

Supplementary Material

GENERAL METHODS

Melting points were taken on a Mel-Temp apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on Varian Gemini-200 and Mercury-400 MHz. Chemical shifts are reported in ppm scale, using as internal standards residual chloroform, and coupling constants (J) are reported in Hertz. Infrared spectra were recorded as nujol mulls on a Nicolet 205 FT-IR spectrophotometer and are given in cm^{-1} . Optical rotation measurements were carried out on a Perkin-Elmer 343 Polarimeter and specific rotation $[\alpha]_D^{20}$ was reported in deg per dm at the specified temperature and with the concentration (c) given in g per 100 mL in CHCl_3 . THF, toluene, and heptane were distilled from benzophenone ketyl. *N*-Trialkylsilylimines were prepared according to reported procedures^{1,10} starting from the parent aldehydes

PREPARATIONS

Synthesis of azadiene: General procedure.

A solution of *N*-trimethylsilyl imine **2** was prepared by the dropwise addition of a heptane solution (5mL) of aldehyde (1.0 mmol) to a cooled (0 °C) hexane solution of lithium bis(trimethylsilyl)amide (LHMDS) (1.1 mL, 1.1 mmol). The reaction mixture was stirred for 30 min. at this temperature. The formation of the imine was confirmed by an infrared spectrum of the reaction mixture ($\nu_{\text{CN}}=1685\text{ cm}^{-1}$). The imine solution was then warmed to room temperature, trimethylsilyl chloride (0.15 mL, 1.1 mmol) was added in one portion, and this mixture was allowed to stir for 1h. The mixture was then cooled to 0 °C and triethylamine (0.30 mL, 2.2 mmol) was added in one portion. After stirring this mixture for 5 min. at 0 °C, a toluene solution of α -halo-acetyl chloride (1 mmol) was added very slowly (over 5 min.) via syringe. Stirring was maintained for 30 min. at 0 °C and 30 min. at room temperature. This yellow-orange mixture was then filtered through Celite. An aliquot of this mixture, after removing the solvent was analyzed by IR, ^1H and ^{13}C NMR and mass spectroscopy. Spectral data showed the crude be constituted essentially by the compound **4**. The crude mixture was refluxed in toluene overnight to give the target compound in yields and diastereomeric ratio reported in Tables 1 and 2.

1-Bromo-2(trimethylsilyl)oxy-3-aza-4-phenyl-1,3-butadiene (4a)

IR (CDCl_3): 3155, 2960, 1620, 1589, 1566, 1295; ^1H -NMR (200 MHz CDCl_3): 8.39 (s, 1 H), 7.42 (m, 5 H), 5.97 (s, 1 H), 0.38 (m, 9 H); ^{13}C (50 MHz, CDCl_3): 155.77, 155.19, 135.49, 131.48, 128.92, 128.79, 88.37, 0.74; MS (m/z): 298 (M^+), 226, 218, 202, 192, 184, 147, 105, 91, 77, 59.

(±)-(Trans)-3-Bromo-4-phenyl-azetidin-2-one (5a)¹⁶

m.p.: 125-128 °C; IR (CHCl_3) 3411, 1782; ^1H -NMR (200 MHz CDCl_3): 7.40 (s, 5H), 6.58 (bs, 1H), 4.81 (d, 1H, J= 1.9 Hz), 4.53 (t, 1H, J= 2.0); ^{13}C -NMR (50 MHz CDCl_3): 164.04, 137.18, 129.25, 129.18, 125.67, 62.38, 51.32; MS (m/z): 184 (M^+ -43), 182, 103, 91.

1-Chloro-2(trimethylsilyl)oxy-3-aza-4-phenyl-1,3-butadiene (4b)

IR (CDCl_3): 3155, 2960, 1620, 1589, 1568, 1295; ^1H -NMR (200 MHz CDCl_3): 8.39 (s, 1 H), 7.42 (m, 5 H), 5.97 (s, 1 H), 0.38 (m, 9 H); ^{13}C (50 MHz, CDCl_3): 155.18, 153.46, 135.65, 131.73, 128.89, 128.79, 101.50, 0.65; MS (m/z): 253

m.p.: 125-128 °C; IR (CHCl_3): 3411, 1779, 1457; ^1H -NMR (200 MHz CDCl_3): 7.40 (m, 5H), 6.68 (b.s., 1H), 4.73 (d, 1H, J= 1.9 Hz), 4.52 (dd, 1H, J= 1.9, 1.8 Hz); ^{13}C -NMR (100 MHz CDCl_3): 164.26, 136.96, 129.21, 129.16, 125.73, 64.38, 62.58; MS (m/z): 138 (M^+ -43), 103, 77, 51.

1-Bromo-2(trimethylsilyl)oxy-3-aza-4-p-nitro-phenyl-1,3-butadiene (4c)

IR (CHCl_3): 3020, 1684, 1623, 1562, 1525, 1347; ^1H -NMR (200 MHz CDCl_3): 8.42 (s, 1H), 8.28 (m, 2H), 7.95 (m, 2H), 6.18 (s, 1H), 0.35 (s, 9H); ^{13}C (50 MHz, CDCl_3): 154.43, 152.33, 149.11, 141.10, 129.40, 124.00, 93.53, 0.77; MS (m/z): 344 (M^+), 342, 263, 247, 217, 202, 189, 75, 59.

(±)(Trans)-3-Bromo-4-p-nitro-phenyl-azetidin-2-one (5c)

m.p.: 144-146 °C; IR (CHCl_3): 3406, 1790, 1608, 1528; ^1H -NMR (200 MHz CDCl_3): 8.28 (m, 2H), 7.60 (m, 2H), 6.70 (bs, 1H), 4.93 (d, 1H, J= 2.1 Hz), 4.59 (dd, 1H, J= 2.1, 1.5 Hz); ^{13}C -NMR (50 MHz CDCl_3): 163.39, 148.51, 144.15, 126.64, 124.46, 61.49, 51.02; MS (m/z): 229 (M^+ -43), 197, 169, 102, 90;

1-Chloro-2(trimethylsilyl)oxy-3-aza-4-p-nitro-phenyl-1,3-butadiene (4d)

IR (CHCl_3): 3020, 1684, 1622, 1561, 1525, 1347; ^1H -NMR (200 MHz CDCl_3): 8.42 (s, 1H), 8.28 (m, 2H), 7.95 (m, 2H), 6.15 (s, 1H), 0.32 (s, 9H); ^{13}C (100 MHz, CDCl_3): 152.88, 151.92, 149.03, 141.17, 129.33, 123.95, 105.21, 0.63; MS (m/z): 298 (M^+), 263, 247, 217, 202, 167, 149, 129, 73, 59.

(±)3-Chloro-4-p-nitro-phenyl-azetidin-2-one (5d)

m.p.: 130-133 °C; IR (CHCl_3): 3407, 1795, 1608, 1528; ^1H -NMR (200 MHz CDCl_3): 8.28 (m, 2H), 7.60 (m, 2H), 6.70 (bs, 1H), 4.82 (d, 1H, J= 2.1 Hz), 4.55 (dd, 1H, J= 2.1, 1.4 Hz); ^{13}C -NMR (50 MHz CDCl_3): 163.44, 148.53, 143.89, 126.71, 124.45, 64.48, 61.69; MS (m/z): 183 (M^+ -43), 153, 125, 102, 89, 75;

1-Chloro-2(trimethylsilyl)oxy-3-aza-4-p-chloro-phenyl-1,3-butadiene (4e)

IR (CDCl_3): 3155, 1647, 1621, 1597, 1489, 1389; ^1H -NMR (200 MHz CDCl_3): 8.33 (s, 1H), 7.73 (m, 2H), 7.40 (m, 2H), 6.00 (s, 1H), 0.32 (s, 9H); ^{13}C (100 MHz, CDCl_3): 153.52, 153.11, 137.34, 134.08, 129.95, 129.05, 102.31, 0.63; MS (m/z): 287 (M^+), 252, 236, 172, 149, 139, 111.

(±)(Trans)-3-chloro-4-p-chloro-phenyl-azetidin-2-one (5e)

IR (CHCl_3): 3410, 1790, 1493; ^1H -NMR (200 MHz CDCl_3): 7.35 (m, 4H), 6.88 (bs, 1H), 4.70 (d, 1H, J= 2.0 Hz), 4.48 (dd, 1H, J= 2.0, 1.5 Hz); ^{13}C -NMR (50 MHz CDCl_3): 164.16, 135.41, 135.17, 129.37, 127.10, 64.35, 61.94; MS (m/z): 215 (M^+), 180, 172, 152, 137, 125, 111, 102.

1-Chloro-2(trimethylsilyl)oxy-3-aza-4-p-methoxy-phenyl-1,3-butadiene (4f)

IR (CDCl_3): 3155, 2961, 1681, 1621, 1607, 1512, 1255; ^1H -NMR (200 MHz CDCl_3): 8.32 (s, 1H), 7.75 (m, 2H), 6.95 (m, 2H), 5.89 (s, 1H), 3.83 (s, 3H) 0.33 (s, 9H); ^{13}C (50MHz, CDCl_3): 154.62, 153.36, 130.59, 128.56, 114.22, 99.70, 55.38, 0.61; MS (m/z): 283 (M^+), 248, 232, 189, 168, 149, 91, 73, 55.

IR (CHCl₃): 3411, 3026, 1780, 1614; ¹H-NMR (200 MHz CDCl₃): 7.28 (m, 2H), 6.95 (bs, 1H), 6.90 (m, 2H), 4.65 (d, 1H, J= 1.9 Hz), 4.42 (dd, 1H, J= 1.9, 1.8 Hz), 3.78 (s, 3H); ¹³C-NMR (50 MHz CDCl₃): 164.55, 160.25, 128.88, 127.05, 114.47, 64.27, 62.17, 55.35; MS (m/z): 176 (M⁺-Cl), 168, 155, 148, 134, 125, 89.

(5 S)-1-Chloro-2-(trimethylsilyloxy)-3-aza-5(triisopropylsilyloxy)-hexa-1,3-diene. 4g

IR (CDCl₃): 3155, 1637, 1607, 1466, 1383; ¹H-NMR (200 MHz CDCl₃): 7.72 (d, 1H, J= 5.0 Hz), 5.79 (s, 1H), 4.45 (dq, 1H, J= 5.0, 6.5 Hz), 1.30 (d, 3H, J= 6.5 Hz), 1.01 (m, 21H), 0.26 (s, 9H); ¹³C (100MHz, CDCl₃): 164.08, 152.42, 100.94, 70.56, 22.06, 17.90, 12.09, 0.54; MS (m/z): 378 (M⁺), 334, 198, 177, 150, 74.

(3S,4S)-3-Chloro-4-[(1S)-(1-triisopropylsilyloxy)ethyl-azetid-2-one. (5g)

$[\alpha]_D^{20} = -6.57$ (c 0.70, CHCl₃); IR (CHCl₃): 3419, 2946, 2868, 1781, 1464, 1142, 883; ¹H-NMR (200 MHz CDCl₃): 6.23 (bs, 1H), 4.73 (dd, 1H, J= 1.9, 2.1 Hz), 4.15 (dq, 1H, J= 2.8, 6.3 Hz), 3.64 (dd, 1H, J= 1.9, 2.8), 1.25 (d, 3H, J= 6.3 Hz), 1.05 (s, 21 H); ¹³C-NMR (50 MHz CDCl₃): 164.23, 66.82, 65.16, 56.51, 20.33, 18.08, 12.47; MS (m/z): 262, 186, 177, 162, 149, 134, 116, 98, 75, 61.

(3R,4R)-3-Chloro-4-[(1S)-(1-triisopropylsilyloxy)ethyl-azetid-2-one. d-5g

$[\alpha]_D^{20} = +24.47$ (c 0.85, CHCl₃); IR (CHCl₃): 3419, 2946, 2868, 1781, 1464, 1142, 883; ¹H-NMR (200 MHz CDCl₃): 6.18 (bs, 1H), 4.50 (dd, 1H, J= 1.9, 2.1 Hz), 4.06 (dq, 1H, J= 6.2, 6.0 Hz), 3.60 (dd, 1H, J= 6.0, 2.1), 1.25 (d, 3H, J= 6.2 Hz), 1.05 (s, 21 H); ¹³C-NMR (50 MHz CDCl₃): 163.64, 68.86, 65.37, 57.61, 19.95, 18.07, 12.50; MS (m/z): 262, 186, 177, 162, 149, 134, 116, 98, 75, 61.

(5S)-1-Chloro-2-(ter-butylidimethylsilyloxy)-3-aza-5(triisopropylsilyloxy)-hexa-1,3-diene. 4h

IR (CDCl₃): 3560, 1637, 1607, 1466, 1383; ¹H-NMR (200 MHz CDCl₃): 7.78 (d, 1H, J= 4.9 Hz), 5.63 (s, 1H), 4.45 (dq, 1H, J= 4.9, 6.4 Hz), 1.29 (d, 3H, J= 6.4 Hz), 1.02 (m, 21H), 0.95 (s, 9H), 0.20 (s, 3H), 0.18 (s, 3H); ¹³C (50 MHz, CDCl₃): 164.54, 157.72, 98.13, 70.55, 25.80, 21.99, 18.14, 17.92, 12.16, -2.64, -3.63; MS (m/z): 420 (M⁺), 376, 289, 220, 198, 184, 149, 74

(3S,4S)-1-ter-Butyldimethylsilyl-3-chloro-4-[(1S)-1-triisopropylsilyloxy]ethyl-azetid-2-one. 5h

$[\alpha]_D^{20} = +12.0$ (c 1.50, CHCl₃); IR (CHCl₃): 2947, 2868, 1753, 1464; ¹H-NMR (200 MHz CDCl₃): 4.75(d, 1H, J= 2.0 Hz), 4.20 (dq, 1H, J= 6.4, 1.1 Hz), 3.51 (dd, J= 2.0, 1.1 Hz), 1.23 (d, 3H, J= 6.4), 1.03 (m, 21H), 0.92 (s, 9H), 0.33 (s, 3H), 0.15 (s, 3H); ¹³C-NMR (50 MHz CDCl₃): 169.28, 67.54, 67.25, 56.47, 26.36, 20.77, 19.54, 18.22, 12.82, -5.23, -5.46; MS (m/z): 376, 362, 300, 226, 219, 189, 157, 142, 115, 100, 73, 41.

(3R,4R)-1-ter-Butyldimethylsilyl-3-chloro-4-[(1S)-1-triisopropylsilyloxy]ethyl-azetid-2-one. d-5h

$[\alpha]_D^{20} = -6.10$ (c 0.30, CHCl₃); IR (CHCl₃): 2947, 2867, 1752, 1464; ¹H-NMR (200 MHz CDCl₃): 4.68 (d, 1H, J= 2.0 Hz), 4.25 (dq, 1H, J= 6.4, 4.3 Hz), 3.71 (dd, J= 2.0, 4.3 Hz), 1.12 (d, 3H, J= 6.4 Hz), 1.05 (m, 21H), 0.95 (s, 9H), 0.20 (s, 3H), 0.15 (s, 3H); ¹³C-NMR (50 MHz CDCl₃): 169.28, 67.54, 67.25, 56.47, 26.36, 20.77, 19.54, 18.22, 12.82, -5.23, -5.46; MS (m/z): 376, 362, 300, 226, 219, 189, 157, 142, 115, 100, 73, 41.

-5.29, -5.47; MS (m/z): 376, 362, 300, 219, 175, 157, 142, 115, 100, 73, 41.

(5 S)-1-Bromo-2-(trimethylsilyloxy)-3-aza-5(ter-butylidimethylsilyloxy)-hexa-1,3-diene. 4i

IR (CDCl₃): 3155, 1666, 1605, 1471, 1380; ¹H-NMR (200 MHz CDCl₃): 7.70 (d, 1H, J= 4.9 Hz), 5.78 (s, 1H), 4.35 (dq, 1H, J= 4.9, 6.5 Hz), 1.27 (d, 3H, J= 6.5 Hz), 0.88 (s, 9 H), 0.27 (s, 3H), 0.15 (s, 3H), 0.06 (s, 9H); ¹³C (50MHz, CDCl₃): 164.33, 154.27, 87.09, 70.46, 25.72, 21.46, 18.12, 0.68, -4.71, -4.78; MS (m/z): 323, 300, 250, 149, 130, 95, 73, 57.

(3S,4S)-3-bromo-4-[(1S)-1-ter-butylidimethylsilyloxy]ethyl-azetid-2-one. 5i

$[\alpha]_{Hg365}^{20} = +28.7$ (c 0.60, CHCl₃); IR (CHCl₃): 3416, 2956, 2931, 2859, 1779, 1471; ¹H-NMR (400 MHz CDCl₃): 6.16 (bs, 1H), 4.73 (dd, 1H, J= 2.8, 2.0 Hz), 3.97 (dq, 1H, J= 6.0, 2.8 Hz), 3.70 (dd, 1H, J= 2.0, 2.8 Hz), 1.22 (d, 3H, J= 6.0 Hz), 0.90 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H); ¹³C-NMR (100 MHz CDCl₃): 165.11, 68.11, 65.84, 44.61, 26.92, 21.48, 19.22, -3.14, -3.67; MS (m/z): 278, 262, 209, 172, 141, 130, 115, 75.

(3R,4R)-3-bromo-4-[(1S)-1-ter-butylidimethylsilyloxy]ethyl-azetid-2-one. d-5i

$[\alpha]_D^{20} = +52.8$ (c 0.80, CH₃OH); IR (CHCl₃): 3416, 2956, 2931, 2859, 1779, 1471; ¹H-NMR (400 MHz CDCl₃): 6.27 (bs, 1H), 4.42 (dd, 1H, J= 2.8, 2.4 Hz), 3.88 (dq, 1H, J= 6.0, 6.4 Hz), 3.66 (dd, 1H, J= 6.4, 2.4 Hz), 1.21 (d, 3H, J= 6.0 Hz), 0.89 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H); ¹³C-NMR (100 MHz CDCl₃): 163.45, 68.89, 65.03, 44.51, 25.78, 20.03, 18.05, -4.05, -4.66; MS (m/z): 278, 262, 209, 172, 141, 130, 115, 75.

(5 S)-1-Chloro-2-(trimethylsilyloxy)-3-aza-5(ter-butylidimethylsilyloxy)-hepta-1,3-diene. 4j

¹H-NMR (200 MHz CDCl₃): 7.64 (d, 1H, J= 5.4 Hz), 5.80 (s, 1H), 4.11 (m, 1H), 1.57 (m, 2H), 0.84 (m, 12H), 0.22 (s, 3H), 0.07 (s, 3H), 0.05 (m, 9H).

(±)(3S,4S)-3-Chloro-4-[(1S)-1-triisopropylsilyloxy]propyl-azetid-2-one. 5j

IR (CHCl₃): 3416, 2931, 2859, 1781, 1464; ¹H-NMR (200 MHz CDCl₃): 6.00 (bs, 1H), 4.70 (dd, 1H, J= 2.2, 1.9 Hz), 3.85 (ddd, 1H, J= 5.8, 5.8, 2.4 Hz), 3.63 (dd, 1H, J= 2.2, 2.4 Hz), 1.50 (m, 2H), 0.91 (dd, 3H, J= 7.4, 7.6 Hz), 0.80 (s, 9H), -0.07 (s, 3H), -0.05 (s, 3H); ¹³C-NMR (50 MHz CDCl₃): 164.22, 71.40, 63.34, 56.64, 27.69, 25.74, 18.05, 9.15, -4.42, -4.70; MS (m/z): 248, 220, 205, 186, 177, 144, 128, 115, 93, 82, 73, 57, 41;

(±)(3R,4R)-3-Chloro-4-[(1S)-1-triisopropylsilyloxy]propyl-azetid-2-one. d-5j

IR (CHCl₃): 3425, 2957, 2932, 2859, 1782, 1464; ¹H-NMR (200 MHz C₆D₆): 5.99 (bs, 1H), 4.13 (dd, 1H, J= 2.1, 1.8 Hz), 3.25 (dd, 1H, J= 2.1, 6.3 Hz), 3.10 (ddd 1H, J= 6.3, 5.8, 5.8, Hz), 1.10 (m, 2H), 0.88 (s, 9H), 0.62 (dd, 3H, J= 7.5, 7.3 Hz), -0.07 (s, 3H), -0.10 (s, 3H); ¹³C-NMR (50 MHz C₆D₆): 163.16, 73.55, 63.19, 58.50, 26.99, 25.85, 18.08, 9.01, -4.31, -4.59; MS (m/z): 262, 233, 186, 157, 144, 129, 111, 95, 83, 67, 55;

(5 S)-1-Chloro-2-(trimethylsilyloxy)-3-aza-5(tri-

(d, 3H, J= 5.1 Hz), 0.93 (d, 3H, J= 5.00 Hz), 0.30 (s, 9H); ¹³C (100 MHz, CDCl₃): 162.92, 152.71, 101.28, 79.06, 22.06, 34.84, 18.17, 12.57, 0.79; MS (m/z): 406 (M⁺), 362, 290, 215, 177, 149, 73.

(3S,4S)-3-Chloro-4-[(1S)-1-triisopropylsilyloxy-2-methyl]propyl-azetidin-2-one. 5k

[α]_D²⁰ = +13.92 (c 1.20, CHCl₃); IR (CHCl₃): 3414, 2947, 2869, 1780, 1466; ¹H-NMR (200 MHz CDCl₃): 6.46 (bs, 1H), 4.83 (dd, 1H, J= 1.9, 1.7 Hz), 3.91 (dd, 1H, J= 3.6, 1.4 Hz), 3.72 (dd, 1H, J= 1.9, 1.4 Hz), 1.96 (ddq, 1H, J= 3.6, 6.4, 6.4 Hz), 1.07 (m, 21H), 0.96 (d, 6H, J= 6.4 Hz); ¹³C-NMR (50 MHz CDCl₃): 164.84, 75.18, 61.04, 57.04, 33.42, 18.88, 18.15, 16.06, 12.85; MS (m/z): 290, 247, 214, 170, 149, 75, 61.

(3R,4R)-3-Chloro-4-[(1S)-1-triisopropylsilyloxy-2-methyl]propyl-azetidin-2-one. d-5k

[α]_D²⁰ = +35.40 (c 0.84, CHCl₃); IR (CHCl₃): 3426, 2947, 2869, 1781, 1465; ¹H-NMR (200 MHz CDCl₃): 6.12 (bs, 1H), 4.45 (dd, 1H, J= 2.0, 1.9 Hz), 3.79 (dd, 1H, J= 6.8, 3.3 Hz), 3.71 (dd, 1H, J= 6.8, 2.0 Hz), 1.95 (ddq, 1H, J= 3.3, 7.0, 7.0 Hz), 1.08 (m, 21H), 0.96 (d, 6H, J= 7.0 Hz); ¹³C-NMR (50 MHz CDCl₃): 163.47, 77.49, 61.15, 58.71, 33.16, 18.30, 18.18, 16.77, 12.99; MS (m/z): 290, 247, 214, 170, 149, 75, 61.

(5S)-1-Bromo-2-(trimethylsilyloxy)-3-aza-5-(triisopropylsilyloxy)-6-methyl-hepta-1,3-diene. 4l

IR (CDCl₃): 3155, 2962, 2867, 1662, 1605, 1464; ¹H-NMR (200 MHz CDCl₃): 7.70 (d, 1H, J= 6.1 Hz), 5.78 (s, 1H), 4.11 (dd, 1H, J= 6.1, 4.8 Hz), 1.91 (m, 1H), 1.03 (m, 21H), 0.96 (d, 3H, J= 5.6 Hz), 0.93 (d, 3H, J= 5.9 Hz), 0.30 (s, 9H); ¹³C (50 MHz, CDCl₃): 163.21, 154.38, 88.08, 78.71, 34.56, 18.24, 12.38, 0.70; MS (m/z): 408 (M⁺-i-Prop), 370, 298, 242, 214, 195, 149, 123, 73, 57.

(3S,4S)-3-Bromo-4-[(1S)-1-triisopropylsilyloxy-2-methyl]propyl-azetidin-2-one. 5l

[α]_D²⁰ = +12.76 (c 0.97, CHCl₃); IR (CHCl₃): 3412, 2947, 2869, 1775, 1466, 1372, 1110, 883; ¹H-NMR (200 MHz CDCl₃): 6.86 (bs, 1H), 4.82 (dd, 1H, J= 1.9, 1.9 Hz), 3.89 (dd, 1H, J= 1.9, 3.7 Hz), 3.80 (dd, 1H, J= 3.7, 1.6 Hz), 1.92 (ddq, 1H, J= 1.6, 6.6, 6.6 Hz), 1.05 (m, 21H), 0.98 (d, 3H, J= 6.6 Hz), 0.95 (d, 3H, J= 6.6 Hz); ¹³C-NMR (50 MHz CDCl₃): 165.27, 75.54, 61.11, 44.88, 33.42, 18.88, 18.15, 16.34, 12.84; MS (m/z): 336, 293, 214, 184, 170, 149, 121, 75, 61.

(3R,4R)-3-Bromo-4-[(1S)-1-triisopropylsilyloxy-2-methyl]propyl-azetidin-2-one d-5l

[α]_D²⁰ = +27.30 (c 1.70, CHCl₃); IR (CHCl₃): 3424, 2947, 2869, 1780, 1466, 1370, 1106, 883; ¹H-NMR (200 MHz C₆D₆): 6.24 (bs, 1H), 4.17 (dd, 1H, J= 2.0, 2.0 Hz), 3.49 (dd, 1H, J= 2.0, 6.6 Hz), 3.43 (dd, 1H, J= 6.6, 3.1 Hz), 1.58 (ddq, 1H, J= 3.1, 7.1, 7.1 Hz), 0.98 (m, 21H), 0.73 (d, 3H, J= 7.1 Hz), 0.65 (d, 3H, J= 7.1 Hz); ¹³C-NMR (50 MHz CDCl₃): 163.65, 77.69, 61.09, 45.72, 33.10, 18.30, 18.15, 16.80, 12.97; MS (m/z): 378 (M⁺), 334, 248, 214, 170, 149, 75, 67, 55.

(5S)-1-Bromo-2-(trimethylsilyloxy)-3-aza-5-(tert-butylsilyloxy)-6,6-dimethyl-hepta-1,3-diene. 4m

IR (CDCl₃): 3155, 1666, 1605, 1471, 1380; ¹H-NMR (200

35.86, 28.38, 26.35, 18.17, 0.73, -4.58, -4.82; MS (m/z): 323 (M -t-But), 300, 250, 149, 130, 95, 73, 57.

(±)(3S,4S)-3-Bromo-4-[(1S)-1-ter-butylsilyloxy-2,2-dimethyl]propyl-azetidin-2-one. 5m

IR (CHCl₃): 3412, 2858, 1776, 1472; ¹H-NMR (200 MHz CDCl₃): 6.15 (bs, 1H), 4.78 (dd, 1H, J= 1.7, 2.1 Hz), 3.97 (dd, 1H, J= 1.0, 1.7 Hz), 3.47 (d, 1H, 1.0 Hz), 0.98 (s, 9H), 0.91 (s, 9H), 0.70 (s, 6H); ¹³C-NMR (50 MHz CDCl₃): 164.56, 78.72, 61.15, 44.75, 35.33, 26.71, 26.18, 18.50, -3.32, -4.18; MS (m/z): 336, 292, 251, 227, 201, 172, 156, 116, 100, 73, 57, 41.

(±)(3R,4R)-3-Bromo-4-[(1S)-1-ter-butylsilyloxy-2,2-dimethyl]propyl-azetidin-2-one. d-5m

IR (CHCl₃): 2958, 2858, 1780, 1472; ¹H-NMR (200 MHz CDCl₃): 5.85 (bs, 1H), 4.39 (dd, 1H, J= 1.9, 2.1 Hz), 3.79 (dd, 1H, J= 1.9, 7.9 Hz), 3.31 (d, 1H, 7.9 Hz), 0.95 (s, 9H), 0.89 (s, 9H), 0.10 (s, 6H); ¹³C-NMR (50 MHz CDCl₃): 163.19, 81.40, 61.27, 47.39, 35.14, 26.27, 26.08, 18.49, -3.06, -3.64; MS (m/z): 294, 251, 214, 201, 172, 116, 100, 73, 57, 41

(5S)-1-Chloro-2-(trimethylsilyloxy)-3-aza-5-(triisopropylsilyloxy)-5-phenyl-1,3-penta-diene. 4n

IR (CDCl₃): 3065, 1673, 1633, 1605, 1464; ¹H-NMR (200 MHz CDCl₃): 7.65 (d, 1H, J= 6.1 Hz), 7.25 (m, 5H), 5.82 (s, 1H), 5.35 (d, 1H, J= 6.1 Hz), 1.01 (m, 21H), 0.16 (s, 9H); ¹³C (100 MHz, CDCl₃): 161.42, 152.42, 140.59, 128.30, 127.73, 126.09, 101.31, 76.62, 17.90, 12.05, 0.38; MS (m/z): 438 (M⁺), 396, 246, 177, 149, 73.

(3S,4S)-3-Chloro-4-[(1S)-1-triisopropylsilyloxy]benzil-azetidin-2-one. 5n

[α]_D²⁰ = +13.60 (c 0.36, CHCl₃); IR (CHCl₃): 3419, 2947, 2869, 1781, 1464, 1107, 884; ¹H-NMR (200 MHz CDCl₃): 7.34 (m, 5H), 5.78 (bs, 1H), 4.86 (d, 1H, J= 4.9 Hz), 4.70 (dd, 1H, J= 1.9, 1.8 Hz), 3.81 (dd, 1H, J= 4.9, 1.8 Hz), 0.95 (m, 21H); ¹³C-NMR (50 MHz CDCl₃): 163.93, 139.93, 128.64, 128.57, 126.32, 74.63, 65.24, 57.27, 17.66, 12.29; MS (m/z): 324, 263, 248, 214, 206, 179, 149, 129, 91, 75.

(3R,4R)-3-Chloro-4-[(1S)-1-triisopropylsilyloxy]benzil-azetidin-2-one. d-5n

[α]_D²⁰ = +41.15 (c 1.13, CHCl₃); IR (CHCl₃): 3419, 2947, 2869, 1781, 1464, 1109, 883; ¹H-NMR (200 MHz CDCl₃): 7.35 (m, 5H), 6.22 (bs, 1H), 4.90 (d, 1H, J= 5.4 Hz), 4.55 (dd, 1H, J= 2.0, 1.9 Hz), 3.82 (dd, 1H, J= 2.0, 5.4 Hz), 0.98 (m, 21H); ¹³C-NMR (50 MHz CDCl₃): 163.54, 139.75, 128.76, 128.65, 126.35, 74.93, 65.42, 57.24, 17.96, 12.38; MS (m/z): 324, 263, 248, 206, 179, 115, 91, 75.

(5S)-1-Bromo-2-(trimethylsilyloxy)-3-aza-5-(triisopropylsilyloxy)-5-phenyl-1,3-penta-diene. 4o

IR (CDCl₃): 3066, 1673, 1633, 1605, 1464; ¹H-NMR (200 MHz CDCl₃): 7.67 (d, 1H, J= 6.1 Hz), 7.26 (m, 5H), 5.82 (s, 1H), 5.33 (d, 1H, J= 6.1 Hz), 1.02 (m, 21H), 0.17 (s, 9H); ¹³C (100 MHz, CDCl₃): 161.98, 152.44, 140.41, 128.20, 127.78, 126.12, 88.69, 76.68, 17.90, 12.04, 0.51; MS (m/z): 438 (M⁺), 396 (M -i-Pr), 246, 177, 149, 73

(3S,4S)-3-Bromo-4-[(1S)-1-triisopropylsilyloxy]benzil-azetidin-2-one. 5o

[α]_D²⁰ = +16.46 (c 0.65, CHCl₃); IR (CHCl₃): 3413, 2946,

J=4.7, 1.9 Hz), 0.95 (m, 21H); ¹³C-NMR (50 MHz CDCl₃): 163.91, 139.84, 128.72, 128.62, 126.53, 75.22, 65.08, 44.38, 17.87, 12.35; MS (m/z): 368, 325, 264, 248, 221, 195, 177, 149, 139, 115, 91, 75, 43.

(3R,4R)-3-Bromo-4-[(1S)-1-triisopropylsilyloxy]benzyl-azetidin-2-one. d-5o

[α]_D²⁰ = +43.23 (c 0.77, CHCl₃); IR (CHCl₃): 3419, 2947, 2869, 1779, 1464; ¹H-NMR (200 MHz CDCl₃): 7.33 (m, 5H), 6.31 (bs, 1H), 4.87 (d, 1H, J= 5.4 Hz), 4.55 (dd, 1H, J= 2.0, 2.0 Hz), 3.30 (dd, 1H, J= 5.4, 2.0 Hz), 0.98 (m, 21H); ¹³C-NMR (50 MHz CDCl₃): 163.54, 139.68, 128.74, 128.64, 126.36, 75.19, 65.30, 44.07, 17.96, 12.36; MS (m/z): 368, 327, 265, 248, 221, 195, 177, 162, 139, 115, 83, 75, 47.

(5 S)-1-Bromo-2-(trimethylsilyloxy)-3-aza-5(tert-butyl)dimethylsilyloxy-5-phenyl-1,3-penta-diene. 4p

IR (CDCl₃): 3155, 1679, 1602, 1471, 1254; ¹H-NMR (200 MHz CDCl₃): 7.65 (d, 1H, J= 6.0 Hz), 7.26 (m, 5H), 5.81 (s, 1H), 5.26 (d, 1H, J= 6.0 Hz), 0.90 (s, 9H), 0.20 (s, 9H), 0.08 (s, 3H), 0.03 (s, 3H); ¹³C (50MHz, (CDCl₃): 161.78, 154.25, 140.10, 128.47, 127.97, 126.06, 88.04, 76.45, 25.77, 18.24, 0.57, -4.58, -4.82; MS (m/z): 443 (M⁺), 384, 362, 305, 251, 190, 149, 73.

(3S,4S)-3-Bromo-4-[(1S)-1-ter-

butyldimethylsilyloxy]benzil-azetidin-2-one. 5p

[α]_D²⁰ = +30.51 (c 0.78, CHCl₃); IR (CHCl₃): 3423, 2930, 2858, 1780, 1472, 1260, 1105, 839; ¹H-NMR (200 MHz C₆D₆): 7.05 (m, 5H), 5.44 (bs, 1H), 4.69 (dd, 1H J=1.9, 2.1 Hz), 4.18 (d, 1H, J= 5.1 Hz), 3.50 (dd, 1H, J= 1.9, 5.1 Hz), 0.90 (s, 9H), -0.05 (s, 3H), -0.22 (s, 3H); ¹³C-NMR (50 MHz C₆D₆): 163.04, 140.39, 126.64, 126.33, 75.24, 70.95, 64.91, 45.43, 25.81, 18.21, -4.68, -5.14; MS (m/z): 371 (M⁺), 314, 293, 234, 221, 192, 165, 115, 91, 75, 55;

(3R,4R)-3-Bromo-4-[(1S)-1-ter-butyl)dimethylsilyloxy]benzil-azetidin-2-one. d-5p

[α]_D²⁰ = +52.90 (c 0.86, CHCl₃); IR (CHCl₃): 3419, 2956, 2859, 1779, 1472, 1260, 1106, 840; ¹H-NMR (200 MHz CDCl₃): 7.33 (m, 5H), 6.08 (bs, 1H), 4.75 (d, 1H, J= 5.1 Hz), 4.55 (dd, 1H, J= 1.9, 2.1 Hz), 3.85 (dd, 1H, J= 1.9, 5.1 Hz), 0.89 (s, 9H), -0.05 (s, 3H), -0.16 (s, 3H); ¹³C-NMR (50 MHz CDCl₃): 163.39, 139.67, 128.82, 128.51, 125.99, 74.45, 65.14, 44.05, 25.70, 18.11, -4.56, -5.18; MS (m/z): 314, 234, 221, 192, 165, 115, 91, 73, 55;

General procedure for dehalogenation reaction.

Under inert atmosphere, azetidinone **5** (0.40 mmol) was dissolved in toluene (5 ml). To this solution tris(trimethylsilyl)silane (0.155 ml, 0.5 mmol) and a catalytic amount of AIBN were added. The resulting mixture was heated at 100 °C for 2 hrs. The solvent was removed and the crude chromatographed on a short column of silica gel eluting with CH₂Cl₂/acetone 90/10. The target **7** was obtained in the yields reported in Table 3.

(±)4-Phenyl-azetidin-2-one 7a¹⁷

IR (CHCl₃): 3414, 3012, 1760, 1216. ¹H-NMR (200 MHz CDCl₃): 7.35(m, 5H), 6.70 (bs, 1H), 4.70 (dd, 1H, J= 2.6, 5.3 Hz), 3.41 (ddd, 1H, J= 5.3, 2.4, 14.8 Hz), 2.83 (ddd, 1H, J= 14.8, 2.6, 0.90 Hz). ¹³C-NMR (50 MHz CDCl₃): 168.30, 140.16, 128.75, 128.10, 125.57, 50.28, 47.83. MS (m/z):

IR (CHCl₃): 3018, 2930, 1768, 1524, 1349, 854. ¹H-NMR (200 MHz CDCl₃): 8.25 (m, 2H), 7.57 (m, 2H), 6.23 (b.s., 1H), 4.85 (dd, 1H, J= 2.7, 5.6 Hz), 3.55 (ddd, 1H, J= 5.6, 2.8, 14.9 Hz), 2.88 (ddd, 1H, J= 14.9, 2.7, 0.7 Hz). ¹³C-NMR (50 MHz CDCl₃): 157.61, 130.89, 128.80, 126.55, 124.22, 49.71, 48.43; MS (m/z): 149, 119, 103, 91, 83, 77, 51, 42.

(±)4-p-Chloro-phenyl-azetidin-2-one. 7c

IR (CHCl₃): 3412, 1764, 1494; ¹H-NMR (200 MHz CDCl₃): 7.32 (m, 4H), 6.55 (bs, 1H), 4.70 (dd, 1H, J= 2.5, 5.3 Hz), 3.43 (ddd, 1H, J= 5.3, 2.4, 14.9 Hz), 2.83 (ddd, 1H, J= 14.9, 2.5, 0.8 Hz). ¹³C-NMR (50 MHz CDCl₃): 167.89, 138.72, 133.97, 129.01, 127.01, 49.78, 48.08. MS (m/z): 183, 181, 140, 138, 103, 77, 63.

(±)4-p-Methoxy-phenyl-azetidin-2-one. 7d

IR (CHCl₃): 3413, 1759, 1614, 1516, 1249, 1176, 1035, 832. ¹H-NMR (200 MHz CDCl₃): 7.28 (m, 2H), 6.89 (m, 2H), 6.29 (bs, 1H), 4.67 (dd, 1H, J= 2.6, 5.3 Hz), 3.40 (ddd, 1H, J= 5.3, 2.4, 14.9 Hz), 2.83 (ddd, 1H, J= 14.9, 2.6, 0.8 Hz). ¹³C-NMR (50 MHz CDCl₃): 168.21, 159.57, 132.07, 126.90, 114.21, 55.33, 49.99, 47.99. MS (m/z): 177, 176, 146, 135, 134, 119, 91, 77, 65, 42.

(4R)-4-[(1S)-1-ter-Butyldimethylsilyloxy]ethyl-azetidin-2-one. 7e

m.p.: 60-63 °C; [α]_D²⁰ = +120.20 (c 0.71, CHCl₃); IR (CHCl₃): 3419, 2931, 2858, 1760, 1255; ¹H-NMR (400 MHz CDCl₃): 5.82 (bs, 1H), 3.91 (dq, 1H, J= 6.4, 3.6 Hz), 3.54 (ddd, 1H, J= 2.8, 4.8, 3.6 Hz), 2.88 (ddd, 1H, J= 14.6, 4.8, 2.0 Hz) 2.82 (ddd, 1H, J= 14.6, 2.8, 1.6 Hz), 1.14 (d, 1H, J= 6.4 Hz), 0.85 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ¹³C-NMR (50 MHz CDCl₃): 168.41, 68.36, 52.90, 39.03, 25.70, 19.93, 17.97, -4.48, -4.89; MS (m/z): 172, 130, 115, 103, 75, 59.

(4S)-4-[(1S)-1-ter-Butyldimethylsilyloxy]ethylazetidin-2-one. 7f

[α]_D²⁰ = +16.30 (c 1.65, CHCl₃); IR (CHCl₃): 3427, 2932, 2859, 1759, 1259; ¹H-NMR (200 MHz CDCl₃): 5.92 (bs, 1H), 3.71 (dq, 1H, J= 6.2, 7.6 Hz), 3.46 (ddd, 1H, J= 7.6, 5.1, 2.5 Hz), 2.95 (ddd, 1H, J= 5.1, 14.7, 2.0 Hz) 2.53 (ddd, 1H, J= 14.7, 2.5, 1.4 Hz), 1.13 (d, 1H, J= 6.2 Hz), 0.85 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ¹³C-NMR (50 MHz CDCl₃): 167.52, 71.54, 53.50, 40.19, 25.77, 19.91, 18.04, -4.24, -4.70; MS (m/z): 185, 172, 130, 115, 73, 59.

(4R)-4-[(1S)-1-triisopropylsilyloxy-2-methyl]propyl-azetidin-2-one. 7g

[α]_D²⁰ = +36.28 (c 1.20, CHCl₃); IR (CHCl₃): 3415, 2947, 2869, 1757, 1465; ¹H-NMR (400 MHz CDCl₃): 5.74 (bs, 1H), 3.87 (dd, 1H, J= 3.2, 3.2 Hz), 3.70 (ddd, 1H, J= 4.8, 2.4, 3.2 Hz), 3.10 (dd, 1H, J= 14.8, 2.4 Hz), 2.81 (ddd, 1H, J= 14.8, 2.4, 4.8 Hz), 1.89 (ddq, 1H, J= 7.2, 7.2, 3.2 Hz), 1.06 (m, 21H), 0.93 (d, 3H, J= 7.2 Hz), 0.89 (d, 3H, J= 7.2 Hz). ¹³C-NMR (100 MHz CDCl₃): 168.57, 76.03, 49.11, 39.88, 33.48, 18.51, 18.22, 16.81, 12.97. MS (m/z): 256, 214, 128, 115, 99, 75, 59, 43.

(4S)-4-[(1S)-1-triisopropylsilyloxy-2-methyl]propyl-azetidin-2-one 7h

[α]_D²⁰ = +8.60 (c 1.25, CH₂Cl₂); IR (CHCl₃): 3427, 2963,

(m, 21H), 0.73 (d, 3H, J= 7.2 Hz), 0.56 (d, 3H, J= 7.2 Hz). ¹³CNMR (50 MHz CDCl₃): 167.47, 79.47, 49.51, 41.12, 32.94, 18.28, 18.21, 17.40, 13.03. MS (m/z): 256, 214, 128, 115, 99, 75, 59, 43.

(±)(4R)-4-[(1S)-1-*ter*-butyldimethylsilyloxy-2,2-dimethyl]propyl-azetidin-2-one 7i

IR (CHCl₃): 3415, 2959, 2903, 2858, 1755, 1472. ¹HNMR (200 MHz CDCl₃): 5.59 (bs, 1H), 3.87 (ddd, 1H, J= 1.2, 2.5, 5.0 Hz), 3.47 (d, 1H, J= 1.2 Hz), 3.10 (dd, 1H, J= 2.5, 14.6 Hz), 2.74 (ddd, 1H, J= 5.0, 14.6, 2.7), 0.94 (s, 9H); 0.89 (s, 9 H). 0.09 (s, 3 H), 0.08 (s, 3 H). ¹³CNMR (100 MHz CDCl₃): 168.55, 78.35, 48.79, 38.98, 35.42, 26.71, 26.17, 18.51, -3.37, -4.16. MS (m/z): 214, 172, 116, 99, 83, 73, 57.

(±)(4S)-4-[(1S)-1-triisopropylsilyloxy-2,2-dimethyl]propyl-azetidin-2-one 7j

IR (CHCl₃): 3432, 2959, 2904, 2858, 1756, 1464. ¹HNMR (400 MHz CDCl₃): 5.73 (bs, 1H), 3.67 (ddd, 1H, J= 2.6, 8.2, 5.0 Hz), 3.27 (d, 1H, J= 8.2 Hz), 3.00 (ddd, 1H, J= 2.4, 5.0, 14.8 Hz), 2.66 (ddd, 1H, J= 1.2, 14.8, 2.6), 0.93(s, 9H); 0.89 (s, 9 H). 0.05 (s, 3 H), 0.04 (s, 3 H). ¹³CNMR (100 MHz CDCl₃): 167.27, 82.46, 49.18, 42.99, 35.41, 26.56, 26.09, 18.48, -2.99, -3.56. MS (m/z): 214, 172, 116, 100, 83, 73, 57.

(4R)-4-[(1S)-1-triisopropylsilyloxy]benzyl-azetidin-2-one 7k

$[\alpha]_D^{20} = +56.02$ (c 0.98, CHCl₃); IR (CHCl₃): 3416, 2946, 2868, 1758, 1464. ¹HNMR (200 MHz CDCl₃): 7.30 (m, 5H), 5.66 (bs, 1H), 4.81 (d, 1H, J= 5.1 Hz), 3.73 (ddd, 1H, J= 5.1, 3.9, 3.4 Hz), 2.89 (m, 2H), 0.98 (m, 21H). ¹³CNMR (100 MHz CDCl₃): 167.64, 140.95, 128.36, 128.14, 126.56, 76.09, 53.55, 39.99, 17.85, 12.29. MS (m/z): 290, 263, 248, 115, 91, 75, 59, 43.

(4S)-4-[(1S)-1-triisopropylsilyloxy]benzyl-azetidin-2-one 7l

$[\alpha]_D^{20} = +29.60$ (c 0.71, CHCl₃). IR (CHCl₃): 3425, 2946, 2868, 1758, 1464, 1098, 883. ¹HNMR (200 MHz CDCl₃): 7.32 (m, 5H), 6.02 (bs, 1H), 4.66 (d, 1H, J= 7.4 Hz), 3.74 (ddd, 1H, J= 7.4, 5.0, 2.7 Hz), 2.75 (ddd, 1H, J= 15.0, 5.0, 2.1 Hz), 2.62 (ddd, 1H, J= 15.0, 2.7, 1.3 Hz), 0.97 (m, 21H). ¹³CNMR (50 MHz CDCl₃): 167.83, 141.02, 128.49, 128.32, 126.69, 78.58, 54.12, 40.13, 17.86, 12.34. MS (m/z): 290, 264, 248, 115, 91, 75, 59, 43.

¹⁶ Chem. Abstr.; 74; 12982 (Patent; Hoechst AG; 1914386; 1970)

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