A Mild and Efficient Synthesis of (*Z*)-α-Chloroalkylidene-β-Lactones via the $PdCl_2$-Catalyzed Cyclocarbonylation of 2-Alkynols

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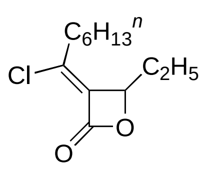
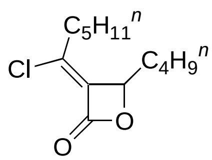
Supporting information

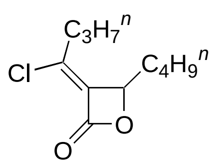
General Procedure for $PdCl_2$-Catalyzed Cyclocarbonylation of Secondary Propargylic Alcohols with 5 equiv of $CuCl_2$: In a flame-dried argon-flushed flask, a solution of **1a** (157 mg, 0.93 mmol) and anhydrous $CuCl_2$ (635 mg, 4.7 mmol) in 9.3 mL of dry THF was stirred for 5 min at rt followed by the addition of $PdCl_2$ (16.5 mg, 0.093 mmol). Then the flask was transferred to a Parr pressure reactor. The Parr reactor was charged with 20 atm of CO gas. After the mixture was stirred for 4 h at 30°C, the gas was ventilated, and the residue was diluted with Et_2O. Filtration through a short column of silica gel, evaporation and flash chromatography on silica gel (eluent : petroleum ether: ethyl acetate = 40 : 1) afforded 184 mg (86% yield) of (***Z***)-**2a**.



(1) (*Z*)-α-(1-Chloroheptylidene)-β-ethyl-β-lactone ((*Z*)-2a): The reaction of **1a** (157 mg, 0.93 mmol) afforded 184 mg (86% yield) of **(*Z*)-2a**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.96 (dd, *J* = 3.0 and 7.5 Hz, 1H), 2.32 (t, *J* = 7.5 Hz, 2 H), 2.10-1.90 (m, 1 H), 1.90-1.50 (m, 3 H), 1.25-1.17 (m, 6 H), 1.05 (t, *J* = 7.4 Hz, 3 H), 0.88 (t, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.59, 139.07, 132.93, 80.21, 36.46, 31.62, 28.66, 26.92, 26.41, 22.66, 14.22, 8.80; MS (ESI) *m/z* (%) 255 (MNa^+(^{37}Cl), 10.02), 253 (MNa^+(^{35}Cl), 41.79), 233 (MH^+(^{37}Cl), 26.73), 231 (MH^+(^{35}Cl), 100); IR (neat) 2931, 2859, 1813, 1703, 1108, 844 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{19}{}^{35}ClO_2$ 230.1074. Found 230.1044.

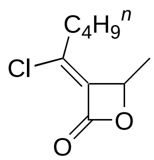


(2) (*Z*)-α-(1-Chlorohexylidene)-β-(*n*-butyl)-β-lactone ((*Z*)-2b): The reaction of **1b** (165 mg, 0.91 mmol) afforded 168 mg (76% yield) of **(*Z*)-2b**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.98 (dd, *J* = 3.3 and 8.1 Hz, 1 H), 2.31 (t, *J* = 7.2 Hz, 2 H), 2.02-1.10 (m, 12 H), 0.98-0.70 (m, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.32, 138.60, 133.10, 79.05, 36.10, 32.69, 30.78, 26.45, 26.33, 22.25, 22.23, 13.76; MS (EI) *m/z* (%) 189 (M^+(^{37}Cl)-C_4H_9, 18.24), 187 (M^+(^{35}Cl)-C_4H_9, 54.15), 41 (100); IR (neat) 2958, 2933, 2862, 1814, 1702, 1114 cm^{-1}; HRMS (EI) calcd for $C_{13}H_{21}{}^{35}ClO_2$ 244.1230. Found 244.1189.

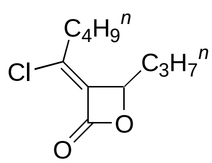


(3) (*Z*)-α-(1-Chlorobutylidene)-β-(*n*-butyl)-β-lactone ((*Z*)-2c): The reaction of **1c** (151 mg, 0.98 mmol) afforded 157 mg (74% yield) of **(*Z*)-2c**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.96 (dd, *J* = 3.0 and 8.4 Hz, 1 H), 2.28 (t, *J* = 7.5 Hz, 2 H), 2.00-1.84 (m, 1 H), 1.84-1.55 (m, 3 H), 1.50-1.20 (m, 4 H), 0.98-0.78 (m, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.55, 138.57, 133.60, 79.39, 38.08, 32.97, 26.76, 22.50, 20.25, 14.02, 13.31; MS (EI) *m/z* (%) 161

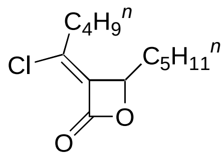
(M^+(^{37}Cl)-C_4H_9, 25.76), 159 (M^+(^{35}Cl)-C_4H_9, 78.08), 41 (100); IR (neat) 2962, 2935, 2874, 1814, 1703, 1112, 832 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{17}{}^{35}ClO_2$ 216.0917. Found 216.0875.



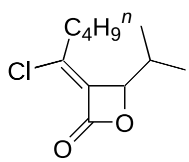
(4) (*Z*)-α-(1-Chloropentylidene)-β-methyl-β-lactone ((*Z*)-2d): The reaction of **1d** (123 mg, 0.98 mmol) afforded 117 mg (64% yield) of **(*Z*)-2d**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.08 (q, *J* = 4.7 Hz, 1 H), 2.32 (t, *J* = 7.4 Hz, 2 H), 1.73-1.50 (m, 5 H), 1.50-1.20 (m, 2 H), 0.92 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.43, 139.13, 134.49, 75.60, 35.88, 29.00, 22.11, 19.30, 13.95; MS (EI) *m/z* (%) 190 (M^+(^{37}Cl), 2.14), 188 (M^+(^{35}Cl), 7.14), 102 (100); IR (neat) 2960, 2933, 2873, 1811, 1703, 1111, 819 cm^{-1}; HRMS (EI) calcd for $C_9H_{13}{}^{35}ClO_2$ 188.0604. Found 188.0608.



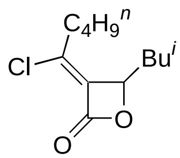
(5) (*Z*)-α-(1-Chloropentylidene)-β-(*n*-propyl)-β-lactone ((*Z*)-2e): The reaction of **1e** (129 mg, 0.84 mmol) afforded 131 mg (72% yield) of **(*Z*)-2e**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.98 (dd, *J* = 3.2 and 8.0 Hz, 1 H), 2.31 (t, *J* = 7.5 Hz, 2 H), 1.97-1.82 (m, 1 H), 1.82-1.22 (m, 7 H), 0.95 (t, *J* = 7.5 Hz, 3 H), 0.90 (t, *J* = 7.5 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.59, 138.86, 133.36, 79.18, 36.14, 35.29, 29.01, 22.09, 18.13, 13.94, 13.91; MS (EI) *m/z* (%) 175 (M^+(^{37}Cl)-C_3H_7, 30.69), 173 (M^+(^{35}Cl)-C_3H_7, 90.47), 91 (100); IR (neat) 2961, 2935, 2874, 1813, 1703, 1111, 816 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{17}{}^{35}ClO_2$ 216.0917. Found 216.0916.



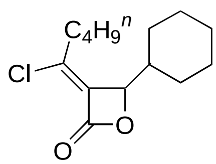
(6) (*Z*)-α-(1-Chloropentylidene)-β-(*n*-pentyl)-β-lactone ((*Z*)-2f): The reaction of **1f** (170 mg, 0.93 mmol) afforded 152 mg (67% yield) of **(*Z*)-2f**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.99 (dd, *J* = 3.3 and 8.4 Hz, 1 H), 2.33 (t, *J* = 7.5 Hz, 2 H), 2.00-1.30 (m, 12 H), 1.00-0.80 (m, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.36, 138.61, 133.12, 79.09, 35.93, 33.03, 31.34, 28.78, 24.12, 22.38, 21.89, 13.88, 13.70; GCMS (EI) *m/z* (%) 247 (M^++1(^{37}Cl), 27), 245 (M^++1(^{35}Cl), 83), 91 (100); IR (neat) 2958, 2933, 2863, 1815, 1703, 1113 cm^{-1}; Anal. Calcd for $C_{13}H_{21}ClO_2$: C, 63.79; H, 8.65. Found: C, 63.82; H, 8.63.



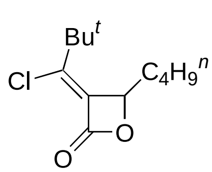
(7) (*Z*)-α-(1-Chloropentylidene)-β-(*i*-propyl)-β-lactone ((*Z*)-2g): The reaction of **1g** (168 mg, 1.0 mmol) afforded 154 mg (71% yield) of **(*Z*)-2g**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.87 (d, *J* = 3.3 Hz, 1 H), 2.32 (t, *J* = 7.7 Hz, 2 H), 2.22-2.02 (m, 1 H), 1.76-1.45 (m, 2 H), 1.45-1.25 (m, 2 H), 1.06 (d, *J* = 7.2 Hz, 3 H), 0.96 (d, *J* = 6.6 Hz, 3 H), 0.90 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.69, 139.12, 132.10, 83.72, 36.45, 31.08, 29.00, 22.18, 18.61, 15.73, 13.92; MS (EI) *m/z* (%) 175 (M^+(^{37}Cl)-C_3H_7, 32.66), 173 (M^+(^{35}Cl)-C_3H_7, 100); IR (neat) 2964, 2934, 2875, 1813, 1702, 1109, 846 cm^{-1}; HRMS (EI) calcd for $C_{11}H_{17}{}^{35}ClO_2$ 216.0917. Found 216.0909.



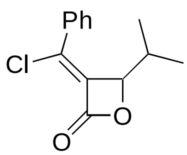
(8) (*Z*)-α-(1-Chloropentylidene)-β-(*i*-butyl)-β-lactone ((*Z*)-2h): The reaction of **1h** (141 mg, 0.84 mmol) afforded 173 mg (90% yield) of **(*Z*)-2h**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.00 (dd, *J* = 5.9 and 7.1 Hz, 1 H), 2.29 (t, *J* = 7.5 Hz, 2 H), 1.93-1.72 (m, 1 H), 1.72-1.42 (m, 4 H), 1.42-1.20 (m, 2 H), 1.02-0.80 (m, 9 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.57, 138.71, 133.89, 78.13, 42.23, 36.07, 29.01, 25.29, 23.28, 22.06, 13.92; MS (EI) *m/z* (%) 175 (M^+(^{37}Cl)-C_4H_9, 16.20), 173 (M^+(^{35}Cl)-C_4H_9, 48.07), 91 (100); IR (neat) 2959, 2933, 2873, 1814, 1703, 1110, 812 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{19}{}^{35}ClO_2$ 230.1074. Found 230.1122.



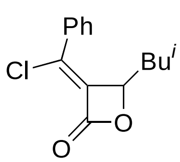
(9) (*Z*)-α-(1-Chloropentylidene)-β-cyclohexyl-β-lactone ((*Z*)-2i): The reaction of **1i** (161 mg, 0.83 mmol) afforded 173 mg (82% yield) of **(*Z*)-2i**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.84 (d, *J* = 3.0 Hz, 1 H), 2.34 (t, *J* =7.4 Hz, 2 H), 1.90-1.47 (m, 8 H), 1.47-1.05 (m, 7 H), 0.92 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.74, 138.88, 131.92, 83.29, 40.73, 36.49, 29.01, 26.25, 26.17, 26.10, 25.81, 22.15, 13.98; MS (EI) *m/z* (%) 175 (M^+(^{37}Cl)-C_6H_{11}, 33.12), 173 (M^+(^{35}Cl)-C_6H_{11}, 76.59), 55 (100); IR (neat) 2930, 2856, 1813, 1701, 1110, 829 cm^{-1}; HRMS (EI) calcd for $C_{14}H_{21}{}^{35}ClO_2$ 256.1230. Found 256.1219.



(10) (*Z*)-α-(1-Chloro-2,2-dimethylpropylidene)-β-(*n*-butyl)-β-lactone ((*Z*)-2j): The reaction of **1j** (153 mg, 0.91 mmol) afforded 187 mg (89% yield) of **(*Z*)-2j**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.10 (dd, *J* = 2.4 and 8.4 Hz, 1 H), 2.10-1.95 (m, 1 H), 1.90-1.70 (m, 1 H), 1.50-1.28 (m, 4 H), 1.21 (s, 9 H), 0.87 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 162.59, 148.72, 131.33, 80.79, 40.02, 34.06, 28.71, 26.52, 22.45, 14.06; MS (EI) *m/z* (%) 175 (M^+(^{37}Cl)-C_4H_9, 4.19), 173 (M^+(^{35}Cl)-C_4H_9, 12.33), 109 (100); IR (neat) 2961, 2873, 1816, 1672, 1144, 838 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{19}{}^{35}ClO_2$ 230.1074. Found 230.1066.

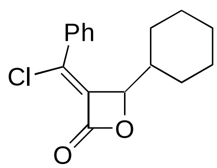


(11) (*Z*)-α-(1-Chlorobenzylidene)-β-(*i*-propyl)-β-lactone ((*Z*)-2k): The reaction of **1k** (173 mg, 0.99 mmol) afforded 200 mg (91% yield) of **(*Z*)-2k**: solid, mp 82-84 °C (ethyl acetate/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.40 (m, 5 H), 5.27 (d, *J* = 3.3 Hz, 1 H), 2.08-1.90 (m, 1 H), 0.93 (d, *J* = 7.2 Hz, 3 H), 0.78 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.75, 134.26, 133.90, 132.07, 131.38, 128.87, 128.04, 84.44, 29.45, 18.19, 15.21; MS (EI) *m/z* (%) 238 (M^+(^{37}Cl), 3.51), 236 (M^+(^{35}Cl), 11.24), 193 (100); IR (KBr) 2968, 1800, 1670, 1072, 845 cm^{-1}; Anal Calcd for $C_{13}H_{13}ClO_2$: C, 65.97; H, 5.54. Found: C, 65.94; H 5.33.

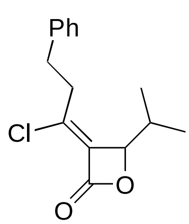


(12) (*Z*)-α-(1-Chlorobenzylidene)-β-(*i*-butyl)-β-lactone ((*Z*)-2l): The reaction of **1l** (191 mg, 1.01 mmol) afforded 205 mg (81% yield) of **(*Z*)-2l**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$)

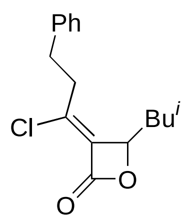
δ 7.60-7.40 (m, 5 H), 5.40 (dd, J = 3.9 and 8.4 Hz, 1 H), 1.90-1.70 (m, 1 H), 1.70-1.40 (m, 2 H), 0.93 (d, J = 6.3 Hz, 3 H), 0.88 (d, J = 6.9 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.76, 133.65, 133.30, 131.44, 128.87, 128.07, 128.05, 79.20, 39.83, 24.78, 22.92, 21.66; MS (EI) *m/z* (%) 195 (M^+(^{37}Cl)-C_4H_9, 17.44), 193 (M^+(^{35}Cl)-C_4H_9, 53.87), 129 (100); IR (neat) 2961, 2871, 1798, 1672, 1079, 766 cm^{-1}; Anal Calcd for $C_{14}H_{15}ClO_2$: C, 67.07; H, 6.03. Found: C, 66.93; H, 6.17.



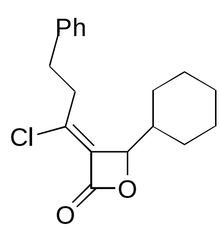
(13) (*Z*)-α-(1-Chlorobenzylidene)-β-cyclohexyl-β-lactone ((*Z*)-2m): The reaction of **1m** (187 mg, 0.87 mmol) afforded 188 mg (78% yield) of **(*Z*)-2m**: solid, mp 102-104 ^{o}C (ethyl acetate/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.38 (m, 5 H), 5.23 (d, J = 3.6 Hz, 1 H), 1.80-1.40 (m, 6 H), 1.30-0.90 (m, 5 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.81, 134.02, 133.87, 131.68, 131.33, 128.81, 128.03, 83.99, 39.12, 28.38, 25.70, 25.63, 25.60, 25.28; MS (EI) *m/z* (%) 278 (M^+(^{37}Cl), 4.39), 276 (M^+(^{35}Cl), 13.05), 193 (100); IR (KBr) 2926, 2854, 1802, 1676, 1073, 827 cm^{-1}; Anal Calcd for $C_{16}H_{17}ClO_2$: C, 69.44; H, 6.19. Found: C, 69.34; H, 6.25.



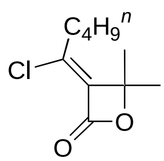
(14) (*Z*)-α-(1-Chloro-3-phenylpropylidene)-β-(*i*-propyl)-β-lactone ((*Z*)-2n): The reaction of **1n** (127 mg, 0.63 mmol) afforded 104 mg (63% yield) of **(*Z*)-2n**: solid, mp 48-50 ^{o}C (ethyl acetate/*n*-hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.12 (m, 5 H), 4.35 (d, *J* = 3.3 Hz, 1 H), 3.06-2.88 (m, 2 H), 2.72-2.50 (m, 2 H), 2.00-1.83 (m, 1 H), 0.97 (d, *J* = 7.2 Hz, 3 H), 0.78 (d, *J* = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.51, 139.37, 137.12, 133.28, 129.04, 128.72, 127.15, 83.69, 39.15, 32.90, 30.94, 18.64, 15.55; MS (ESI) *m/z* (%) 289 (MNa^+(^{37}Cl), 12.46), 287 (MNa^+(^{35}Cl), 42.08), 267 (MH^+(^{37}Cl), 29.09), 265 (MH^+(^{35}Cl), 100); IR (neat) 2967, 2933, 1813, 1701, 1105, 844 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{17}{}^{35}ClO_2$ 264.0917. Found 264.0954.



(15) (*Z*)-α-(1-Chloro-3-phenylpropylidene)-β-(*i*-butyl)-β-lactone ((*Z*)-2o): The reaction of **1o** (212 mg, 0.98 mmol) afforded 143 mg (52% yield) of **(*Z*)-2o**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.10 (m, 5 H), 4.43 (dd, *J* = 3.6 and 9.6 Hz, 1 H), 3.20-2.85 (m, 2 H), 2.70-2.50 (m, 2 H), 1.80-1.60 (m, 1 H), 1.35-1.15 (m, 2 H), 0.84 (d, *J* = 6.9 Hz, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.15, 139.08, 136.23, 134.78, 128.65, 128.51, 126.77, 77.78, 41.09, 38.71, 32.45, 24.68, 22.93, 21.46; MS (ESI) *m/z* (%) 303 (MNa^+(^{37}Cl), 11.40), 301 (MNa^+(^{35}Cl), 32.10), 298 (MNH_4^+(^{37}Cl), 37.72), 296 (MNH_4^+(^{35}Cl), 100), 281 (MH^+(^{37}Cl), 11.98), 279 (MH^+(^{35}Cl), 27.07); IR (neat) 3028, 2954, 2870, 1795, 1706, 1107, 798 cm^{-1}; Anal Calcd for $C_{16}H_{19}ClO_2$: C, 68.94; H, 6.87. Found: C, 68.94; H, 6.59.

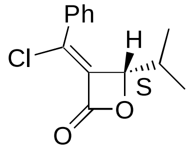


(16) (*Z*)-α-(1-Chloro-3-phenylpropylidene)-β-cyclohexyl-β-lactone ((*Z*)-2p): The reaction of **1p** (236 mg, 0.98 mmol) afforded 181 mg (61% yield) of **(*Z*)-2p**: solid, mp 92-94 ^oC (ethyl acetate/*n*-hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.35-7.05 (m, 5 H), 4.30 (d, J = 3.6 Hz, 1 H), 3.10-2.80 (m, 2 H), 2.75-2.50 (m, 2 H), 1.85-1.30 (m, 6 H), 1.30-0.85 (m, 5 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.16, 139.04, 136.59, 132.61, 128.60, 128.32, 126.71, 82.90, 39.96, 38.77, 32.50, 28.51, 25.72, 25.64, 25.47; MS (EI) *m/z* (%) 237 (M^++1(^{37}Cl)-C_5H_{10}, 24.46), 235 (M^++1(^{35}Cl)-C_5H_{10}, 42.46), 193 (100); IR (KBr) 2939, 2915, 2854, 1797, 1704, 1107, 820 cm^{-1}; Anal Calcd for $C_{18}H_{21}ClO_2$: C, 70.93; H, 6.94. Found: C, 70.80; H, 6.89.

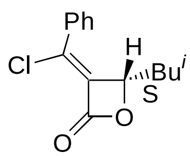


(17) (*Z*)-α-(1-Chloropentylidene)-β-dimethyl-β-lactone ((*Z*)-2q): The reaction of **1q** (275 mg, 1.96 mmol) afforded 198 mg (50% yield) of **(*Z*)-2q**: liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 2.31 (t, J = 7.5 Hz, 2 H), 1.72-1.55 (m, 2 H), 1.66 (s, 6 H), 1.42-1.25 (m, 2 H), 0.94 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 161.11, 137.90, 137.03, 84.20, 34.91, 28.83, 25.09, 21.98, 13.76; MS (EI) *m/z* (%) 189 (M^+(^{37}Cl)-CH_3, 7.76), 187 (M^+(^{35}Cl)-CH_3, 23.13), 43 (100); IR (neat) 2960, 2932, 2874, 1793, 1703, 1201, 1075, 788 cm^{-1}; Anal Calcd for $C_{10}H_{15}ClO_2$: C, 59.26; H, 7.46. Found: C, 59.21; H, 7.30.

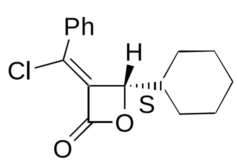
Optically active secondary propargylic alcohols **(*S*)-1** were prepared according to Carreira's method.[1] The enantioselective addition reaction was conducted using 1.1 equiv of $Zn(OTf)_2$, 1.2 equiv of (-)-N-methylephedrine, and 1.2 equiv of Et_3N in toluene (1.0 M) at 23^{o}C. The absolute stereochemistry was established by comparison with the literature data.[1]



(18) (*S*)-(*Z*)-α-(1-Chlorobenzylidene)-β-(*i*-propyl)-β-lactone ((*S*)-(*Z*)-2k): The reaction of (*S*)-**1k** (146 mg, 0.84 mmol, >91% ee) afforded 166 mg (89% yield) of **(*S*)-(Z)-2k** with 92% ee as determined by HPLC analysis (Chiralcel OD-H, 10% *i*-PrOH in hexane, 254 nm), t_r 14.8 (major), 16.0 (minor); $[\alpha]^{20}_{D}$-78.5^o (c = 1.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.40 (m, 5 H), 5.27 (d, *J* = 3.6 Hz, 1 H), 2.10-1.90 (m, 1 H), 0.94 (d, *J* = 7.2 Hz, 3 H), 0.79 (d, *J* = 6.9 Hz, 3 H).

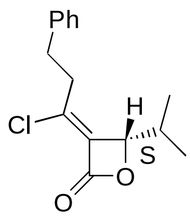


(19) (*S*)-(*Z*)-α-(1-Chlorobenzylidene)-β-(*i*-butyl)-β-lactone ((*S*)-(*Z*)-2l): The reaction of **(S)-1l** (168 mg, 0.89 mmol, >83% ee) afforded 140 mg (63% yield) of **(*S*)-(*Z*)-2l** with 85% ee as determined by HPLC analysis (Chiralcel AS, 2% *i*-PrOH in hexane, 230 nm), t_r 14.5 (major), 19.5 (minor); $[\alpha]^{20}_{D}$ –111.0^o (c = 1.05, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.40 (m, 5 H), 5.40 (dd, *J* = 3.9 and 8.4 Hz, 1 H), 1.90-1.70 (m, 1 H), 1.70-1.40 (m, 2 H), 0.93 (d, *J* =6.3 Hz, 3 H), 0.88 (d, *J* = 6.9 Hz, 3 H).

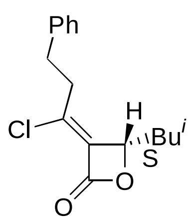


(20) (*S*)-(*Z*)-α-(1-Chlorobenzylidene)-β-cyclohexyl-β-lactone ((*S*)-(*Z*)-2m): The reaction of **(*S*)-1m** (185 mg, 0.86 mmol, 96% ee) afforded 199 mg (83% yield) of **(*S*)-(*Z*)-2m** with 96% ee as determined by HPLC analysis (Chiralcel OD-H, 10% *i*-PrOH in hexane, 254 nm),

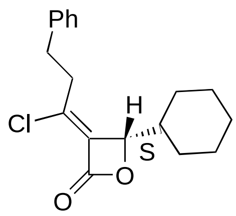
t_r 14.5 (major), 16.4 (minor); $[\alpha]^{20}_D$ –130.4° (c = 0.95, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65-7.40 (m, 5 H), 5.24 (d, *J* = 3.9 Hz, 1 H), 1.80-1.40 (m, 6 H), 1.30-0.90 (m, 5 H).



(21) (*S*)-(*Z*)-α-(1-Chloro-3-phenylpropylidene)-β-(*i*-propyl)-β-lactone ((*S*)-(*Z*)-2n): The reaction of **(*S*)-1n** (170 mg, 0.84 mmol, 97% ee) afforded 152 mg (68% yield) of **(*S*)-(*Z*)-2n** with 97% ee as determined by HPLC analysis (Chiralcel AS, 2% *i*-PrOH in hexane, 230 nm), t_r 16.1 (major), 18.8 (minor); $[\alpha]^{20}_D$ –37.2° (c = 1.35, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.10 (m, 5 H), 4.35 (d, *J* = 3.3 Hz, 1 H), 3.10-2.90 (m, 2 H), 2.75-2.55 (m, 2 H), 2.00-1.85 (m, 1 H), 0.98 (d, *J* = 6.6 Hz, 3 H), 0.79 (d, *J* = 7.2 Hz, 3 H).



(22) (*S*)-(*Z*)-α-(1-Chloro-3-phenylpropylidene)-β-(*i*-butyl)-β-lactone ((*S*)-(*Z*)-2o): The reaction of **(*S*)-1o** (167 mg, 0.77 mmol, 95% ee) afforded 138 mg (64% yield) of **(*S*)-(*Z*)-2o** with 92% ee as determined by HPLC analysis (Chiralcel AS, 1% *i*-PrOH in hexane, 230 nm), t_r 18.0 (major), 20.6 (minor); $[\alpha]^{20}_D$ –63.5° (c = 1.20, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.10 (m, 5 H), 4.42 (dd, *J* = 3.3 and 9.9 Hz, 1 H), 3.15-2.80 (m, 2 H), 2.70-2.50 (m, 2 H), 1.80-1.60 (m, 1 H), 1.40-1.12 (m, 2 H), 0.84 (d, *J* = 6.0 Hz, 6 H).



(23) (*S*)-(*Z*)-α-(1-Chloro-3-phenylpropylidene)-β-cyclohexyl-β-lactone ((*S*)-(*Z*)-2p): The reaction of **(*S*)-1p** (222 mg, 0.92 mmol, 98% ee) afforded 176 mg (63% yield) of **(*S*)-(*Z*)-2p** with 98% ee as determined by HPLC analysis (Chiralcel AS, 5% *i*-PrOH in hexane, 230 nm), t_r 12.1 (major), 14.2 (minor); $[\alpha]^{20}_{D}$-66.8^o (c = 1.15, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.10 (m, 5 H), 4.32 (d, *J* = 3.3 Hz, 1 H), 3.10-2.90 (m, 2 H), 2.75-2.50 (m, 2 H), 1.85-1.35 (m, 6 H), 1.35-0.90 (m, 5 H).

References:

(1) Frantz, D. E.; Fässler, R.; Carreira, E. M. *J. Am. Chem. Soc.* **2000**, *122*, 1806.