7.05, N 4.70.

(3*R*,4*S*)-4-[(*R*)-1-Hydroxy-2-methyl-2,3-butadienyl]-1-(*p*-methoxyphenyl)-3-(2-propenyloxy)-2-azetidinone, (+)-13d. From 26 mg (0.099 mmol) of aldehyde (+)-**1e**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound (+)-**13d** (25 mg, 80%) as a colorless oil; $[\alpha]_D$ = +211.3 (*c* = 1.4 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.33 and 6.87 (dd, *J* = 6.8, 2.2 Hz, each 2H), 5.94 (m, 1H), 5.33 (m, 2H), 4.84 (d, *J* = 5.3 Hz, 1H), 4.76 and 4.66 (dt, *J* = 10.3, 3.0 Hz, each 1H), 4.57 (dq, *J* = 5.9, 3.0 Hz, 1H), 4.43 (d, *J* = 5.3 Hz, 1H), 4.42 and 4.27 (ddt, *J* = 12.5, 5.9, 1.4 Hz, each 1H), 3.79 (s, 3H), 3.12 (d, *J* = 10.2 Hz, 1H), 1.83 (td, *J* = 2.1, 0.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 205.5, 164.3, 156.7, 133.0, 129.9, 119.6, 118.5, 99.1, 81.8, 76.5, 72.9, 69.2, 68.9, 59.1, 55.5,

15.8; IR ($CHCl_3$): ν = 3420, 2991, 1941, 1748•cm^{-1}; MS (CI): *m/z* (%): 316 (100) $[M + H]^+$, 315 (22) $[M]^+$; elemental analysis calcd (%) for $C_{18}H_{21}NO_4$ (315.37): C 68.55, H 6.71, N 4.44; found C 68.74, H 6.69, N 4.43.

(3*RS*,4*SR*)-4-[(*RS*)-1-Hydroxy-2-methyl-2,3-butadienyl]-1-(*p*-methoxyphenyl)-3-(2-propenyl)-2-azetidinone, (±)-13e. From 67 mg (0.273 mmol) of aldehyde (±)-**1f**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound (±)-**13e** (73 mg, 90%) as a colorless oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 7.29 and 6.87 (dd, *J* = 6.6, 2.2 Hz, each 2H), 5.99 (m, 1H), 5.16 (m, 2H), 4.75 and 4.58 (m, each 1H), 4.59 (m, 1H), 4.31 (t, *J* = 5.4 Hz, 1H), 3.79 (s, 3H), 2.63 (m, 2H), 1.96 (d, *J* = 4.2 Hz, 1H), 1.74 (t, *J* = 3.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ = 205.9, 167.9, 156.3, 136.4, 130.4, 119.9, 116.1, 114.2, 98.9, 76.9, 69.5, 57.2, 55.4, 51.6, 29.5, 15.2; IR ($CHCl_3$): ν = 3424, 2992, 1940, 1745•cm^{-1}; MS (CI): *m/z* (%): 316 (100) $[M + H]^+$, 315 (22) $[M]^+$; elemental analysis calcd (%) for $C_{18}H_{21}NO_3$ (315.37): C 72.22, H 7.07, N 4.68; found C 72.30, H 7.05, N 4.69.

Preparation of α-allenic alcohols (±)-13j and (±)-14j. From 159 mg (0.654 mmol) of aldehyde (±)-**1m**, and after chromatography of the residue using dichloromethane/ethyl acetate (9:1) as eluent, 17 mg (9%) of the less polar compound (±)-**14j** and 157 mg (81%) of the more polar compound (±)-**13j** were obtained.

(3*RS*,4*SR*)-4-[(*RS*)-1-Hydroxy-2-methyl-2,3-butadienyl]-1-(*p*-methoxyphenyl)-3-(2-propynyl)-2-azetidinone, (±)-13j. Colorless oil; ^1H NMR (300 MHz, $CDCl_3$, 25 ºC): δ = 7.28 and 6.86 (dd, *J* = 6.6, 2.2 Hz, each 2H), 4.70 (m, 3H), 4.35 (dd, *J* = 5.4, 4.6 Hz, 1H), 3.78 (s, 3H), 3.58 (m, 1H), 2.87 (td, *J* = 6.3, 2.7 Hz, 1H), 2.40 (brs, 1H), 2.09 (t, *J* = 2.7 Hz, 1H), 1.75 (t, *J* = 3.0 Hz,

3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 205.8, 166.2, 156.5, 130.2, 119.9, 114.3, 98.7, 81.9, 77.6, 69.7, 68.9, 57.1, 55.4, 50.7, 15.2, 14.8; IR ($CHCl_3$): ν = 3422, 2990, 1940, 1749•cm^{-1}; MS (CI): *m/z* (%): 298 (100) [*M* + H]$^+$, 297 (25) [*M*]$^+$; elemental analysis calcd (%) for $C_{18}H_{19}NO_3$ (237.3): C 72.71, H 6.44, N 4.71; found C 72.78, H 6.46, N 4.70.

(3*RS*,4*SR*)-4-[(*SR*)-1-Hydroxy-2-methyl-2,3-butadienyl]-1-(*p*-methoxyphenyl)-3-(2-propynyl)-2-azetidinone, (±)-14j. Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.39 and 6.85 (dd, *J* = 6.6, 2.2 Hz, each 2H), 4.81 (m, 1H), 4.53 (m, 1H), 4.47 (m, 2H), 3.79 (s, 3H), 3.54 (dt, *J* = 9.0, 5.4 Hz, 1H), 2.91 (ddd, *J* = 17.6, 9.0, 2.7 Hz, 1H), 2.73 (dq, *J* = 17.6, 2.7 Hz, 1H), 2.07 (t, *J* = 2.7 Hz, 1H), 2.02 (brs, 1H), 1.85 (t, *J* = 3.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 205.0, 166.2, 156.4, 130.9, 120.6, 113.9, 100.1, 81.3, 78.8, 70.2, 56.8, 55.5, 49.9, 15.6, 14.5; IR ($CHCl_3$): ν = 3420, 2990, 1941, 1745•cm^{-1}; MS (CI): *m/z* (%): 298 (100) [*M* + H]$^+$, 297 (32) [*M*]$^+$; elemental analysis calcd (%) for $C_{18}H_{19}NO_3$ (237.3): C 72.71, H 6.44, N 4.71; found C 72.77, H 6.43, N 4.73.

(3*R*,4*S*)-4-[(*R*)-1-Hydroxy-2-phenyl-2,3-butadienyl]-3-methoxy-1-(2-propynyl)-2-azetidinone, (+)-13l. From 53 mg (0.320 mmol) of aldehyde (+)-**1g**, and after chromatography of the residue using dichloromethane/ethyl acetate (9:1) as eluent gave compound (+)-**13l** (54 mg, 60%) as a colorless oil; $[\alpha]_D$ = +66.6 (*c* = 0.5 in $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.47 (m, 2H), 7.33 (m, 3H), 5.30 (m, 2H), 4.96 (m, 1H), 4.49 (d, *J* = 4.9 Hz, 1H), 4.39 (dd, *J* = 17.6, 2.4 Hz, 1H), 4.16 (t, *J* = 4.9 Hz, 1H), 3.98 (dd, *J* = 17.6, 2.4 Hz, 1H), 3.53 (s, 3H), 2.54 (d, *J* = 5.4 Hz, 1H), 2.23 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$, 25 ^{o}C): δ = 207.6, 168.9, 133.9, 128.6, 127.4, 126.8, 106.9, 83.8, 80.7, 77.2, 72.5,

68.7, 59.8, 59.7, 31.0; IR ($CHCl_3$): ν = 3425, 2990, 1941, 1747•cm^{-1}; MS (CI): *m/z* (%): 284 (100) $[M + H]^+$, 283 (18) $[M]^+$; elemental analysis calcd (%) for $C_{17}H_{17}NO_3$ (283.3): C 72.07, H 6.05, N 4.94; found C 72.05, H 6.03, N 4.93.

(3*R*,4*S*)-4-[(*R*)-1-hydroxy-2-phenyl-2,3-butadienyl]-3-methoxy-1-(*p*-methoxyphenyl)-2-azetidinone, (+)-13m. From 46 mg (0.197 mmol) of aldehyde (+)-**1j**, and after chromatography of the residue using dichloromethane/ethyl acetate (9.5:0.5) as eluent gave compound (+)-**13m** (58 mg, 84%) as a colorless oil; $[\alpha]_D$ = +99.8 (*c* = 1.3 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.51 (m, 2H), 7.32 and 6.87 (dd, *J* = 6.8, 2.2 Hz, each 2H), 7.31 (m, 3H), 5.22 (m, 3H), 4.72 (d, *J* = 4.9 Hz, 1H), 4.48 (dd, *J* = 4.9, 2.7 Hz, 1H), 3.79 and 3.69 (s, each 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 208.2, 164.4, 156.8, 133.9, 129.6, 128.6, 127.3, 126.8, 119.8, 114.5, 106.0, 84.3, 80.2, 67.1, 60.0, 59.4, 55.5; IR ($CHCl_3$): ν = 3419, 2989, 1940, 1746•cm^{-1}; MS (CI): *m/z* (%): 352 (100) $[M + H]^+$, 351 (34) $[M]^+$; elemental analysis calcd (%) for $C_{21}H_{21}NO_4$ (289.3): C 71.78, H 6.02, N 3.99; found C 71.86, H 6.00, N 3.97.

Preparation of α-allenic alcohols (±)-13n and (±)-14n. From 54 mg (0.233 mmol) of aldehyde (±)-**1l**, and after chromatography of the residue using dichloromethane/ethyl acetate (9:1) as eluent, 7 mg (9%) of the less polar compound (+)-**14n** and 65 mg (80%) of the more polar compound (+)-**13n** were obtained.

(3*RS*,4*SR*)-4-[(*RS*)-1-hydroxy-2-phenyl-2,3-butadienyl]-3-methoxy-1-(*p*-methoxyphenyl)-2-azetidinone, (±)-13n. Colorless solid; m. p. 46–48 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.46 (m, 2H), 7.36 (m, 2H), 7.29 (m, 3H), 6.87 (dd, *J* = 6.8, 2.4 Hz, 2H), 6.28 (m, 1H), 5.48 (m, 2H), 5.33 (m, 2H), 5.18 (m, 1H), 4.49 (dd, *J* = 5.6, 3.9 Hz, 1H), 4.09 (m, 1H), 3.79 (s, 3H), 2.21 (d, *J* = 5.6

Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 207.9, 165.6, 156.5, 133.6, 130.4, 130.0, 128.7, 127.5, 126.7, 120.5, 120.0, 114.4, 106.0, 81.1, 67.1, 55.7, 55.5; IR ($CHCl_3$): ν = 3419, 2993, 1943, 1747•cm^{-1}; MS (CI): *m/z* (%): 290 (100) $[M + H]^+$, 289 (16) $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{21}NO_3$ (347.4): C 76.06, H 6.09, N 4.03; found C 76.14, H 6.11, N 4.01.

(3*RS*,4*SR*)-4-[(*SR*)-1-hydroxy-2-phenyl-2,3-butadienyl]-3-methoxy-1-(*p*-methoxyphenyl)-2-azetidinone, (±)-14n. Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.46 (d, *J* = 9.0 Hz, 2H), 7.40 (m, 3H), 7.30 (m, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 5.96 (m, 1H), 5.38 (m, 2H), 5.27 and 4.98 (dd, *J* = 12.2, 2.4 Hz, each 1H), 4.87 (m, 1H), 4.57 (m, 1H), 3.99 (m, 1H), 3.79 (s, 3H), 2.25 (brs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 207.4, 165.9, 156.4, 133.4, 131.2, 128.9, 128.8, 128.7, 126.6, 121.4, 120.5, 113.9, 106.7, 81.4, 69.9, 58.6, 55.5, 55.2; IR ($CHCl_3$): ν = 3421, 2992, 1940, 1745•cm^{-1}; MS (CI): *m/z* (%): 290 (100) $[M + H]^+$, 289 (22) $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{21}NO_3$ (347.4): C 76.06, H 6.09, N 4.03; found C 76.00, H 6.06, N 4.04.

General Procedure for the Preparation of the *O*-Acetylmandelates of alcohols 3, 7 and 13. The appropriate (*R*)- or (*S*)-*O*-acetylmandelic acid (0.10 mmol), 4-dimethylaminopyridine (DMAP) (cat.), and a solution of dicyclohexylcarbodiimide (DCC) (0.18 mmol) in dichloromethane (500 mL) were sequentially added at 0 ^{o}C to a solution of the corresponding alcohol **3**, **7** or **13** (0.09 mmol) in dichloromethane (1.0 mL). The reaction mixture was allowed to warm to room temperature and stirred for 16 h. The solvent was removed under reduced pressure and diethyl ether was added. The mixture was then filtered and the filtrate was concentrated under reduced pressure. Chromatography of the residue

eluting with hexanes/ethyl acetate mixtures gave analytically pure *O*-acetylmandelates.

(*R*)-*O*-Acetylmandelate of (3*R*,4*S*)-4-[(*R*)-1-hydroxy-3-chloro-4-trimethylsilyl-2-butenyl]-3-methoxy-1-(2-propenyl)-2-azetidinone. From 26 mg (0.082 mmol) of 2-chloro-3-silapropenyl alcohol (+)-**3a**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave the (*R*)-*O*-acetylmandelate (34 mg, 80%) as a colorless oil; $[\alpha]_D$ = –21.1 (*c* = 2.4 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.41 (m, 5H), 5.92 (brs, 1H), 5.83 (dd, *J* = 8.8, 5.1 Hz, 1H), 5.59 (m, 1H), 5.39 (d, *J* = 8.8 Hz, 1H), 5.11 (m, 2 H), 4.35 (d, *J* = 4.6 Hz, 1H), 3.89 (ddt, *J* = 15.6, 5.4, 1.7 Hz, 1H), 3.85 (t, *J* = 4.6 Hz, 1H), 3.27 (s, 3 H), 3.23 (ddt, *J* = 15.6, 6.8, 1.2 Hz, 1H), 2.18 (s, 3H), 1.92 (s, 2H), 0.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 170.1, 167.3, 167.2, 140.1, 133.5, 131.1, 129.3, 128.8, 127.9, 127.6, 118.5, 117.1, 83.6, 74.4, 72.1, 59.1, 58.3, 43.4, 31.4, 20.6, –1.4; IR ($CHCl_3$): ν 1751, 1748•cm^{-1}; MS (CI): *m/z* (%): 497 (40) $[M + 3]^+$, 495 (100) $[M + H]^+$; elemental analysis calcd (%) for $C_{24}H_{32}NO_6SiCl$ (494.1): C 58.35, H 6.53, N 2.83, Cl 11.15; found C 58.42, H 6.55, N 2.84, Cl 11.17.

(*S*)-*O*-Acetylmandelate of (3*R*,4*S*)-4-[(*R*)-1-hydroxy-3-chloro-4-trimethylsilyl-2-butenyl]-3-methoxy-1-(2-propenyl)-2-azetidinone. From 26 mg (0.082 mmol) of 2-chloro-3-silapropenyl alcohol (+)-**3a**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave the (*S*)-*O*-acetylmandelate (32 mg, 76%) as a colorless oil; $[\alpha]_D$ = +64.2 (*c* = 1.6 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.39 (m, 5H), 5.93 (dd, *J* = 8.8, 5.6 Hz, 1H), 5.89 (s, 1H), 5.67 (m, 1H), 5.23 (m, 2 H), 5.20 (d, *J* = 7.1 Hz, 1H), 4.51 (d, *J* = 4.6 Hz, 1H), 4.12 (ddt, *J* = 15.6, 5.1,

1.7 Hz, 1H), 3.95 (dd, *J* = 5.6, 4.6 Hz, 1H), 3.58 (ddt, *J* = 15.6, 7.1, 1.7 Hz, 1H), 3.46 (s, 3 H), 2.20 (s, 3H), 1.82 (s, 2H), –0.01 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 170.2, 167.3, 167.2, 140.4, 133.4, 131.3, 129.2, 128.7, 127.8, 118.9, 116.5, 83.9, 74.5, 72.1, 59.4, 58.4, 43.5, 31.4, 20.7, –1.7; IR ($CHCl_3$): ν = 1752, 1749•cm^{-1}; MS (CI): *m/z* (%): 497 (42) [*M* + 3]$^+$, 495 (100) [*M* + H]$^+$; elemental analysis calcd (%) for $C_{24}H_{32}NO_6SiCl$ (494.1): C 58.35, H 6.53, N 2.83, Cl 11.15; found C 58.28, H 6.56, N 2.81, Cl 11.11.

(*R*)-*O*-Acetylmandelate of (3*R*,4*S*)-4-[(*R*)-1-Hydroxy-3-butynyl]-3-methoxy-1-(*p*-methoxyphenyl)-2-azetidinone. From 39 mg (0.142 mmol) of homopropargyl alcohol (+)-**7f**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave the (*R*)-*O*-acetylmandelate (63 mg, 98%) as a colorless oil; $[\alpha]_D$ = +12.2 (*c* = 0.7 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.27 (m, 7H), 6.80 (dd, *J* = 7.1, 2.3 Hz, 2H), 5.79 (s, 1 H), 4.70 (t, *J* = 5.3 Hz, 1H), 4.50 (d, *J* = 5.4 Hz, 1H), 3.79 and 3.34 (s, each 3H), 2.71 (m, 2H), 2.16 (s, 3H), 2.14 (t, *J* = 2.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 170.2, 167.8, 164.7, 156.7, 132.8, 130.4, 129.1, 128.6, 127.6, 119.4, 114.2, 82.2, 78.4, 74.6, 71.7, 70.8, 59.2, 56.1, 55.4, 21.5, 20.5; IR ($CHCl_3$): ν 1751, 1746•cm^{-1}; MS (CI): *m/z* (%): 452 (100) [*M* + H]$^+$, 451 (36) [*M*]$^+$; elemental analysis calcd (%) for $C_{25}H_{25}NO_7$ (451.4): C 66.51, H 5.58, N 3.10; found C 66.59, H 5.55, N 3.12.

(*S*)-*O*-Acetylmandelate of (3*R*,4*S*)-4-[(*R*)-1-Hydroxy-3-butynyl]-3-methoxy-1-(*p*-methoxyphenyl)-2-azetidinone. From 33 mg (0.12 mmol) of homopropargyl alcohol (+)-**7f**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave the (*S*)-*O*-acetylmandelate (55 mg, 98%) as a colorless oil; $[\alpha]_D$ =

+70.1 (*c* = 0.7 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.30 (m, 5H), 7.39 and 6.87 (dd, *J* = 6.8, 2.2 Hz, each 2H), 5.57 (s, 1 H), 5.32 (dd, *J* = 11.7 , 5.8 Hz, 1H), 4.67 (dd, *J* = 11.5 , 5.4 Hz, 1H), 4.63 (d, *J* = 5.1 Hz, 1H), 3.79 and 3.58 (s, each 3H), 2.58 (m, 2H), 2.12 (s, 3H), 1.89 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 169.7, 167.6, 164.7, 156.8, 133.4, 130.3, 129.0, 128.6, 127.7, 119.8, 114.2, 82.3, 78.1, 74.2, 71.4, 71.3, 59.4, 56.5, 55.4, 20.9, 20.6; IR ($CHCl_3$): ν 1750, 1746•cm^{-1}; MS (CI): *m/z* (%): 452 (100) $[M + H]^+$, 451 (32) $[M]^+$; elemental analysis calcd (%) for $C_{25}H_{25}NO_7$ (451.4): C 66.51, H 5.58, N 3.10; found C 66.43, H 5.60, N 3.11.

(*R*)-*O*-Acetylmandelate of (3*R*,4*S*)-4-[(*R*)-1-Hydroxy-2-methyl-2,3-propadienyl]-3-methoxy-1-(*p*-methoxyphenyl)-2-azetidinone. From 48 mg (0.216 mmol) of α-allenic alcohol (+)-**13f**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave the (*R*)-*O*-acetylmandelate (81 mg, 94%) as a colorless oil; $[\alpha]_D$ = –75.2 (*c* = 0.8 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.48 (m, 2H), 7.40 (m, 3H), 5.91 (s, 1 H), 5.33 (dt, *J* = 7.8, 1.8 Hz, 1H), 4.87 (m, 2H), 4.39 (d, *J* = 5.1 1H), 4.10 (dd, *J* = 7.8, 5.1 Hz, 1H), 3.89 (dd, *J* = 17.8, 2.7 Hz, 1H), 3.37 (s, 3H), 2.61 (dd, *J* = 17.8, 2.7 Hz, 1H), 2.21 (s, 3H), 2.20 (t, *J* = 2.7 Hz, 1H), 1.79 (t, *J* = 3.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 206.9, 170.2, 167.8, 166.9, 133.2, 129.5, 128.9, 127.9, 97.3, 83.6, 77.7, 76.4, 74.5, 74.4, 72.6, 59.3, 57.4, 30.0, 20.6, 16.3; IR ($CHCl_3$): ν 1750, 1747•cm^{-1}; MS (CI): *m/z* (%): 398 (100) $[M + H]^+$, 397 (31) $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{23}NO_6$ (397.4): C 66.49, H 5.83, N 3.52; found C 66.57, H 5.86, N 3.54.

(*S*)-*O*-Acetylmandelate of (3*R*,4*S*)-4-[(*R*)-1-Hydroxy-2-methyl-2,3-propadienyl]-3-methoxy-1-(*p*-methoxyphenyl)-2-azetidinone. From

41 mg (0.185 mmol) of α-allenic alcohol (+)-**13f**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave the (*S*)-*O*-acetylmandelate (68 mg, 92%) as a colorless oil; $[\alpha]_D$ = +6.1 (*c* = 0.8 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 7.49 (m, 2H), 7.39 (m, 3H), 5.92 (s, 1 H), 5.39 (dt, *J* = 8.3, 1.5 Hz, 1H), 4.67 and 4.54 (m, each 1H), 4.39 (dd, *J* = 17.8, 2.4 Hz, 1H), 4.13 (dd, *J* = 8.5, 5.1 Hz, 1H), 3.83 (dd, *J* = 17.8, 2.4 Hz, 1H), 3.50 (s, 3H), 2.31 (t, *J* = 2.4 Hz, 1H), 2.21 (s, 3H), 1.47 (t, *J* = 3.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^oC): δ = 206.9, 170.3, 167.9, 133.3, 129.2, 128.7, 127.6, 96.7, 83.6, 77.4, 76.8, 74.8, 74.4, 72.6, 59.3, 57.8, 30.5, 20.6, 15.8; IR ($CHCl_3$): ν 1750, 1746•cm^{-1}; MS (CI): *m/z* (%): 398 (100) $[M + H]^+$, 397 (35) $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{23}NO_6$ (397.4): C 66.49, H 5.83, N 3.52; found C 66.42, H 5.85, N 3.49.

General Procedure for the Preparation of α-Allenic Acetates. Acetic anhydride (1.20 mmol), DMAP (cat.), and triethylamine (2.40 mmol) were sequentially added dropwise to a stirred solution of the corresponding a-allenic alcohol **13** (1.0 mmol), in dichloromethane (10 mL) at 0 ^oC, and the mixture was stirred for 2 h at room temperature. The organic phase was washed with water (2 x 5 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate/triethylamine mixtures gave analytically pure acetates.

Acetate of (3*R*,4*S*)-4-[(*R*)-1-Hydroxy-2-methyl-2,3-butadienyl]-3-methoxy-1-(2-propynyl)-2-azetidinone, (+)-17. From 100 mg (0.452 mmol) of allenol (+)-**13f**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave compound (+)-**17** (103 mg, 86%) as a colorless oil; $[\alpha]_D$ = +1.6 (*c* = 1.1 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 ^oC): δ = 5.39 (dt, *J* = 7.7, 1.9 Hz, 1H),

4.85 (m, 2H), 4.48 (d, *J* = 4.9 Hz, 1H), 4.26 (dd, *J* = 17.8, 2.4 Hz, 1H), 4.14 (dd, *J* = 7.6, 4.9 Hz, 1H), 3.73 (dd, *J* = 17.8, 2.4 Hz, 1H), 3.51 (s, 3H), 2.26 (t, *J* = 2.4 Hz, 1H), 2.09 (s, 3H), 1.77 (t, *J* = 3.2, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C): δ = 206.8, 169.9, 166.9, 97.5, 83.7, 77.5, 76.6, 72.4, 59.5, 58.4, 30.7, 21.0, 16.3; IR ($CHCl_3$): ν = 1747, 1742•cm^{-1}; MS (CI): *m/z* (%): 264 (100) [*M* + H]$^+$, 263 (16) [*M*]$^+$; elemental analysis calcd (%) for $C_{14}H_{17}NO_4$ (263.3): C 63.87, H 6.51, N 5.32; found C 63.80, H 6.54, N 5.34.

Spectroscopic and analytical data for some representative pure forms of **18** follow.

Tricyclic azetidinone (+)-18b. From 51 mg (0.194 mmol) of allenyne (+)-**17**, and after chromatography of the residue using ethyl acetate as eluent gave compound (+)-**18b** (24 mg, 42%) as a colorless oil; $[\alpha]_D$ = +3.6 (*c* = 0.6 in $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6, 25 ^{o}C): δ = 6.11 (s, 1H), 5.97 (t, *J* = 1.9 Hz, 1H), 5.06 (d, *J* = 1.9 Hz, 1H), 3.86 (d, *J* = 5.1 Hz, 1H), 3.09 (m, 1H), 3.08 (s, 3H), 2.85 (d, *J* = 5.1 Hz, 1H), 2.55 (m, 2H), 1.63 (s, 3H), 0.96 (d, *J* = 6.8 Hz, 3H); IR ($CHCl_3$): ν = 1746, 1743, 1705 cm^{-1}; MS (CI): *m/z* (%): 292 (100) [*M* + H]$^+$, 291 (15) [*M*]$^+$; elemental analysis calcd (%) for $C_{15}H_{17}NO_5$ (291.3): C 61.85, H 5.88, N 4.81; found C 61.92, H 5.85, N 4.83.

Procedure for the Preparation of Tosylcarbamate (–)-20. *p*-Toluenesulfonyl isocyanate (76 mg, 0.393 mmol) was added dropwise to a stirred solution of the α-allenic alcohol (+)-**13f** (79 mg, 0.357 mmol), in tetrahydrofuran (3 mL) at 0 ^{o}C, and the mixture was stirred for 2 h at room temperature. The organic phase was washed with water (2 x 3 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with

hexanes/ethyl acetate (2:1) gave 140 mg (94%) of analytically pure compound (–)-**20**.

Tosylcarbamate (–)-20. Colorless oil; $[\alpha]_D$ = –48.5 (*c* = 1.1 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.94 and 7.34 (d, *J* = 8.5 Hz, each 2H), 5.25 (dt, *J* = 6.3, 2.0 Hz, 1H), 4.79 (q, *J* = 3.2 Hz, 2H), 4.45 (d, *J* = 4.9 Hz, 1H), 4.15 and 3.63 (dd, *J* = 17.8, 2.4 Hz, each 1H), 4.09 (dd, *J* = 6.6, 4.9 Hz, 1H), 3.56 and 2.44 (s, each 3H), 2.13 (t, *J* = 2.4 Hz, 1H), 1.69 (t, *J* = 3.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 206.6, 167.1, 149.7, 144.9, 135.6, 129.7, 128.4, 96.9, 83.5, 77.9, 76.7, 74.7, 72.6, 59.4, 58.1, 30.6, 21.6, 16.1; IR ($CHCl_3$): ν = 3244, 1752, 1746, 1350 cm^{-1}; MS (CI): *m/z* (%): 419 (100) $[M + H]^+$, 418 (42) $[M]^+$; elemental analysis calcd (%) for $C_{20}H_{22}N_2SO_6$ (418.5): C 57.41, H 5.30, N 6.69; found C 57.49, H 5.32, N 6.66.

Spectroscopic and analytical data for some representative pure forms of **26** follow.

Bridged Tricyclic Azetidinone (+)-26b. From 56 mg (0.238 mmol) of allenynol (+)-**13g**, 19 mg (26%) of compound (+)-**26b** were obtained as a colorless oil; $[\alpha]_D$ = +3.5 (*c* = 0.8 in $CHCl_3$); ^1H NMR (500 MHz, CD_3COCD_3, 25 °C): δ = 6.41 (d, *J* = 2.0 Hz, 1H), 5.01 (brs, 1H), 4.75 (m, 1H), 4.54 (d, *J* = 4.9 Hz, 1H), 4.49 (dd, *J* = 12.0, 2.2 Hz, 1H), 4.15 (d, *J* = 4.9 Hz, 1H), 3.62 (m, 2H), 3.45 (s, 3H), 2.90 (m, 2H), 1.87 (s, 3H); IR ($CHCl_3$): ν = 1746 cm^{-1}; MS (ESI): *m/z* (%): 338 (100) $[M\ (^{81}Br) + Na]^+$, 336 (84) $[M\ (^{79}Br) + Na]^+$; elemental analysis calcd (%) for $C_{13}H_{16}NO_3Br$ (314.2): C 49.70, H 5.13, N 4.46; found C 49.62, H 5.15, N 4.47.