# Supporting Information for the Paper

# Domino metal-free allene-β-lactam-based access to functionalized pyrroles

Benito Alcaide,*[a] Pedro Almendros,*[b] and María C. Redondo[a]

[a]*Departamento de Química Orgánica I, Facultad de Química, Universidad Complutense de Madrid, 28040-Madrid, Spain*

[b]*Instituto de Química Orgánica General, CSIC, Juan de la Cierva 3, 28006-Madrid, Spain*

E-mail: alcaideb@quim.ucm.es; iqoa392@iqog.csic.es

## Table of Contents

General procedure for the synthesis of α-allenic alcohols **1a–e** and **2a–b** S1

Characterization of α-allenic alcohols **1a–e** and **2a–b** S2

General procedure for the synthesis of α-allenyl methyl ethers **3a–e** and **4a–b** S7

Characterization of α-allenyl methyl ethers **3a–e** and **4a–b** S7

Preparation and characterization of pyrroles **5a–e** S11

Preparation and characterization of pyrroles **6a–b** S14

**Indium-promoted reaction between 3-substituted prop-2-ynyl bromides and carbonyl-β-lactams; general procedure for the synthesis of α-allenic alcohols 1a–e and 2a–b.** 1-Bromo-2-butyne or 1-bromo-3-phenyl-2-propyne (3.0 mmol) was added to a well stirred suspension of the corresponding 4-oxoazetidine-2-carbaldehydes or

 

azetidine-2,3-diones (1.0 mmol) and indium powder (6.0 mmol) in THF/$NH_4Cl$ (aq. sat.) (1:5, 5 mL) at 0 °C. After disappearance of the starting material (TLC) 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 or dichloromethane/ethyl acetate mixtures gave analytically pure compounds. Spectroscopic and analytical data for some representative pure forms of **1** and **2** follow.

**Preparation of α-allenic alcohols (+)-1a and *anti*-(+)-1a.** From 92 mg (0.38 mmol) of the appropriate aldehyde, and after chromatography of the residue using dichloromethane/ethyl acetate (9.5:0.5) as eluent, 104 mg (75%) of the more polar compound (+)-**1a** and 12 mg (9%) of the less polar compound *anti*-(+)-**1a** were obtained.

**α-Allenic alcohol (+)-1a.** 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 (ES): *m/z* (%): 352 (100) $[M + H]^+$, 351 (34) $[M]^+$; elemental analysis calcd (%) for $C_{21}H_{21}NO_4$ (351.4): C 71.78, H 6.02, N 3.99; found C 71.90, H 6.00, N 3.97.

**α-Allenic alcohol *anti*-(+)-1a.** Colorless oil; $[\alpha]_D$ = +86.2 (*c* = 0.6 in $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.34 (m, 7H), 6.88 (d, *J* = 8.5 Hz, 2H), 5.17 and 4.77 (dd, *J* = 12.0, 2.5 Hz,

 

each 1H), 5.09 (m, 1H), 4.59 (m, 2H), 3.79 and 3.63 (s, each 3H), 1.82 (br s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 208.6, 165.5, 156.9, 134.2, 131.1, 129.2, 128.7, 127.9, 121.0, 114.3, 106.8, 83.2, 81.1, 68.6, 60.3, 60.2, 55.9; IR ($CHCl_3$): ν = 3422, 2995, 1944, 1748 $cm^{-1}$; MS (ES): *m/z* (%): 352 (100) $[M + H]^+$, 351 (26) $[M]^+$; elemental analysis calcd (%) for $C_{21}H_{21}NO_4$ (351.4): C 71.78, H 6.02, N 3.99; found C 71.92, H 6.06, N 3.96.

**Preparation of a-allenic alcohols (+)-1b and *anti*-(+)-1b.** From 198 mg (0.66 mmol) of the appropriate aldehyde, and after chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent, 115 mg (42%) of the more polar compound (+)-**1b** and 30 mg (11%) of the less polar compound *anti*-(+)-**1b** were obtained.

**a-Allenic alcohol (+)-1b.** Colorless solid; m. p. 129–131 °C; $[\alpha]_D$ = +149.0 (*c* = 0.7 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.52 (d, *J* = 9.0 Hz, 2H), 7.30 (m, 7H), 6.98 (m, 3H), 6.84 (d, *J* = 9.0 Hz, 2H), 5.27 (d, *J* = 5.3 Hz, 1H), 5.02 (m, 2H), 4.82 (dd, *J* = 6.3, 1.9 Hz, 1H), 4.72 (dd, *J* = 6.3, 5.4 Hz, 1H), 3.66 (s, 3H), 2.50 (br s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 207.9, 163.9, 157.6, 156.6, 133.8, 130.7, 129.4, 128.7, 127.4, 126.6, 122.4, 120.3, 115.9, 113.9, 106.6, 80.7, 79.5, 69.3, 60.5, 55.4; IR (KBr): ν = 3420, 2990, 1942, 1751 $cm^{-1}$; MS (EI): *m/z* (%): 413 (10) $[M]^+$, 262 (100) $[M-151]^+$; elemental analysis calcd (%) for $C_{26}H_{23}NO_4$ (413.4): C 75.53, H 5.61, N 3.39; found C 75.66, H 5.57, N 3.36.

**a-Allenic alcohol *anti*-(+)-1b.** Colorless oil; $[\alpha]_D$ = +200.0 (*c* = 1.2 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.37 (m, 9H), 7.12 (m, 3H), 6.91 (d, *J* = 9.0 Hz, 2H), 5.37 (d, *J* = 5.0 Hz, 1H), 5.24 (d, *J* = 10.5 Hz, 1H), 4.99 (dd, *J* = 4.4, 2.9 Hz, 1H), 4.64 (dd, *J* = 5.0, 3.2 Hz, 1H), 3.81 (s, 3H), 3.06 (d, *J* = 11.2 Hz,

1H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 208.0, 162.8, 157.5, 156.9, 131.6, 129.7, 128.7, 128.3, 127.4, 126.7, 123.0, 119.7, 116.4, 114.6, 105.7, 81.7, 80.6, 66.7, 59.6, 55.3; IR ($CHCl_3$): ν = 3411, 2988, 1940, 1750 $cm^{-1}$; MS (EI): *m/z* (%): 413 (14) $[M]^+$, 262 (100) $[M-151]^+$; elemental analysis calcd (%) for $C_{26}H_{23}NO_4$ (413.4): C 75.53, H 5.61, N 3.39; found C 75.64, H 5.58, N 3.42.

**a-Allenic alcohol (+)-1c.** From 56 mg (0.331 mmol) of the appropriate aldehyde, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave compound (+)-**1c** (60 mg, 64%) as a colorless oil; $[\alpha]_D$ = +70.6 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.39 (m, 5H), 5.78 (m, 1H), 5.24 (m, 3H), 4.94 (m, 1H), 4.47 (d, *J* = 4.9 Hz, 1H), 4.16 (ddt, *J* = 15.5, 5.3, 1.6 Hz, 1H), 4.04 (dd, *J* = 5.6, 4.9 Hz, 1H), 3.82 (ddt, *J* = 15.5, 6.7, 1.0 Hz, 1H), 3.63 (d, *J* = 4.9 Hz, 1H), 3.53 (s, 3H), 2.58 (d, *J* = 5.1 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 207.7, 167.4, 133.9, 132.0, 128.6, 127.4, 126.7, 118.2, 107.0, 83.6, 80.6, 68.7, 59.8, 59.6, 44.1; IR ($CHCl_3$): ν = 3424, 2991, 1940, 1748 $cm^{-1}$; MS (ES): *m/z* (%): 286 (100) $[M + H]^+$, 285 (31) $[M]^+$; elemental analysis calcd (%) for $C_{17}H_{19}NO_3$ (285.3): C 71.56, H 6.71, N 4.91; found C 71.48, H 6.69, N 4.92.

**Preparation of a-allenic alcohols (±)-1d and *anti*-(±)-1d.** From 200 mg (0.91 mmol) of the appropriate aldehyde, and after chromatography of the residue using dichloromethane/ethyl acetate (25:1) as eluent, 101 mg (33%) of the more polar compound (±)-**1d** and 140 mg (46%) of the less polar compound *anti*-(±)-**1d** were obtained.

**a-Allenic alcohol (±)-1d.** Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.34 (m, 7H), 6.79 (d, *J* = 9.2 Hz, 2H), 5.24 and

5.03 (dd, *J* = 12.4, 2.0 Hz, each 1H), 4.80 (dt, *J* = 7.6, 2.0 Hz, 1H), 4.44 (dd, *J* = 7.8, 5.8 Hz, 1H), 3.73 (s, 3H), 3.28 (dd, *J* = 7.8, 5.8 Hz, 1H), 2.71 (br s, 1H), 1.21 (d, *J* = 7.8 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 207.5, 169.3, 156.3, 133.7, 131.6, 128.9, 128.7, 126.6, 120.5, 113.9, 107.0, 81.2, 70.1, 58.2, 55.5, 46.0, 9.3; IR ($CHCl_3$): ν = 3425, 2993, 1943, 1749 $cm^{-1}$; MS (EI): *m/z* (%): 335 (27) $[M]^+$, 279 (100) $[M-56]^+$; elemental analysis calcd (%) for $C_{21}H_{21}NO_3$ (335.4): C 75.20, H 6.31, N 4.18; found C 75.32, H 6.27, N 4.15.

**a-Allenic alcohol *anti*-(±)-1d.** Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.30 (m, 7H), 6.77 (d, *J* = 9.0 Hz, 2H), 5.18 (m, 1H), 5.09 (dd, *J* = 4.4, 2.9 Hz, 2H), 4.33 (dd, *J* = 5.4, 4.8 Hz, 1H), 3.73 (s, 3H), 3.41 (dd, *J* = 7.6, 5.3 Hz, 1H), 2.67 (br s, 1H), 1.46 (d, *J* = 7.6 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 208.3, 169.4, 156.5, 134.6, 130.4, 128.8, 127.6, 127.0, 120.5, 114.5, 106.6, 80.5, 67.7, 57.6, 55.6, 47.3, 10.2; IR ($CHCl_3$): ν = 3422, 2991, 1940, 1750 $cm^{-1}$; MS (EI): *m/z* (%): 335 (33) $[M]^+$, 279 (100) $[M-56]^+$; elemental analysis calcd (%) for $C_{21}H_{21}NO_3$ (335.4): C 75.20, H 6.31, N 4.18; found C 75.34, H 6.35, N 4.14.

**a-Allenic alcohol (+)-1e.** From 170 mg (0.61 mmol) of the appropriate aldehyde, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave compound (+)-**1e** (180 mg, 75%) as a colorless oil; $[\alpha]_D$ = +65.8 (*c* = 0.8 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.31 (m, 7H), 6.83 (d, *J* = 9.0 Hz, 2H), 5.78 (m, 1H), 5.16 (m, 4H), 4.73 (dd, *J* = 11.5, 1.9 Hz, 1H), 4.31 (d, *J* = 3.6 Hz, 1H), 3.79 and 3.68 (s, each 3H), 2.80 (dd, *J* = 14.3, 6.3 Hz, 1H), 2.54 (dd, *J* = 14.4, 7.0 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 208.3, 165.8, 156.6, 131.6, 131.0,

128.7, 127.3, 126.6, 121.1, 118.2, 114.6, 113.8, 106.8, 88.0, 80.6, 67.8, 63.3, 55.4, 54.1, 34.8; IR ($CHCl_3$): $\nu$ = 3417, 2993, 1942, 1749 $cm^{-1}$; MS (EI): *m/z* (%): 391 (21) $[M]^+$, 127 (100) $[M-194]^+$; elemental analysis calcd (%) for $C_{24}H_{25}NO_4$ (391.5): C 73.64, H 6.44, N 3.58; found C 73.51, H 6.40, N 3.61.

**a-Allenic alcohol (+)-2a.** From 50 mg (0.17 mmol) of the appropriate azetidine-2,3-dione, 53 mg (76%) of compound (+)-**2a** was obtained as a colorless oil; $[\alpha]_D$ = +48.2 (*c* = 0.9 in $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.64 and 7.35 (m, each 2H), 7.28 (m, 1H), 6.84 and 7.57 (dd, each 2H, *J* = 7.0, 2.5 Hz), 5.29 (s, 2H), 4.55 (q, 1H, *J* = 6.8 Hz), 4.37 (d, 1H, *J* = 6.8 Hz), 4.28 (dd, 1H, *J* = 8.8, 6.8 Hz), 4.00 (brs, 1H), 3.79 (s, 3H), 3.77 (dd, 1H, *J* = 8.8, 6.8 Hz), 1.46 and 1.36 (s, each 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 207.6, 166.1, 156.7, 132.5, 130.7, 128.6, 128.4, 127.8, 120.1, 113.9, 109.8, 105.9, 84.2, 80.9, 76.5, 66.7, 66.3, 55.4, 26.4, 25.2; IR ($CHCl_3$): $\nu$ = 3332, 2988, 1938, 1746 $cm^{-1}$; MS (ES): *m/z* (%): 408 (100) $[M + H]^+$, 407 (15) $[M]^+$; elemental analysis calcd (%) for $C_{24}H_{25}NO_5$ (407.5): C 70.75, H 6.18, N 3.44; found C 70.87, H 6.14, N 3.41.

**a-Allenic alcohol (−)-2b.** From 58 mg (0.257 mmol) of the appropriate azetidine-2,3-dione, 54 mg (62%) of compound (−)-**2b** was obtained as a colorless oil; $[\alpha]_D$ = −75.8 (*c* = 0.7 in $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.59 (m, 2H), 7.28 (m, 3H), 5.61 (m, 1H), 5.21 (s, 2H), 5.13 (m, 2H), 4.47 (s, 1H), 4.44 (dd, 1H, *J* = 7.1, 5.6 Hz), 4.22 (ddt, 1H, *J* = 15.4, 4.6, 1.7 Hz), 4.17 (dd, 1H, *J* = 8.8, 6.8 Hz), 3.80 (d, 1H, *J* = 7.1 Hz), 3.68 (m, 1H), 3.67 (dd, 1H, *J* = 8.8, 5.4 Hz), 1.34 and 1.40 (s, each 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 207.3, 168.8, 132.8, 131.3, 128.5, 127.6,

118.3, 109.7, 105.8, 84.8, 80.3, 76.0, 66.6, 64.9, 43.4, 26.5, 25.0; IR ($CHCl_3$): $\nu$ = 3334, 2991, 1940, 1745 $cm^{-1}$; MS (ES): *m/z* (%): 342 (100) $[M + H]^+$, 341 (24) $[M]^+$; elemental analysis calcd (%) for $C_{20}H_{23}NO_4$ (341.4): C 70.36, H 6.79, N 4.10; found C 70.44, H 6.82, N 4.12.

**Reaction between methyl sulfate and α-allenic alcohols 1 and 2; general procedure for the synthesis of α-allenyl methyl ethers 3a–e and 4a–b.** Tetrabutyl ammonium iodide (cat), 50% aqueous sodium hydroxide (18 mL) and dimethyl sulfate (0.60 mmol) were sequentially added at room temperature to a solution of the corresponding α-allenol (0.92 mmol) in dichloromethane (18 mL). The reaction was stirred for 24 h and then aqueous ammonia (30%) was added (2.5 mL), before being partitioned between dichloromethane and water. The aqueous phase was extracted with dichloromethane (3 x 15 mL), the combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes or dichloromethane/ethyl acetate mixtures gave analytically pure compounds. Spectroscopic and analytical data for some representative pure forms of **3** and **4** follow.

**α-Allenyl methyl ether (+)-3a.** From 95 mg (0.27 mmol) of α-allenic alcohol (+)-**1a**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave the α-allenyl methyl ether (+)-**3a** (67 mg, 68%) as a colorless solid; m. p. 138–140 °C; $[\alpha]_D$ = +26.4 (*c* = 0.5 in $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 7.56 (m, 3H), 7.31 (m, 4H), 6.84 (d, *J* = 9.2 Hz, 2H), 5.21 (m, 2H), 4.52 (m, 3H), 3.78 and 3.44 (s, each 3H), 3.22 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 209.6, 165.6, 156.4, 134.9,

131.7, 128.7, 127.3, 127.0, 119.9, 113.9, 104.4, 83.0, 80.8, 78.9, 60.8, 60.0, 57.3, 55.5; IR (KBr): ν = 2985, 1942, 1748 $cm^{-1}$; MS (ES): *m/z* (%): 366 (100) $[M + H]^+$, 365 (22) $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{23}NO_4$ (365.4): C 72.31, H 6.34, N 3.83; found C 72.44, H 6.38, N 3.80.

**α-Allenyl methyl ether *anti*-(+)-3a.** From 80 mg (0.22 mmol) of α-allenic alcohol *anti*-(+)-**1a**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave the α-allenyl methyl ether *anti*-(+)-**3a** (51 mg, 64%) as a colorless oil; $[\alpha]_D$ = +24.8 (*c* = 1.0 in $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.27 (m, 5H), 6.88 and 6.60 (d, *J* = 9.2 Hz, each 2H), 4.95 and 4.67 (d, *J* = 12.2 Hz, each 2H), 4.70 (d, *J* = 4.4 Hz, 1H), 4.57 (dd, *J* = 8.7, 4.4 Hz, 1H), 4.46 (d, *J* = 8.7 Hz, 1H), 3.72 and 3.63 (s, each 3H), 3.40 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C): δ = 210.4, 164.8, 156.4, 133.6, 129.4, 128.1, 126.9, 126.8, 120.7, 113.4, 102.3, 83.8, 80.5, 77.5, 59.8, 55.8, 55.2; IR ($CHCl_3$): ν = 2989, 1944, 1751 $cm^{-1}$; MS (ES): *m/z* (%): 366 (100) $[M + H]^+$, 365 (14) $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{23}NO_4$ (365.4): C 72.31, H 6.34, N 3.83; found C 72.45, H 6.30, N 3.80.

**α-Allenyl methyl ether (+)-3b.** From 115 mg (0.27 mmol) of α-allenic alcohol (+)-**1b**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave the α-allenyl methyl ether (+)-**3b** (85 mg, 74%) as a colorless oil; $[\alpha]_D$ = +10.0 (*c* = 0.6 in $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.64 (d, *J* = 9.0 Hz, 2H), 7.34 (m, 8H), 7.00 (m, 1H), 6.87 (m, 3H), 5.26 (d, *J* = 4.8 Hz, 1H), 4.95 (m, 2H), 4.73 (m, 2H), 3.81 and 3.31 (s, each 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C): δ = 210.1, 164.1, 157.8, 156.5, 134.6, 131.4, 129.4, 128.7, 127.3, 127.1, 122.2, 120.0, 115.7,

113.8, 103.3, 81.1, 79.1, 78.6, 60.1, 56.9, 55.4; IR ($CHCl_3$): ν = 2994, 1944, 1749 $cm^{-1}$; 428 (100) $[M + H]^+$, 427 (18) $[M]^+$; elemental analysis calcd (%) for $C_{27}H_{25}NO_4$ (427.5): C 75.86, H 5.89, N 3.28; found C 76.00, H 5.86, N 3.25.

**α-Allenyl methyl ether (–)-3c.** From 200 mg (0.70 mmol) of α-allenic alcohol (+)-**1c**, and after chromatography of the residue using hexanes/ethyl acetate (1:1) as eluent gave the α-allenyl methyl ether (–)-**3c** (140 mg, 67%) as a colorless oil; $[\alpha]_D$ = –51.0 (*c* = 0.7 in $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.52 (m, 2H), 7.29 (m, 3H), 5.79 (m, 1H), 5.21 (m, 2H), 4.47 (d, *J* = 9.2 Hz, 1H), 4.37 (d, *J* = 4.9 Hz, 1H), 4.12 (ddt, *J* = 15.4, 5.1, 1.4 Hz, 1H), 4.05 (dd, *J* = 9.2, 4.6 Hz, 1H), 3.83 (ddt, *J* = 15.1, 6.6, 1.0 Hz, 1H), 3.37 and 3.31 (s, each 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C): δ = 209.9, 167.6, 131.9, 131.5, 128.6, 128.4, 127.1, 127.0, 117.9, 83.7, 80.8, 78.6, 59.5, 59.2, 55.4, 44.1; IR ($CHCl_3$): ν = 2995, 1945, 1750 $cm^{-1}$; MS (ES): *m/z* (%): 300 (100) $[M + H]^+$, 299 (17) $[M]^+$; elemental analysis calcd (%) for $C_{18}H_{21}NO_3$ (299.4): C 72.22, H 7.07, N 4.68; found C 72.35, H 7.02, N 4.71.

**α-Allenyl methyl ether (±)-3d.** From 120 mg (0.35 mmol) of α-allenic alcohol (±)-**1d**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave the α-allenyl methyl ether (±)-**3d** (95 mg, 78%) as a colorless oil; $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.33 (m, 5H), 6.94 and 6.69 (d, *J* = 9.0 Hz, each 2H), 4.95 and 4.58 (d, *J* = 12.4 Hz, 1H), 4.48 (dd, *J* = 8.5, 5.3 Hz, 1H), 4.32 (d, *J* = 8.5 Hz, 1H), 3.75 (s, 3H), 3.52 (dd, *J* = 7.5, 5.3 Hz, 1H), 3.35 (s, 3H), 1.44 (d, *J* = 7.8 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C): δ = 210.5, 169.1, 156.3, 133.5, 129.9, 128.4, 127.3, 127.2, 121.1, 113.7, 102.5, 81.7, 77.5, 56.1, 55.9,

55.3, 47.2, 9.0; IR ($CHCl_3$): ν = 2988, 1940, 1748 $cm^{-1}$; MS (ES): *m/z* (%): 350 (100) $[M + H]^+$, 349 (15) $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{23}NO_3$ (349.4): C 75.62, H 6.63, N 4.01; found C 75.49, H 6.67, N 3.98.

**a-Allenyl methyl ether (+)-3e.** From 70 mg (0.17 mmol) of α-allenic alcohol (+)-**1e**, and after chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent gave the α-allenyl methyl ether (+)-**3e** (50 mg, 70%) as a colorless oil; $[\alpha]_D$ = +41.7 (*c* = 1.7 in $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.54 (m, 3H), 7.34 and 6.85 (d, *J* = 9.0 Hz, each 2H), 7.32 (m, 2H), 5.56 (m, 1H), 5.17 (m, 2H), 4.97 (m, 2H), 4.54 (d, *J* = 8.5 Hz, 1H), 4.34 (d, *J* = 8.5 Hz, 1H), 3.79 and 3.55 (s, each 3H), 3.25 (s, 3H), 2.55 (dd, *J* = 14.1, 6.6 Hz, 1H), 2.41 (dd, *J* = 14.1, 7.5 Hz, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C): δ = 210.0, 166.6, 156.4, 135.6, 131.8, 131.2, 128.6, 128.3, 127.2, 120.4, 119.6, 113.7, 104.2, 87.9, 81.3, 78.9, 63.9, 56.9, 55.5, 54.3, 35.9; IR ($CHCl_3$): ν = 2995, 1945, 1747 $cm^{-1}$; MS (ES): *m/z* (%): 406 (100) $[M + H]^+$, 405 (11) $[M]^+$; elemental analysis calcd (%) for $C_{25}H_{27}NO_4$ (405.5): C 74.05, H 6.71, N 3.45; found C 74.19, H 6.67, N 3.42.

**a-Allenyl methyl ether (+)-4a.** From 111 mg (0.27 mmol) of α-allenic alcohol (+)-**2a**, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent gave the α-allenyl methyl ether (+)-**4a** (70 mg, 62%) as a colorless solid; m. p. 112–114 °C; $[\alpha]_D$ = +203.4 (*c* = 0.5 in $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.63 and 6.85 (d, 1H, *J* = 9.0 Hz, each 2H), 7.32 (m, 5H), 5.18 (q, 1H, *J* = 12.7 Hz), 4.42 (q, 1H, *J* = 7.3 Hz), 4.16 (dd, 1H, *J* = 8.5, 6.3 Hz), 4.05 (d, 1H, *J* = 8.5 Hz), 3.79 and 3.70 (s, each 3H), 3.39 (dd, 1H, *J* = 8.7, 7.5 Hz), 1.36 and 1.29 (s, each 3H);

$^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 209.4, 163.5, 156.4, 133.6, 131.7, 128.6, 128.1, 127.9, 119.9, 113.8, 109.3, 101.2, 78.9, 76.9, 67.2, 67.0, 55.4, 54.6, 26.4, 25.2; IR (KBr): ν = 2987, 1940, 1748 $cm^{-1}$; MS (EI): *m/z* (%): 421 (32) $[M]^+$, 171 (100) $[M-250]^+$; elemental analysis calcd (%) for $C_{25}H_{27}NO_5$ (421.5): C 71.24, H 6.46, N 3.32; found C 71.39, H 6.42, N 3.30.

**a-Allenyl methyl ether (+)-4b.** From 74 mg (0.21 mmol) of α-allenic alcohol (−)-**2c**, and after chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent gave the α-allenyl methyl ether (+)-**4b** (46 mg, 62%) as a colorless oil; $[\alpha]_D$ = +8.7 (*c* = 0.4 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.33 (m, 5H), 5.70 (m, 1H), 5.19 (m, 2H), 5.14 (m, 2H), 4.34 (dt, 1H, *J* = 8.8, 6.3 Hz), 4.20 (ddt, 1H, *J* = 15.6, 4.6, 1.7 Hz), 4.07 (dd, 1H, *J* = 8.5, 6.3 Hz), 3.73 (ddt, 1H, *J* = 16.6, 7.0, 1.0 Hz), 3.59 (s, 3H), 3.53 (d, 1H, *J* = 8.8 Hz), 3.34 (dd, 1H, *J* = 8.5, 6.6 Hz), 1.31 and 1.29 (s, each 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 209.1, 165.9, 133.6, 131.5, 128.4, 127.7, 127.6, 117.8, 109.0, 101.3, 90.0, 78.8, 76.7, 66.8, 65.4, 55.2, 43.2, 26.5, 25.3; IR ($CHCl_3$): ν = 2995, 1943, 1748 $cm^{-1}$; MS (ES): *m/z* (%): 356 (100) $[M + H]^+$, 355 (11) $[M]^+$; elemental analysis calcd (%) for $C_{21}H_{25}NO_4$ (355.4): C 70.96, H 7.09, N 3.94; found C 71.11, H 7.05, N 3.97.

**Sodium methoxide promoted reaction of 2-azetidinone-tethered-a-allenyl ethers 3a–e. General procedure for the preparation of pyrrole derivatives 5a–e.** Sodium methoxide (0.6 mmol) was added in portions at 0 °C to a solution of the appropriate allene-β-lactam **3** (0.15 mmoll) in methanol (3 mL). The reaction was stirred at room temperature under argon atmosphere until complete disappearance of the starting material (TLC) and then water was added (0.5 mL). The

methanol was concentrated under reduced pressure, the aqueous residue was extracted with ethyl acetate (5 x 3 mL), the organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. Chromatography of the residue on deactivated silica gel eluting with ethyl acetate/hexanes mixtures gave analytically pure compounds **5a–e**.

**Pyrrole (–)-5a.** From 67 mg (0.18 mmol) of allene-β-lactam (+)-**3a**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave the pyrrole (–)-**5a** (52 mg, 77%) as a colorless oil; $[\alpha]_D$ = –30.0 (*c* = 0.4 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.32 (m, 6H), 7.02 (m, 3H), 6.45 (s, 1H), 4.52 (s, 1H), 3.88 and 3.71 (s, each 3H), 3.24 (s, 3H), 2.13 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 170.6, 159.4, 136.7, 130.1, 129.8, 128.3, 128.0, 127.9, 127.5, 125.3, 121.7, 114.2, 114.1, 109.2, 74.7, 56.7, 55.5, 52.2, 12.0; IR ($CHCl_3$): ν = 1742, 750 $cm^{-1}$; MS (ES): *m/z* (%): 366 (100) $[M + H]^+$, 365 (5) $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{23}NO_4$ (365.4): C 72.31, H 6.34, N 3.83; found C 72.17, H 6.30, N 3.85.

**Pyrrole (–)-5b.** From 80 mg (0.18 mmol) of allene-β-lactam (+)-**3b**, and after chromatography of the residue using hexanes/ethyl acetate (20:1) as eluent gave the pyrrole (–)-**5b** (40 mg, 50%) as a colorless oil; $[\alpha]_D$ = –28.5 (*c* = 0.4 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.38 (m, 7H), 6.92 (m, 3H), 6.76 (m, 4H), 6.59 (s, 1H), 5.32 (s, 1H), 3.82 and 3.74 (s, each 3H), 2.16 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 169.8, 159.4, 131.5, 129.9, 129.8, 129.6, 129.5, 129.4, 128.8, 128.3, 128.2, 127.9, 126.4, 125.5, 121.7, 115.6, 115.4, 114.2, 109.8, 71.7, 55.5, 52.5, 12.1; IR ($CHCl_3$): ν = 1745, 745 $cm^{-1}$; MS (ES): *m/z* (%): 428 (100) [*M* +

H]$^+$, 427 (11) [*M*]$^+$; elemental analysis calcd (%) for $C_{27}H_{25}NO_4$ (427.5): C 75.86, H 5.89, N 3.28; found C 75.98, H 5.92, N 3.25.

**Pyrrole (–)-5c.** From 60 mg (0.20 mmol) of allene-β-lactam (–)-**3c**, and after chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent gave the pyrrole (–)-**5c** (30 mg, 50%) as a colorless oil; $[\alpha]_D$ = –10.6 (*c* = 1.5 in acetone); $^1$H NMR (300 MHz, acetone-$d_6$, 25 °C): δ = 7.36 (m, 4H), 7.19 (m, 1H), 6.25 (s, 1H), 5.97 (m, 1H), 5.14 (dd, 1H, *J* = 10.4, 1.6 Hz), 4.96 (s, 1H), 4.85 (dd, 1H, *J* = 17.2, 1.6 Hz), 4.68 (m, 2H), 3.73 and 3.37 (s, each 3H), 2.30 (s, 3H); $^{13}$C NMR (75 MHz, acetone-$d_6$, 25 °C): δ = 170.5, 137.6, 135.2, 131.7, 128.7, 128.1, 127.6, 125.4, 121.5, 115.1, 109.8, 75.8, 56.3, 51.7, 46.5, 10.5; IR ($CHCl_3$): ν = 1747, 740 cm$^{-1}$; MS (EI): *m/z* (%): 299 (18) [*M*]$^+$, 240 (100) [*M–59*]$^+$; elemental analysis calcd (%) for $C_{18}H_{21}NO_3$ (299.2): C 72.22, H 7.07, N 4.68; found C 72.36, H 7.03, N 4.71.

**Pyrrole (±)-5d.** From 28 mg (0.08 mmol) of allene-β-lactam (±)-**3d**, and after chromatography of the residue using hexanes/ethyl acetate (9:2) as eluent gave the pyrrole (±)-**5d** (15 mg, 54%) as a colorless oil; $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.45 and 7.37 (d, each 2H, *J* = 8.0 Hz), 7.20 (m, 3H), 7.00 (d, 2H, *J* = 7.0 Hz), 6.31 (s, 1H), 3.88 and 3.58 (s, each 3H), 3.50 (q, 1H, *J* = 7.2 Hz), 2.12 (s, 3H), 1.45 (d, 3H, *J* = 7.2 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 174.4, 159.3, 137.0, 132.0, 130.7, 130.2, 129.5, 128.3, 127.7, 126.3, 125.1, 121.0, 114.3, 114.2, 105.7, 55.5, 51.9, 37.5, 17.8, 12.0; IR ($CHCl_3$): ν = 1738, 741 cm$^{-1}$; MS (EI): *m/z* (%): 349 (35) [*M*]$^+$, 290 (100) [*M–59*]$^+$; elemental analysis calcd (%) for $C_{22}H_{23}NO_4$ (349.4): C 75.62, H 6.63, N 4.01; found C 75.49, H 6.67, N 4.04.

 

**Pyrrole (–)-5e.** From 25 mg (0.06 mmol) of allene-β-lactam (+)-**3e**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave the pyrrole (–)-**5e** (13 mg, 53%) as a colorless oil; $[\alpha]_D$ = –42.8 (*c* = 0.6 in acetone); $^1$H NMR (300 MHz, acetone-$d_6$, 25 °C): δ = 7.48 and 7.38 (dd, each 2H, *J* = 8.0, 2.0 Hz), 7.22 and 7.00 (m, 2H), 6.77 (m, 1H), 6.59 (s, 1H), 5.66 (m, 1H), 5.03 (m, 2H), 3.86 and 3.39 (s, each 3H), 3.11 (s, 3H), 2.78 (m, 2H), 2.02 (s, 3H); $^{13}$C NMR (75 MHz, acetone-$d_6$, 25 °C): δ = 171.0, 160.0, 137.5, 133.0, 131.7, 131.2, 130.9, 130.7, 130.2, 128.7, 127.9, 125.4, 120.5, 117.5, 115.0, 114.0, 110.8, 80.3, 55.3, 51.3, 49.5, 38.3, 11.6; IR ($CHCl_3$): ν = 1748, 750 cm$^{-1}$; MS (EI): *m/z* (%): 405 (14) $[M]^+$, 362 (100) $[M-43]^+$; elemental analysis calcd (%) for $C_{25}H_{27}NO_4$ (405.5): C 74.05, H 6.71, N 3.45; found C 74.20, H 6.67, N 3.42.

**Sodium methoxide promoted reaction of 2-azetidinone-tethered-α-allenyl ethers 4a–b. General procedure for the preparation of pyrrole derivatives 6a–b.** Sodium methoxide (0.6 mmol) was added in portions at 0 °C to a solution of the appropriate allene-β-lactam **4** (0.15 mmoll) in methanol (3 mL). The reaction was stirred at reflux temperature under argon atmosphere until complete disappearance of the starting material (TLC). The mixture was allowed to cool to room temperature and then water was added (0.5 mL). The methanol was concentrated under reduced pressure, the aqueous residue was extracted with ethyl acetate (5 x 3 mL), the organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. Chromatography of the residue on deactivated silica gel eluting with ethyl acetate/hexanes mixtures gave analytically pure compounds **6a–b.**

 

**Pyrrole (+)-6a.** From 53 mg (0.12 mmol) of allene-β-lactam (+)-**4a**, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent gave the pyrrole (+)-**6a** (26 mg, 49%) as a pale yellow oil; $[\alpha]_D$ = +98.8 (*c* = 1.0 in $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.29 (m, 7H), 6.98 (d, *J* = 9.5 Hz, 2H), 5.66 (dd, *J* = 8.9, 6.7 Hz, 1H), 4.06 (t, *J* = 6.9 Hz, 1H), 3.87 and 3.60 (s, each 3H), 3.83 (m, 1H), 1.82 (s, 3H), 1.29 and 1.03 (s, each 3H); $^{13}$C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 166.6, 159.6, 136.2, 131.6, 131.5, 130.5, 130.4, 129.4, 128.2, 128.1, 128.0, 126.5, 114.8, 114.2, 109.2, 71.1, 68.8, 55.9, 51.4, 26.0, 25.6, 11.5; IR ($CHCl_3$): ν = 1704 $cm^{-1}$; MS (ES): *m/z* (%): 422 (100) $[M + H]^+$, 421 (17) $[M]^+$; elemental analysis calcd (%) for $C_{25}H_{27}NO_5$ (421.5): C 71.24, H 6.46, N 3.32; found C 71.11, H 6.51, N 3.36.

**Pyrrole (−)-6b.** From 38 mg (0.10 mmol) of allene-β-lactam (+)-**4b**, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent gave the pyrrole (−)-**6b** (20 mg, 53%) as a colorless oil; $[\alpha]_D$ = −5.9 (*c* = 1.0 in acetone); $^1$H NMR (300 MHz, acetone-$d_6$, 25 °C): δ = 7.25 (m, 5H), 6.11 (t, *J* = 7.8 Hz, 1H), 6.04 (m, 1H), 5.18 (m, 2H), 4.88 (m, 3H), 4.23 and 3.92 (t, *J* = 7.8 Hz, each 1H), 2.84 (s, 3H), 1.57 and 1.38 (s, each 3H); $^{13}$C NMR (75 MHz, acetone-$d_6$, 25 °C): δ = 165.8, 136.7, 135.4, 131.5, 130.6, 129.4, 127.7, 126.2, 122.8, 115.6, 109.3, 70.0, 68.2, 50.2, 47.5, 25.8, 23.7, 9.7; IR ($CHCl_3$): ν = 1698 $cm^{-1}$; MS (EI): *m/z* (%): 355 (9) $[M]^+$, 269 (100) $[M-86]^+$; elemental analysis calcd (%) for $C_{21}H_{25}NO_4$ (355.4): C 70.96, H 7.09, N 3.94; found C 71.09, H 7.04, N 3.92.

 