**Studies on Pd(II)-Catalyzed Synthesis of
(Z)- α -Haloalkylidene- β -lactones from Cyclocarbonylation of
2-Alkynols and the Subsequent Coupling Reaction**

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The ^1H and ^{13}C NMR spectra were taken with a Varian Mercury-300 spectrometer. The IR spectra were recorded with a Perkin-Elmer 983 spectrometer. The MS data were measured with a HP 5989A spectrometer. The HRMS data were collected with a Finnigan MAT 8430 spectrometer.

The following compounds were prepared according to Typical Procedure I.

(1) (*E*)- α -(1-chloropentylidene)- β -(*n*-pentyl)- β -lactone ((*E*)-5f**):**

The reaction of **3f** (183 mg, 1.00 mmol), PdCl_2 (17 mg, 0.10 mmol), and CuCl_2 (678 mg, 5.02 mmol) was stirred at 27 °C for 4 h to afford 160 mg (67%) of (*Z*)-**5f** and 18 mg (9%) of (*E*)-**5f**. (*E*)-**5f**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 4.99 (dd, $J = 3.3$ and 6.6 Hz, 1 H), 2.90-2.70 (m, 2 H), 2.18-2.00 (m, 1 H), 1.90-1.73 (m, 1 H), 1.73-1.55 (m, 3 H), 1.55-1.20 (m, 7 H), 0.94 (t, $J = 7.4$ Hz, 3 H), 0.90 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 161.9, 142.7, 133.5, 79.4, 35.1, 31.6, 31.4, 29.1, 23.9, 22.4, 21.5, 13.9, 13.6; MS (EI) m/z (%) 247 ($\text{M}^+ + 1(^{37}\text{Cl})$, 1.98), 245 ($\text{M}^+ + 1(^{35}\text{Cl})$, 5.88), 41 (100); IR (neat) 1816, 1712 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{21}^{35}\text{ClO}_2$ 244.1230. Found 244.1230.

(2) (*E*)- α -(1-chlorobenzylidene)- β -(*i*-propyl)- β -lactone ((*E*)-5k**) and 4-Chloro-3-phenyl-5-(*i*-propyl)-2(5*H*)-furanone (**6k**):**

The reaction of **3k** (173 mg, 1.00 mmol), PdCl₂ (18 mg, 0.10 mmol), and CuCl₂ (676 mg, 5.01 mmol) was stirred at 30 °C for 4 h to afford 214 mg (91%) of (**Z**)-**5k**, 15 mg (6%) of (**E**)-**5k** and 11mg (4%) of **6k**. (**E**)-**5k**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 8.05-7.94 (m, 2 H), 7.58-7.21 (m, 3 H), 5.03 (d, *J* = 3.6 Hz, 1 H), 2.60-2.44 (m, 1 H), 1.18 (d, *J* = 6.9 Hz, 3 H), 1.04 (d, *J* = 6.6 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 160.8, 138.1, 132.5, 132.2, 131.6, 128.50, 128.48, 83.2, 29.4, 18.4, 15.0; MS (EI) *m/z* (%) 238 (M⁺(³⁷Cl), 7.33), 236 (M⁺(³⁵Cl), 23.46), 193 (100); IR (neat) 1806, 1667 cm⁻¹; HRMS (EI) calcd for C₁₃H₁₃³⁵ClO₂ 236.0604. Found 236.0598. **6k**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.88-7.76 (m, 2 H), 7.55-7.20 (m, 3 H), 4.90 (d, *J* = 2.4 Hz, 1 H), 2.48-2.30 (m, 1 H), 1.24 (d, *J* = 6.9 Hz, 3 H), 0.83 (d, *J* = 6.6 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 169.8, 151.8, 129.51, 128.53, 128.5, 127.625, 126.626, 85.7, 29.8, 19.3, 13.5; MS (EI) *m/z* (%) 238 (M⁺(³⁷Cl), 15.87), 236 (M⁺(³⁵Cl), 46.07), 194 (100); IR (neat) 1764, 1644 cm⁻¹; HRMS (EI) calcd for C₁₃H₁₃³⁵ClO₂ 236.0604. Found 236.0614.

(3) (*E*)-α-(1-chlorobenzylidene)-β-cyclohexyl-β-lactone ((*E*)-5m) and 4-Chloro-3-phenyl-5-cyclohexyl-2(5*H*)-furanone (6m):

The reaction of **3m** (217 mg, 1.01 mmol), PdCl₂ (18 mg, 0.10 mmol), and CuCl₂ (673

mg, 4.99 mmol) was stirred at 30 °C for 4 h to afford 219 mg (78%) of **(Z)-5m**, 15 mg (6%) of **(E)-5m** and 9mg (3%) of **6m**. **(E)-5m**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 8.02-7.89 (m, 2 H), 7.53-7.40 (m, 3 H), 5.00 (d, $J = 3.6$ Hz, 1 H), 2.28-2.10 (m, 1 H), 1.92-1.68 (m, 5 H), 1.50-1.10 (m, 5 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 160.8, 138.1, 132.5, 132.0, 131.6, 128.50, 128.49, 82.8, 38.9, 28.7, 26.2, 26.0, 25.7, 25.4; MS (EI) m/z (%) 278 ($\text{M}^+(\text{}^{37}\text{Cl})$, 9.27), 276 ($\text{M}^+(\text{}^{35}\text{Cl})$, 26.99), 55 (100); IR (neat) 1805, 1665 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{17}^{35}\text{ClO}_2$ 276.0917. Found 276.0903. **6m**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.86-7.70 (m, 2 H), 7.53-7.36 (m, 3 H), 4.86 (d, $J = 2.7$ Hz, 1 H), 2.15-1.98 (m, 1 H), 1.95-1.00 (m, 10 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 169.9, 151.6, 129.5, 128.5, 128.4, 127.7, 126.5, 85.6, 39.2, 29.7, 26.4, 25.8, 25.7, 23.8; MS (EI) m/z (%) 278 ($\text{M}^+(\text{}^{37}\text{Cl})$, 5.32), 276 ($\text{M}^+(\text{}^{35}\text{Cl})$, 15.44), 194 (100); IR (neat) 1767, 1642 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{17}^{35}\text{ClO}_2$ 276.0917. Found 276.0934.

(4) (*E*)- α -(1-chloro-3-phenylpropylidene)- β -(*i*-propyl)- β -lactone ((E)-5n**) and 4-Chloro-3-(2-phenylethyl)-5-(*i*-propyl)-2(*5H*)-furanone (**6n**):**

The reaction of **3n** (200 mg, 0.99 mmol), PdCl_2 (17 mg, 0.10 mmol), and CuCl_2 (673 mg, 4.99 mmol) was stirred at 30 °C for 4 h to afford 172 mg (66%) of **(Z)-5n**, 4 mg (2%) of **(E)-5n** and 5mg (2%) of **6n**. **(E)-5n**: liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.16 (m, 5 H), 4.81 (d, $J = 3.3$ Hz, 1 H), 3.32-3.13 (m, 1 H), 3.08-2.90 (m, 3 H), 2.30-2.10 (m, 1 H), 1.01 (d, $J = 6.9$ Hz, 3 H), 0.78 (d, $J = 6.6$ Hz, 3 H); ^{13}C NMR

(75.4 MHz, CDCl₃) δ 161.8, 141.2, 138.7, 133.3, 128.50, 128.49, 126.5, 83.6, 36.6, 33.1, 29.7, 18.0, 15.3; MS (EI) m/z (%) 267 ($M^+ + 1(^{37}\text{Cl})$, 0.91), 265 ($M^+ + 1(^{35}\text{Cl})$, 2.94), 91 (100); IR (neat) 1811, 1713 cm⁻¹; HRMS (EI) calcd for C₁₅H₁₇³⁵ClO₂ 264.0917. Found 264.0939. **6n**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.32-7.15 (m, 5 H), 4.71 (d, J = 2.1 Hz, 1 H), 2.90 (t, J = 7.7 Hz, 2 H), 2.78-2.60 (m, 2 H), 2.28-2.05 (m, 1 H), 1.12 (d, J = 7.2 Hz, 3 H), 0.60 (d, J = 6.9 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 171.0, 153.2, 140.1, 128.5, 128.44, 128.39, 126.3, 85.9, 32.6, 29.3, 25.4, 19.1, 13.4; MS (EI) m/z (%) 267 ($M^+ + 1(^{37}\text{Cl})$, 0.63), 265 ($M^+ + 1(^{35}\text{Cl})$, 2.65), 91 (100); IR (neat) 1766, 1661 cm⁻¹; HRMS (EI) calcd for C₁₅H₁₇³⁵ClO₂ 264.0917. Found 264.0945.

(5) (*E*)- α -(1-chloro-3-phenylpropylidene)- β -(*i*-butyl)- β -lactone ((*E*)-5o):

The reaction of **3o** (210 mg, 0.97 mmol), PdCl₂ (18 mg, 0.10 mmol), and CuCl₂ (673 mg, 4.99 mmol) was stirred at 30 °C for 6 h to afford 140 mg (52%) of (**Z**)-**5o** and 17 mg (6%) of (**E**)-**5o**. (**E**)-**5o**: liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.40-7.15 (m, 5 H), 4.94 (dd, J = 2.7 and 9.9 Hz, 1 H), 3.20-2.89 (m, 4 H), 1.92-1.75 (m, 2 H), 1.60-1.42 (m, 1 H), 0.95 (d, J = 6.3 Hz, 6 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 161.6, 140.7, 138.8, 134.9, 128.5, 128.4, 126.5, 78.1, 40.4, 36.8, 33.2, 24.8, 23.0, 22.0; MS (EI) m/z (%) 280 ($M^+ (^{37}\text{Cl})$, 0.29), 278 ($M^+ (^{35}\text{Cl})$, 0.72), 91 (100); IR (neat) 1813, 1713 cm⁻¹; HRMS (EI) calcd for C₁₆H₁₉³⁵ClO₂ 278.1074. Found 278.1095.

(6) (*E*)- α -(1-chloro-3-phenylpropylidene)- β -cyclohexyl- β -lactone ((*E*)-5p):

The reaction of **3p** (241 mg, 1.00 mmol), PdCl₂ (17 mg, 0.10 mmol), and CuCl₂ (671 mg, 4.97 mmol) was stirred at 30 °C for 6 h to afford 192 mg (63%) of (**Z**)-**5p** and 20 mg (7%) of (**E**)-**5p**. liquid; ¹H NMR (300 MHz, CDCl₃) δ 7.38-7.16 (m, 5 H), 4.77 (d, J = 3.6 Hz, 1 H), 3.36-3.21 (m, 1 H), 3.08-2.89 (m, 3 H), 1.90-1.55 (m, 5 H), 1.35-0.86 (m, 6 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 161.8, 141.0, 138.7, 133.1, 128.6, 128.5, 126.5, 83.2, 39.1, 36.5, 33.0, 28.3, 25.9, 25.9, 25.7, 25.5; MS (EI) m/z (%) 306 (M^+ (³⁷Cl), 0.53), 304 (M^+ (³⁵Cl), 1.54), 91 (100); IR (neat) 1812, 1713 cm⁻¹; HRMS (EI) calcd for C₁₈H₂₁³⁵ClO₂ 304.1230. Found 304.1227.

The following compounds were prepared according to Typical Procedure II.

(7) (*E*)-3-(1-chloropentylidene)-1-oxa-spiro[3.5]nonan-2-one ((*E*)-5r):

The reaction of **3r** (179 mg, 1.00 mmol), PdCl₂ (18 mg, 0.10 mmol), CuCl₂ (674 mg, 5.00 mmol), and benzoquinone (432 mg, 4.00 mmol) was stirred at 30 °C for 2 h to afford 202 mg (86%) of (**Z**)-**5r** and 15 mg (6%) of (**E**)-**5r**. liquid; ¹H NMR (300 MHz, CDCl₃) δ 2.75 (t, J = 7.2 Hz, 2 H), 2.04 (dt, J = 4.2 and 13.6 Hz, 2 H), 1.95-1.50 (m, 9

H), 1.45-1.20 (m, 3 H), 0.93 (t, $J = 7.4$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 162.3, 141.4, 137.0, 87.4, 35.0, 32.4, 29.1, 24.5, 21.6, 21.4, 13.7; MS (EI) m/z (%) 244 ($\text{M}^+(\text{}^{37}\text{Cl})$, 1.56), 242 ($\text{M}^+(\text{}^{35}\text{Cl})$, 4.14), 55 (100); IR (neat) 2935, 2863, 1809, 1711 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{19}\text{}^{35}\text{ClO}_2$ 242.1074. Found 242.1032.

(8) (Z)-3-(1-Chloropentylidene)-1-oxa-spiro[3.4]octan-2-one ((Z)-5s):

The reaction of **3s** (154 mg, 0.93 mmol), PdCl_2 (18 mg, 0.10 mmol), CuCl_2 (671 mg, 4.97 mmol), and benzoquinone (326 mg, 3.02 mmol) was stirred at 30 $^\circ\text{C}$ for 2 h to afford 97 mg (46%) of **(Z)-5s**. liquid; ^1H NMR (300 MHz, CDCl_3) δ 2.30 (t, $J = 7.5$ Hz, 2 H), 2.27-2.15 (m, 2 H), 2.15-1.98 (m, 2 H), 1.98-1.71 (m, 4 H), 1.71-1.58 (m, 2 H), 1.45-1.30 (m, 2 H), 0.95 (t, $J = 7.5$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 161.6, 137.5, 134.4, 94.4, 36.3, 35.0, 28.8, 24.2, 22.0, 13.7; MS (EI) m/z (%) 230 ($\text{M}^+(\text{}^{37}\text{Cl})$, 0.90), 228 ($\text{M}^+(\text{}^{35}\text{Cl})$, 2.52), 55 (100); IR (neat) 2960, 2874, 1813, 1702 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{17}\text{}^{35}\text{ClO}_2$ 228.0917. Found 228.0937.

(9) (Z)-3-(1-Chloropentylidene)-1-oxa-spiro[3.6]decan-2-one ((Z)-5t):

The reaction of **3t** (194 mg, 1.0 mmol), PdCl_2 (18 mg, 0.10 mmol), CuCl_2 (681 mg, 5.04 mmol), and benzoquinone (329 mg, 3.05 mmol) was stirred at 30 $^\circ\text{C}$ for 2 h to

afford 80 mg (31%) of **(Z)-5t**. liquid; ^1H NMR (300 MHz, CDCl_3) δ 2.35 (t, $J=7.5$ Hz, 2 H), 2.22-2.10 (m, 2 H), 2.10-1.95 (m, 2 H), 1.82-1.50 (m, 10 H), 1.50-1.30 (m, 2 H), 0.96 (t, $J = 7.4$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 161.8, 138.6, 137.2, 90.0, 37.4, 35.6, 28.9, 28.1, 22.4, 22.0, 13.7; MS (EI) m/z (%) 258 ($\text{M}^+(\text{}^{37}\text{Cl})$, 2.41), 256 ($\text{M}^+(\text{}^{35}\text{Cl})$, 6.85), 41 (100); IR (neat) 2931, 2862, 1812, 1698 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{21}\text{}^{35}\text{ClO}_2$ 256.1230. Found 256.1222.

(10) (Z)- α -(1-Chloropentylidene)- β -methyl- β -ethyl- β -lactone ((Z)-5v):

The reaction of **3v** (161 mg, 1.05 mmol), PdCl_2 (18 mg, 0.10 mmol), CuCl_2 (675 mg, 5.0 mmol), and benzoquinone (323 mg, 3.0 mmol) was stirred at 30 $^\circ\text{C}$ for 2 h to afford 169 mg (75%) of **(Z)-5v**. liquid; ^1H NMR (300 MHz, CDCl_3) δ 2.31 (t, $J = 7.4$ Hz, 2 H), 2.06-1.84 (m, 2 H), 1.71-1.58 (m, 2 H), 1.65 (s, 3 H), 1.45-1.30 (m, 2 H), 1.03 (t, $J = 7.4$ Hz, 3 H), 0.95 (t, $J = 7.5$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 161.3, 137.8, 135.8, 87.2, 35.1, 30.8, 28.8, 23.2, 22.0, 13.7, 7.9; MS (EI) m/z (%) 219 ($\text{M}^++1(\text{}^{37}\text{Cl})$, 22.06), 217 ($\text{M}^++1(\text{}^{35}\text{Cl})$, 70.47), 181 (100); IR (neat) 2961, 2875, 1812, 1701 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{17}\text{}^{35}\text{ClO}_2$ 216.0917. Found 216.0903.

(11) (Z)- α -(1-Chloropentylidene)- β -diethyl- β -lactone ((Z)-5w):

The reaction of **3w** (170 mg, 1.01 mmol), PdCl₂ (18 mg, 0.10 mmol), CuCl₂ (675 mg, 5.0 mmol), and benzoquinone (324 mg, 3.0 mmol) was stirred at 30 °C for 2 h to afford 140 mg (60%) of **(Z)-5w**. liquid; ¹H NMR (300 MHz, CDCl₃) δ 2.30 (t, *J* = 7.7 Hz, 2 H), 2.12-1.95 (m, 2 H), 1.95-1.80 (m, 2 H), 1.70-1.60 (m, 2 H), 1.43-1.30 (m, 2 H), 1.01 (t, *J* = 7.4 Hz, 6 H), 0.95 (t, *J* = 7.4 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 161.3, 137.6, 133.8, 90.3, 35.3, 29.3, 28.7, 22.0, 13.7, 7.7 ; MS (EI) *m/z* (%) 233 (M⁺+1(³⁷Cl), 6.97), 231 (M⁺+1(³⁵Cl), 24.10), 201 (100); IR (neat) 2972, 2876, 1809, 1699 cm⁻¹; HRMS (EI) calcd for C₁₂H₁₉³⁵ClO₂ 230.1074. Found 230.1070.

(12) (Z)-α-(1-Chloropentylidene)-β-methyl-β-(*t*-butyl)-β-lactone ((Z)-5x):

The reaction of **3x** (177 mg, 0.97 mmol), PdCl₂ (18 mg, 0.10 mmol), CuCl₂ (667 mg, 4.94 mmol), and benzoquinone (325 mg, 3.0 mmol) was stirred at 30 °C for 2 h to afford 104 mg (44%) of **(Z)-5x**. liquid; ¹H NMR (300 MHz, CDCl₃) δ 2.39 (t, *J* = 7.7 Hz, 2 H), 1.80-1.55 (m, 2 H), 1.63 (s, 3 H), 1.50-1.30 (m, 2 H), 1.07 (s, 9 H), 0.95 (t, *J* = 7.2 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 161.9, 138.3, 135.6, 92.5, 37.4, 35.8, 28.9, 25.4, 22.1, 19.3, 13.7; MS (EI) *m/z* (%) 247 (M⁺+1(³⁷Cl), 21.77), 245 (M⁺+1(³⁵Cl), 66.49), 43 (100); IR (neat) 2962, 2875, 1810, 1691 cm⁻¹; HRMS (EI) calcd for C₁₃H₂₁³⁵ClO₂ 244.1230. Found 244.1204.

(13) (Z)-3-(1-Chlorobenzylidene)-1-oxa-spiro[3.5]nonan-2-one ((Z)-5z):

The reaction of **3z** (200 mg, 1.0 mmol), PdCl₂ (18 mg, 0.10 mmol), CuCl₂ (671 mg, 4.97 mmol), and benzoquinone (323 mg, 3.0 mmol) was stirred at 30 °C for 2 h to afford 187 mg (71%) of **(Z)-5z**. Solid, m.p. 93-95 °C (ethyl acetate/*n*-hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.52-7.42 (m, 5 H), 1.98 (d, *J* = 7.5 Hz, 2 H), 1.80-1.50 (m, 7 H), 1.20-1.00 (m, 1 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 161.9, 137.6, 134.5, 134.3, 130.8, 128.6, 127.7, 88.7, 34.2, 24.2, 21.7; MS (EI) *m/z* (%) 264 (M⁺(³⁷Cl), 1.73), 262 (M⁺(³⁵Cl), 5.26), 129 (100); IR (neat) 2944, 2868, 1807, 1790, 1657 cm⁻¹; Anal Calcd for C₁₅H₁₅ClO₂: C, 68.57; H, 5.75. Found: C, 68.56; H, 5.77.

(14) (S)-(Z)-α-(1-Chloropentylidene)-β-ethyl-β-lactone ((S)-(Z)-5q):

The reaction of **(S)-(-)-3q** (136 mg, 0.97 mmol, 98%ee) afforded 116 mg (59 yield) of **(S)-(Z)-5q** with 98%ee as determined by HPLC analysis (Chiralcel AD-H, *n*-Hexane : *i*-PrOH = 100 : 0.5, 230 nm), *t_r* 9.3 (minor), 14.7 (major); [α]_D²⁰ = -51.2 (c = 1.05, CHCl₃); liquid; ¹H NMR (300 MHz, CDCl₃) δ 4.98 (dd, *J* = 3.6 and 7.8 Hz, 1 H), 2.34 (t, *J* = 7.4 Hz, 2 H), 2.15-1.95 (m, 1 H), 1.94-1.78 (m, 1 H), 1.78-1.54 (m, 2 H), 1.46-1.30 (m, 2 H), 1.07 (t, *J* = 7.5 Hz, 3 H), 0.95 (t, *J* = 7.4 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 161.2, 138.7, 132.6, 79.9, 35.8, 28.7, 26.0, 21.8, 13.6, 8.4; MS (EI) *m/z* (%) 205 (M⁺1(³⁷Cl), 3.33), 203 (M⁺1(³⁵Cl), 9.95), 81 (100); IR (neat) 1813, 1703

cm⁻¹; HRMS (EI) calcd for C₁₀H₁₅³⁵ClO₂ 202.0761. Found 202.0775.

(15) (R)-(Z)-α-(1-Chloropentylidene)-β-ethyl-β-lactone ((R)-(Z)-5q):

(R)-(Z)-5q

The reaction of **(R)-(+)-3q** (141 mg, 1.01 mmol, >95%ee) afforded 119 mg (58 yield) of **(R)-(Z)-5q** with 97%ee as determined by HPLC analysis (Chiralcel AD-H, *n*-Hexane : *i*-PrOH = 100 : 0.5, 230 nm), *t_r* 9.2 (major), 15.8 (minor); [α]_D²⁰ = +51.4 (c = 1.025, CHCl₃).

The following compounds were prepared according to Typical Procedure III.

(16) (Z)-α-(1-Bromoheptylidene)-β-ethyl-β-lactone ((Z)-7a):

The reaction of **3a** (166 mg, 0.99 mmol), Pd(OAc)₂ (12 mg, 0.054 mmol), CuBr₂ (454 mg, 2.03 mmol), and benzoquinone (113 mg, 1.05 mmol) in 10 mL of dry PhH afforded 101 mg (37%) of **(Z)-7a**. liquid; ¹H NMR (300 MHz, CDCl₃) δ 5.00 (dd, *J* = 3.3 and 7.8 Hz, 1 H), 2.45 (t, *J* = 7.5 Hz, 2 H), 2.18-1.96 (m, 1 H), 1.92-1.75 (m, 1 H), 1.75-1.50 (m, 2 H), 1.45-1.25 (m, 6 H), 1.07 (t, *J* = 7.2 Hz, 3 H), 0.90 (t, *J* = 6.8 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 162.0, 135.3, 129.8, 81.4, 37.8, 31.3, 28.2, 27.5, 26.0, 22.3, 13.9, 8.4; MS (EI) *m/z* (%) 277 (M⁺+1(⁸¹Br), 2.94), 275 (M⁺+1(⁷⁹Br),

3.44), 43 (100); IR (neat) 1813, 1698 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{19}^{79}\text{BrO}_2$ 274.0568. Found 274.0532.

(17) (Z)- α -(1-Bromopentylidene)- β -methyl- β -lactone ((Z)-7d):

The reaction of **3d** (138 mg, 1.10 mmol), $\text{Pd}(\text{OAc})_2$ (11 mg, 0.049 mmol), CuBr_2 (447 mg, 2.0 mmol), and benzoquinone (114 mg, 1.06 mmol) in 10 mL of dry PhH afforded 66 mg (26%) of **(Z)-7d**. liquid; ^1H NMR (300 MHz, CDCl_3) δ 5.12 (q, J = 6.4 Hz, 1 H), 2.46 (t, J = 7.7 Hz, 2 H), 1.79-1.50 (m, 2 H), 1.63 (d, J = 6.4 Hz, 3 H), 1.48-1.26 (m, 2 H), 0.95 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 161.8, 136.9, 129.9, 76.7, 37.3, 29.6, 21.7, 19.0, 13.7; MS (EI) m/z (%) 234 ($\text{M}^+(\text{}^{81}\text{Br})$, 0.78), 232 ($\text{M}^+(\text{}^{79}\text{Br})$, 0.79), 67 (100); IR (neat) 1812, 1698 cm^{-1} ; HRMS (EI) calcd for $\text{C}_9\text{H}_{13}^{79}\text{BrO}_2$ 232.0099. Found 232.0061.

(18) (Z)- α -(1-Bromopentylidene)- β -(*n*-propyl)- β -lactone ((Z)-7e):

The reaction of **3e** (152 mg, 0.99 mmol), $\text{Pd}(\text{OAc})_2$ (12 mg, 0.054 mmol), CuBr_2 (452 mg, 2.03 mmol), and benzoquinone (109 mg, 1.02 mmol) in 10 mL of dry PhH afforded 95 mg (37%) of **(Z)-7e**. liquid; ^1H NMR (300 MHz, CDCl_3) δ 5.01 (dd, J = 3.3 and 8.4 Hz, 1 H), 2.45 (t, J = 7.5 Hz, 2 H), 2.01-1.88 (m, 1 H), 1.88-1.25 (m, 7 H),

0.99 (t, $J = 7.5$ Hz, 3 H), 0.95 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 162.0, 135.7, 129.6, 80.3, 37.5, 34.9, 29.6, 21.7, 17.8, 13.6, 13.6; MS (EI) m/z (%) 262 ($\text{M}^+(\text{}^{81}\text{Br})$, 0.69), 260 ($\text{M}^+(\text{}^{79}\text{Br})$, 0.66), 41 (100); IR (neat) 1813, 1698 cm^{-1} ; HRMS (EI) calcd for $\text{C}_8\text{H}_{10}\text{}^{79}\text{BrO}_2(\text{M}^+-\text{C}_3\text{H}_7)$ 216.9864. Found 216.9849.

(19) (Z)- α -(1-Bromopentylidene)- β -(*i*-propyl)- β -lactone ((Z)-7g):

The reaction of **3g** (153 mg, 0.99 mmol), $\text{Pd}(\text{OAc})_2$ (11 mg, 0.049 mmol), CuBr_2 (445 mg, 2.0 mmol), and benzoquinone (114 mg, 1.06 mmol) in 10 mL of dry PhH afforded 136 mg (53%) of **(Z)-7g**, liquid; ^1H NMR (300 MHz, CDCl_3) δ 4.90 (d, $J = 3.9$ Hz, 1 H), 2.45 (t, $J = 8.1$ Hz, 2 H), 2.14-2.04 (m, 1 H), 1.80-1.50 (m, 2 H), 1.45-1.28 (m, 2 H), 1.11 (d, $J = 7.2$ Hz, 3 H), 1.01 (d, $J = 7.2$ Hz, 3 H), 0.95 (t, $J = 7.5$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 162.1, 134.5, 129.9, 84.9, 37.9, 30.7, 29.6, 21.8, 18.3, 15.4, 13.6; MS (EI) m/z (%) 262 ($\text{M}^+(\text{}^{81}\text{Br})$, 2.36), 260 ($\text{M}^+(\text{}^{79}\text{Br})$, 2.06), 217 (100); IR (neat) 1813, 1697 cm^{-1} ; HRMS (EI) calcd for $\text{C}_8\text{H}_{10}\text{}^{79}\text{BrO}_2(\text{M}^+-\text{C}_3\text{H}_7)$ 216.9864. Found 216.9858.

(20) (Z)- α -(1-Bromopentylidene)- β -(*i*-butyl)- β -lactone ((Z)-7h):

The reaction of **3h** (164 mg, 0.98 mmol), $\text{Pd}(\text{OAc})_2$ (11 mg, 0.049 mmol), CuBr_2 (453

mg, 2.03 mmol), and benzoquinone (113 mg, 1.05 mmol) in 10 mL of dry PhH afforded 107 mg (40%) of **(Z)-7h**. liquid; ^1H NMR (300 MHz, CDCl_3) δ 5.05 (dd, $J = 4.5$ and 8.1 Hz, 1 H), 2.45 (t, $J = 7.5$ Hz, 2 H), 2.00-1.82 (m, 1 H), 1.81-1.70 (m, 2 H), 1.70-1.51 (m, 2 H), 1.44-1.28 (m, 2 H), 1.01 (d, $J = 6.6$ Hz, 3 H), 0.99 (d, $J = 6.6$ Hz, 3 H), 0.95 (t, $J = 7.4$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 162.1, 136.3, 129.5, 79.3, 41.9, 37.5, 29.6, 25.0, 23.0, 21.8, 21.7, 13.7; MS (EI) m/z (%) 276 ($\text{M}^+(\text{}^{81}\text{Br})$, 0.99), 274 ($\text{M}^+(\text{}^{79}\text{Br})$, 0.95), 109 (100); IR (neat) 1813, 1698 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{19}\text{}^{79}\text{BrO}_2$ 274.0568. Found 274.0572.

(21) (Z)- α -(1-Bromobenzylidene)- β -(*i*-propyl)- β -lactone ((Z)-7k):

The reaction of **3k** (170 mg, 0.98 mmol), $\text{Pd}(\text{OAc})_2$ (12 mg, 0.054 mmol), CuBr_2 (455 mg, 2.04 mmol), and benzoquinone (114 mg, 1.06 mmol) in 10 mL of dry PhH afforded 97 mg (47%) of **(Z)-7k**. liquid; ^1H NMR (300 MHz, CDCl_3) δ 7.60-7.39 (m, 5 H), 5.24 (d, $J = 5.4$ Hz, 1 H), 2.00-1.83 (m, 1 H), 0.89 (d, $J = 6.9$ Hz, 3 H), 0.78 (d, $J = 6.9$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 162.4, 135.7, 135.2, 131.1, 128.9, 128.9, 124.5, 85.9, 29.7, 18.1, 15.4; MS (EI) m/z (%) 282 ($\text{M}^+(\text{}^{81}\text{Br})$, 11.43), 280 ($\text{M}^+(\text{}^{79}\text{Br})$, 12.56), 129 (100); IR (neat) 1813, 1672 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{13}\text{}^{79}\text{BrO}_2$ 280.0099. Found 280.0090.

(22) (Z)- α -(1-Bromobenzylidene)- β -cyclohexyl- β -lactone ((Z)-7m):

The reaction of **3m** (213 mg, 1.0 mmol), Pd(OAc)₂ (12 mg, 0.054 mmol), CuBr₂ (453 mg, 2.03 mmol), and benzoquinone (219 mg, 2.03 mmol) in 10 mL of dry PhH afforded 92 mg (29%) of **(Z)-7m**. Solid, m.p. 102-103 °C (*n*-Hexane/Ethyl acetate); ¹H NMR (300 MHz, CDCl₃) δ 7.63-7.35 (m, 5 H), 5.22 (d, *J* = 3.6 Hz, 1 H), 1.77-1.38 (m, 6 H), 1.20-0.88 (m, 5 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 162.4, 135.6, 134.8, 131.1, 128.8, 128.5, 124.2, 85.4, 39.3, 28.2, 25.8, 25.7, 25.6, 25.3; MS (EI) *m/z* (%) 322 (M⁺(⁸¹Br), 6.95), 320 (M⁺(⁷⁹Br), 7.44), 129 (100); IR (KBr) 1795, 1648 cm⁻¹; Anal Calcd for C₁₆H₁₇BrO₂: C, 59.83; H, 5.33. Found: C, 60.03; H, 5.46. HRMS (EI) calcd for C₁₆H₁₇⁷⁹BrO₂ 320.0412. Found 320.0366.

Fig. ORTEP drawing of **(Z)-7m**

(23) (Z)-α-(1-Bromo-3-phenylpropylidene)-β-cyclohexyl-β-lactone ((Z)-7p):

The reaction of **3p** (238 mg, 0.98 mmol), Pd(OAc)₂ (12 mg, 0.054 mmol), CuBr₂ (454 mg, 2.03 mmol), and benzoquinone (110 mg, 1.02 mmol) in 10 mL of dry PhH afforded 197 mg (57%) of **(Z)-7p**. Solid, mp 87-88 °C (*n*-Hexane/Ethyl acetate); ¹H NMR (300 MHz, CDCl₃) δ 7.42-7.10 (m, 5 H), 4.28 (d, *J* = 3.9 Hz, 1 H), 2.96 (t, *J* = 6.9 Hz, 2 H), 2.85-2.65 (m, 2 H), 1.85-1.40 (m, 5 H), 1.30-0.96 (m, 6 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 161.9, 139.1, 135.3, 128.6, 128.4, 127.6, 126.8, 84.4, 40.6, 40.0, 33.4, 28.6, 25.8, 25.7, 25.5; MS (ESI) *m/z* (%) 368 (MNH₄⁺(⁸¹Br), 100), 366 (MNH₄⁺(⁷⁹Br), 99.9), 351 (MH⁺(⁸¹Br), 83.4), 349 (MH⁺(⁷⁹Br), 93.6); IR (KBr) 1795, 1699 cm⁻¹; Anal Calcd for C₁₈H₂₁BrO₂: C, 61.90; H, 6.06. Found: C, 61.90; H, 6.13.

(24) (Z)-3-(1-Bromopentylidene)-1-oxa-spiro[3.5]nonan-2-one ((Z)-7r):

The reaction of **3r** (177 mg, 0.98 mmol), Pd(OAc)₂ (12 mg, 0.054 mmol), CuBr₂ (453 mg, 2.03 mmol), and benzoquinone (330 mg, 3.06 mmol) in 10 mL of dry PhH afforded 117 mg (41%) of **(Z)-7r**. liquid; ¹H NMR (300 MHz, CDCl₃) δ 2.44 (t, *J* = 7.5 Hz, 2 H), 1.99 (d, *J* = 13.2 Hz, 2 H), 1.88-1.53 (m, 9 H), 1.46-1.18 (m, 3 H), 0.96 (t, *J* = 7.4 Hz, 3 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 162.3, 139.2, 129.3, 88.6, 37.2, 33.9, 29.9, 24.4, 21.8, 13.8; MS (EI) *m/z* (%) 288 (M⁺(⁸¹Br), 1.57), 286 (M⁺(⁷⁹Br),

1.67), 207 (100); IR (neat) 1812, 1695 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{19}^{79}\text{BrO}_2$ 286.0568. Found 286.0597.

(25) (Z)-3-(1-Bromopentylidene)-1-oxa-spiro[3.4]octan-2-one ((Z)-7s):

The reaction of **3s** (164 mg, 0.99 mmol), $\text{Pd}(\text{OAc})_2$ (11 mg, 0.049 mmol), CuBr_2 (454 mg, 2.03 mmol), and benzoquinone (326 mg, 3.02 mmol) in 10 mL of dry PhH afforded 80 mg (30%) of **(Z)-7s**. liquid; ^1H NMR (300 MHz, CDCl_3) δ 2.42 (t, $J = 7.5$ Hz, 2 H), 2.30-1.98 (m, 4 H), 1.98-1.74 (m, 4 H), 1.74-1.56 (m, 2 H), 1.48-1.25 (m, 2 H), 0.96 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (75.4 MHz, CDCl_3) δ 162.2, 137.0, 128.7, 95.8, 36.6, 36.3, 29.7, 24.2, 21.9, 13.7; MS (EI) m/z (%) 274 ($\text{M}^+(\text{}^{81}\text{Br})$, 1.08), 272 ($\text{M}^+(\text{}^{79}\text{Br})$, 1.10), 193 (100); IR (neat) 1800, 1702 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{17}^{79}\text{BrO}_2$ 272.0412. Found 272.0382.

wb-7-24-1
STANDARD 1H OBSERVE

Archive directory: /export/home/ASM/vnmrsvs/data
Sample directory: auto_25May2003

Pulse Sequence: s2pu1

Solvent: cdcl3

Ambient temperature

File: wb-7-24-102

Mercury-30085 "QMG300"

Relax. delay 1.000 sec

Pulse 45.0 degrees

Acq. time 1.800 sec

Width 18867.9 Hz

4500 repetitions

OBSERVE C13, 75.4420964 MHz

DECOUPLE H1, 300.0294698 MHz

Power 41 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 131072

Total time 3 hr, 37 min, 19 sec

wb-7-41-2-c
 Archive directory: /export/home/masm/vnmrsys/data
 Sample directory:
 File: CARBON
 Pulse Sequence: s2pul
 Solvent: CDCl₃
 Ambient temperature
 Mercury-3000B "DMC300"
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.554 sec
 Width 25082.7 Hz
 SFO00 repetitions
 OBSERVE C13, 75.4420972 MHz
 DECOUPLE H1, 300.0294698 MHz
 Power 41 dB
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 FT size 131072
 Total time 103 hr, 32 min, 2 sec

WB-7-37-1-c
 Archive directory: /export/home/masm/vnmr/sys/data
 Sample directory:
 File: CARBON
 Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
 Mercury-300BS "OMC900"
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.354 sec
 Width 25082.7 Hz
 610 repetitions
 OBSERVE C13, 75.4420886 MHz
 DECOMPL H1, 300.0254886 MHz
 Power 41 dB
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 FT size 131072
 Total time 103 hr, 32 min, 2 sec

wb-7-28-1-c

Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON

Pulse Sequence: s2put
Solvent: CDCl₃
Ambient temperature
Mercury-300BB "QMC300"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.800 sec
Width 18084.0 Hz
382 repetitions
OBSERVE C13, 75.4420961 MHz
DECOUPLE H1, 300.0294698 MHz
Power 41 dB
Continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 131072
Total time 15 hr, 49 min, 18 sec

wb-8-140-c
 Archive directory: /export/home/masm/vnmr/sys/data
 Sample directory:
 File: CARBON
 Pulse Sequence: s2pul

wb-7-71-c

Archive directory: /export/home/masm/vnmrsys/data
 Sample directory:
 File: CARBON

Pulse Sequence: s2pul

2.350	2.311	2.306	2.298	2.281	1.958	1.972	1.946	1.938	1.923	1.914	1.889	1.872	1.667	1.663	1.661	1.646	1.635	1.630	1.627	1.625	1.617	1.593	1.402	1.379	1.353	1.327	1.051	1.027	1.002	0.979	0.954	0.929	0.900
-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------

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wb-7-74-c
Archive directory: /export/home/masm/vnmrsys/data
Sample directory:
File: CARBON
Pulse Sequence: s2pu1
```

wb-7-77-c

Archive directory: /export/home/zhu-hp/vnmr/sys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "DMCS00"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.553 sec
Width 18797.0 Hz
100 repetitions
OBSERVE C13, 75.4421010 MHz
DECOUPLE H1, 300.0294698 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 57 min, 6 sec

wb-7-73-c13

Archive directory: /export/home/masm/vnmr/sys/data
Sample directory:
File: CARBON

Pulse Sequence: s2pu1

wb-7-88-c
 Archive directory: /export/home/masm/vnmrsys/data
 Sample directory:
 File: CARBON
 Pulse Sequence: s2pu1

Wb-7-151-c

Archive directory: /export/home/masm/vnmrsys/data

Sample directory:

File: CARBON

Pulse Sequence: s2pu1

wb-7-150-c
 Archive directory: /export/home/masm/vnmrsys/data
 Sample directory:
 File: CARBON
 Pulse Sequence: s2pu1

wb-7-141-C
 Archive directory: /export/home/zhang-zg/vnmrsys/data
 Sample directory:
 File: CARBON
 Pulse Sequence: s2pu1

Wb-7-157-c
 Archive directory: /export/home/masa/vnmrsvs/data
 Sample directory:
 File: CARBON
 Pulse Sequence: s2pu1