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New Strategies in Carbonylation Chemistry: The Synthesis of δ -Lactones from *Saturated* Alcohols and CO

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Supporting Information

The structure assignments was obtained on the basis of a combination of DEPT, and ^{13}C - ^1H COSY experiments. The separation of *cis/trans* isomers was performed by preparative HPLC (GPC columns (JAIGEL 1H and 2H) using CHCl_3 as an eluent). Alcohols, **1g**, **1o**, and **1p**, were prepared by the hydrogenation of the corresponding aromatic alcohols, 2-phenyl-1-propanol, 1-phenyl-2-propanol, and *trans*-2-phenyl-1-cyclohexanol with 5% Rh/C.

General Procedure for Hydrogenation of Aromatic Alcohol. A mixture of *trans*-2-phenyl-1-cyclohexanol (881 mg, 5 mmol) and 5% Rh/C (515 mg, 0.25 mmol) and anhydrous THF (10 mL, freshly distilled from sodium benzophenone ketyl) were stirred at room temperature with bubbling of hydrogen for 15 h. The reaction mixture was filtered and concentrated. The residue was chromatographed to give *trans*-2-cyclohexyl-1-cyclohexanol **1p** (902 mg, 99% yield) as a white crystal: ^1H NMR (CDCl_3 , 270 MHz) δ 0.92-1.43 (complex m, 10H), 1.42 (br s, 2H), 1.60-1.80 (complex m, 8H), 1.98 (m, 1H), 3.43 (dt-like, 1H, $J \sim 10.0$, 4.3 Hz); ^{13}C NMR (CDCl_3 , 68 MHz) δ 24.97, 25.32, 25.95, 26.91 (two superimposed lines), 27.17, 27.31, 31.53, 36.33, 37.10, 50.69, 71.15.

Procedure for Control Experiments (Tables 1 and 4). A mixture of 1-octanol (**1a**) (2,6-dimethyl-4-heptanol (**1q**) for Table 4), LTA and benzene were placed in a stainless steel autoclave lined with a round bottomed glass tube. The autoclave was sealed, purged twice

with 10 atm of carbon monoxide, and then pressurized with CO, and was heated, with stirring. After one day (three days for **1q**), excess CO was purged at room temperature, then the reaction mixture was poured into 0.4 N aqueous hydrogen chloride. The aqueous layer was extracted with ether (3 x 20 mL) and the combined ether extracts were dried (MgSO₄), then filtered. The filtrate was analyzed by GC. Yields of **2a** and **3a** (**2q** and **1q** for Table 4) were quantified using an internal standard (cyclohexyl acetate) and the separated samples to calibrate the response of the detector.

Tetrahydro-3-butyl-2H-pyran-2-one (2a): According to the general procedure, the title compound **2a** was obtained in 51% yield: a slightly yellow liquid; ¹H NMR (CDCl₃, 270 MHz) δ 0.91 (t, 3H, *J* = 6.8 Hz), 1.25-1.61 (m, 6H), 1.84-1.90 (m, 3H), 2.00-2.16 (m, 1H), 2.34-2.51 (m, 1H, α-CH), 4.25-4.32 (td-like, 2H, *J* ~ 5.9, 2.0 Hz); ¹³C NMR (CDCl₃, 68 MHz) δ 13.86 (q), 21.95 (t), 22.56 (t), 24.54 (t), 28.95 (t), 30.89 (t), 39.50 (d), 68.26 (t), 174.68 (s); IR(neat) 1732 cm⁻¹; EIMS (relative intensity) *m/z* 157 (*M*⁺+1, 2), 127 (2), 113 (26), 100 (100), 85 (4), 73 (5), 55 (20), 41 (14); HREIMS calcd for C₉H₁₆O₂ *m/z* 156.1150, found 156.1155. This compound is already known and the properties (¹H NMR and IR) were consistent with those previously reported.¹ The less polar fraction furnished a mixture of octyl acetate and 2-butyltetrahydrofuran (**3a**). Further purification of the mixture by preparative HPLC gave pure **3a**: a colorless liquid; ¹H NMR (CDCl₃, 270 MHz) δ 0.90 (t, 3H, *J* = 6.9 Hz), 1.20-1.60 (complex m, 7H), 1.75-2.00 (complex m, 3H), 3.66-3.90 (complex m, 3H); ¹³C NMR (CDCl₃, 68 MHz) δ 13.86, 22.64, 25.55, 28.43, 31.23, 35.29, 67.37, 79.25.; HREIMS calcd for C₈H₁₆O *m/z* 128.1201, found 128.1195. This compound is already known.²

Tetrahydro-3-propyl-2H-pyran-2-one (2b): a slightly yellow liquid; ¹H NMR (CDCl₃, 270 MHz) δ 0.91 (t, 3H, *J* = 7.1 Hz), 1.33-1.61 (m, 4H), 1.87-1.95 (m, 3H), 2.04-2.16 (m, 1H), 2.44-2.50 (m, 1H), 4.30 (td, 2H, *J* = 2.0, 5.9 Hz); ¹³C NMR (CDCl₃, 68 MHz) δ 13.91 (q), 19.96 (t), 21.95 (t), 24.53 (t), 33.32 (t), 39.27 (d), 68.28 (t), 174.68 (s); IR(neat) 1734 cm⁻¹; EIMS (relative intensity) *m/z* 143 (*M*⁺+1, 1), 113 (20), 100 (100), 95 (5), 84 (5), 73 (4), 69 (5),

(1) Paterson, I. *Tetrahedron* **1988**, *44*, 4207.

(2) Kharrat, A.; Gardrat, C.; Maillard, B. *Can. J. Chem.* **1984**, *62*, 2385.

55 (23), 41 (15); HREIMS calcd for $C_8H_{14}O_2$ m/z 142.0993, found 142.1018. This compound is already known.³

cis- and trans-Octahydro-1H-2-benzopyran-1-one (2f). Obtained as a *cis/trans*-isomer mixture in a 44/56 ratio: a colorless liquid; 1H NMR ($CDCl_3$, 270 MHz) δ 1.05-2.30 (m, *cis* 11H and *trans* 12H), 2.72 (t-like, *cis* 1H, $J = 4.9$ Hz, α -CH), 4.22-4.42 (m, *cis* 2H and *trans* 2H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 22.39 (t, *cis*), 24.50 (t, *cis*), 25.26 (t, *trans*), 25.66 (t, *cis* or *trans*), 25.72 (t, *cis* or *trans*), 26.68 (t, *trans*), 28.15 (t, *cis*), 29.59 (t, *trans*), 31.15 (t, *cis*), 31.82 (d, *cis*, β -CH), 33.45 (t, *trans*), 36.25 (d, *trans*, β -CH), 40.10 (d, *cis*, α -CH), 45.14 (d, *trans*, α -CH), 66.59 (t, *cis*), 67.71 (t, *trans*), 173.71 (s, *trans*), 174.27 (s, *cis*); IR(neat) 1737 cm^{-1} ; EIMS (relative intensity) m/z 154 (M^+ , 77), 126 (33), 99 (91), 81 (84), 67 (100), 54 (30), 41 (29); HREIMS calcd for $C_9H_{14}O_2$ m/z 154.0994, found 154.0990. These compounds are already known and the properties (1H and ^{13}C NMR) were consistent with those previously reported.⁴

Tetrahydro-6-methyl-3-(1-methylethyl)-2H-pyran-2-one (2m). Obtained as a *cis/trans*-isomer mixture in a 52/48 ratio. These isomers were separated by preparative HPLC. **cis-2m:** a slightly yellow liquid; 1H NMR ($CDCl_3$, 270 MHz) δ 0.92 (d, 3H, $J = 6.3$ Hz, CH_3 of 2-propyl), 0.97 (d, 3H, $J = 6.8$ Hz, CH_3 of 2-propyl), 1.35 (d, 3H, $J = 6.4$ Hz, CH_3CHO), 1.43-1.70 (m, 2H), 1.80-2.00 (m, 2H), 2.38 (m, 1H, α -CH), 2.50 (m, 1H, CH of 2-propyl), 4.36 (m, 1H, δ -CH); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 17.94 (q, CH_3 of 2-propyl), 19.78 (q, CH_3 of 2-propyl), 20.11 (t), 22.07 (q, CH_3CHO), 29.02 (d, CH of 2-propyl), 30.56 (t), 46.35 (d, α -CH), 77.29 (d, δ -CH), 173.25 (s); IR(neat) 1728 cm^{-1} ; EIMS (relative intensity) m/z 156 (M^+ , 4), 141 (17), 114 (100), 101 (21), 84 (27), 73 (55), 55 (39); HREIMS calcd for $C_9H_{16}O_2$ m/z 156.1150, found 156.1142. This compound is already known and the properties (1H NMR) were consistent with those previously reported.⁵ **trans-2m:** a slightly yellow liquid; 1H NMR ($CDCl_3$, 270 MHz) δ 0.94 (d, 3H, $J = 6.8$ Hz, CH_3 of 2-propyl), 1.01 (d, 3H, $J = 6.8$ Hz, CH_3 of

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(4) Fujiwara, Y.; Okamoto, M. *Chem. Pharm. Bull.* **1989**, *37*, 1458.

(5) Bach, M. D.; Bosch, E. *J. Org. Chem.* **1992**, *57*, 4696.

2-propyl), 1.34 (d, 3H, $J = 5.9$ Hz, CH_3CHO), 1.50-1.75 (m, 2H), 1.94 (m, 2H), 2.29 (m, 2H, CH of 2-propyl and α -CH), 4.45 (m, 1H, δ -CH); ^{13}C NMR (CDCl_3 , 68 MHz) δ 18.25 (q, CH_3 of 2-propyl), 18.51 (t), 20.57 (q, CH_3 of 2-propyl), 21.03 (q, CH_3CHO), 27.95 (d, CH of 2-propyl), 28.70 (t), 43.93 (d, α -CH), 74.04 (d, δ -CH), 174.61 (s); IR(neat) 1724 cm^{-1} ; EIMS (relative intensity) m/z 156 (M^+ , 7), 141 (22), 114 (100), 101 (23), 84 (27), 73 (55), 55 (46); HREIMS calcd for $\text{C}_9\text{H}_{16}\text{O}_2$ m/z 156.1150, found 156.1148. This compound is already known and the properties (^1H NMR and MS) were consistent with those previously reported.⁵

Tetrahydro-3,6-dimethyl-2H-pyran-2-one (2n). Obtained as a *cis/trans*-isomer mixture in a 55/45 ratio. These isomers were separated by preparative HPLC. ***cis*-(2*S*, 5*R*)-2n:** a crystal; mp. 51-51.5 °C; ^1H NMR (CDCl_3 , 270 MHz) δ 1.22 (d, 3H, $J = 6.9$ Hz, 2-Me), 1.36 (d, 3H, $J = 6.4$ Hz, 5-Me), 1.40-1.70 (m, 2H), 1.80-2.20 (m, 2H), 2.55-2.64 (m, 1H, α -CH), 4.43-4.51 (m, 1H, δ -CH); ^{13}C NMR (CDCl_3 , 68 MHz) δ 16.11 (q, 2-Me), 21.00 (q, 5-Me), 25.53 (t), 28.32 (t), 32.88 (d, α -CH), 74.34 (d, δ -CH), 176.16 (s); IR(CDCl_3) 1732 cm^{-1} ; EIMS (relative intensity) m/z 128 (M^+ , 5), 113 (4), 84 (43), 69 (20), 56 (100), 42 (50); HREIMS calcd for $\text{C}_7\text{H}_{12}\text{O}_2$ m/z 128.0837, found 128.0824. This compound is already known and the properties (mp., ^1H and ^{13}C NMR, IR, and MS) were consistent with those previously reported.⁶ Optical yield was estimated by GC (column: Chiraldex G-TA 0.25 mm x 20 m). ***trans*-(2*R*, 5*R*)-2n:** a crystal; mp. 52-53 °C; ^1H NMR (CDCl_3 , 270 MHz) δ 1.30 (d, 3H, $J = 6.9$ Hz, 2-Me), 1.37 (d, 3H, $J = 6.4$ Hz, 5-Me), 1.46-1.67 (m, 2H), 1.87-2.10 (m, 2H), 2.39-2.48 (m, 1H, α -CH), 4.40-4.48 (m, 1H, δ -CH); ^{13}C NMR (CDCl_3 , 68 MHz) δ 17.23 (q, 2-Me), 22.03 (q, 5-Me), 28.43 (t), 30.89 (t), 35.65 (d, α -CH), 78.10 (d, δ -CH), 174.29 (s); IR(CDCl_3) 1720 cm^{-1} ; EIMS (relative intensity) m/z 128 (M^+ , 3), 113 (4), 84 (45), 69 (28), 56 (100), 2 (65); HREIMS calcd for $\text{C}_7\text{H}_{12}\text{O}_2$ m/z 128.0837, found 128.0828. This compound is already known and the properties (mp., ^1H and ^{13}C NMR, IR, and MS) were consistent with those previously reported.⁶

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Octahydro-3-methyl-1H-2-benzopyran-1-one (2o). Obtained as a mixture of four diastereomers in a 22/26/24/28 ratio (600 MHz ^1H NMR): ^{13}C NMR (CDCl_3 , 68 MHz) δ 20.88, 20.97, 22.08, 22.30, 22.36, 22.50, 24.10, 25.02, 25.06, 25.17, 25.22, 25.46, 25.92, 26.49 (two superimposed lines), 26.75, 28.23, 31.24, 32.75 (two superimposed lines), 32.84, 34.13, 34.25, 35.85, 35.96, 36.10, 37.00, 38.30, 38.69, 41.37, 42.79, 45.95, 72.36, 73.76, 73.93, 77.06, 172.96, 173.31, 174.91, 175.16. These compounds are already known and the properties (^1H and ^{13}C NMR) were consistent with those previously reported.³

cis- and trans-Tetrahydro-4-methyl-6-(2-methylpropyl)-2H-pyran-2-one (2q). Obtained as a *cis/trans*-isomer mixture in a 59/41 ratio: a colorless liquid; ^1H NMR (CDCl_3 , 270 MHz) δ 0.93 (t, *cis* 6H and *trans* 6H, $J = 6.3$ Hz), 1.02 (d, *cis* 3H, $J = 5.9$ Hz), 1.09 (d, *trans* 3H, $J = 6.4$ Hz), 1.15-2.23 (complex m, *cis* 7H and *trans* 7H), 2.32-2.73 (m, *cis* 1H and *trans* 1H, $\alpha\text{-CHH}$), 4.29-4.39 (m, *cis* 1H, $\delta\text{-CH}$), 4.42-4.52 (m, *trans* 1H, $\delta\text{-CH}$); ^{13}C NMR (CDCl_3 , 68 MHz) δ 21.43 (q, *trans*), 21.64 (q, *cis*), 22.02 (q, *cis* and *trans*), 22.93 (q, *trans*), 22.97 (q, *cis*), 23.80 (d, *trans*), 23.90 (d, *trans*), 24.18 (d, *cis*), 26.71 (d, *cis*), 35.45 (t, *trans*), 37.47 (t, *trans*), 37.55 (t, *cis*), 38.04 (t, *cis*), 44.59 (t, *trans*), 45.23 (t, *cis*), 75.50 (d, *trans*), 78.82 (d, *cis*), 171.51 (s, *cis*), 172.47 (s, *trans*); IR(neat) 1732 cm^{-1} ; EIMS (relative intensity) m/z 170 (M^+ , 2), 152 (6), 128 (5), 113 (100), 85 (17), 69 (33), 56 (25), 43 (11); HREIMS calcd for $\text{C}_{10}\text{H}_{18}\text{O}_2$ m/z 170.1307, found 170.1313. The *cis* isomer is already known and the properties (^1H and ^{13}C NMR and MS) were consistent with those previously reported.⁷

Tetrahydro-4-methyl-2H-pyran-2-one (2r): a slightly yellow liquid; ^1H NMR (CDCl_3 , 600 MHz) δ 1.07 (d, 3H, $J = 6.4$ Hz), 1.45-1.60 (m, 1H, $\beta\text{-CH}$), 1.93 (ddq, 1H, $J = 14.1, 1.5, 4.0$ Hz, $\gamma\text{-CHH}$), 2.06-2.17 (m, 2H, $\alpha\text{-CHHCO}$ and $\gamma\text{-CHH}$), 2.68 (dddd, 1H, $J = 22.1, 10.2, 1.4, 4.0$ Hz, $\alpha\text{-CHH}$), 4.27 (ddd, 1H, $J = 3.8, 10.7, 11.4$ Hz), 4.42 (ddd, 1H, $J = 4.0, 4.9, 11.4$ Hz); ^{13}C NMR (CDCl_3 , 68 MHz) δ 21.41 (q), 26.55 (d, $\beta\text{-CH}$), 30.61 (t, $\gamma\text{-CH}_2$), 38.20 (t, $\alpha\text{-CH}_2$), 68.52 (t), 171.19 (s); IR(neat) 1728 cm^{-1} ; EIMS (relative intensity) m/z 114 (M^+ , 43),

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84 (12), 70 (40), 56 (70), 55 (98), 42 (100); HREIMS calcd for $C_6H_{10}O_2$ m/z 114.0681, found 114.0695. This compound is already known and the properties (1H and ^{13}C NMR) were consistent with those previously reported.⁸

cis- and trans-Tetrahydro-4,6-dimethyl-2H-pyran-2-one (2s). Obtained as a *cis/trans*-isomer mixture in a 56/44 ratio: a slightly yellow liquid; 1H NMR ($CDCl_3$, 600 MHz) δ 1.03 (d, *cis* 3H, J = 6.4 Hz), 1.10 (d, *trans* 3H, J = 6.7 Hz), 1.21 (dt, *cis* 1H, J = 13.8, 11.5 Hz, γ -CHH), 1.37 (d, *cis* 3H, J = 6.3 Hz), 1.38 (d, *trans* 3H, J = 6.3 Hz), 1.62 (ddd, *trans* 1H, J = 4.2, 6.1, 14.1 Hz, γ -CHH), 1.76 (ddd, *trans* 1H, J = 6.4, 8.5, 14.2 Hz, γ -CHH), 1.93 (dm, *cis* 1H, $J_{doublet}$ = 13.8 Hz, γ -CHH), 2.02 (dd, *cis* 1H, J = 16.8, 10.7 Hz, α -CHH), 2.05 (m, *cis* 1H, β -CH), 2.15 (dd, *trans* 1H, J = 16.2, 8.9 Hz, α -CHH), 2.20 (m, *trans* 1H, β -CH), 2.58 (dd, *trans* 1H, J = 16.2, 5.5 Hz, α -CHH), 2.67 (ddd, *cis* 1H, J = 16.8, 4.8, 2.0 Hz, α -CHH), 4.42 (ddq, *cis* 1H, J = 12.6, 2.9, 6.3 Hz, δ -CH), 4.58 (ddq, *trans* 1H, J = 8.8, 4.4, 6.3 Hz, δ -CH); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 21.17 (q, CH_3CHCO *trans*), 21.20 (q, CH_3CHCO *cis*), 21.44 (q, CH_3CHO *trans*), 21.69 (q, CH_3CHO *cis*), 23.55 (d, β -CH *trans*), 26.61 (d, β -CH *cis*), 36.43 (t, *trans*), 37.15 (t, *trans*), 37.61 (t, α -CH₂ *cis*), 38.65 (t, γ -CH₂ *cis*), 73.47 (d, *trans*), 76.85 (d, *cis*), 171.41 (s, *cis*), 172.27 (s, *trans*); IR(neat) 1732 cm^{-1} ; for *cis* isomer: EIMS (relative intensity) m/z 128 (M^+ , 11), 113 (20), 84 (56), 69 (45), 56 (100); for *trans* isomer: EIMS (relative intensity) m/z 128 (M^+ , 12), 113 (16), 84 (58), 69 (42), 56 (100); for *cis* isomer: HREIMS calcd for $C_7H_{12}O_2$ m/z 128.0838, found 128.0843; for *trans* isomer: HREIMS calcd for $C_7H_{12}O_2$ m/z 128.0838, found 128.0812. This compound is already known and the properties (1H and ^{13}C NMR) were consistent with those previously reported.⁹

Tetrahydro-6-propyl-2H-pyran-2-one (2u): a slightly yellow liquid; 1H NMR ($CDCl_3$, 600 MHz) δ 0.94 (t, 3H, J = 7.3 Hz, CH_3), 1.39-1.46 (m, 1H), 1.47-1.60 (m, 3H), 1.66-1.74 (m,

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1H), 1.82-1.95 (m, 3H), 2.45 (ddd, 1H, $J = 7.1, 8.8, 17.6$ Hz, α -CHH), 2.59 (dddd, 1H, $J = 1.3, 4.8, 7.9, 17.6$ Hz, α -CHH), 4.30 (m, 1H, δ -CH); ^{13}C NMR (CDCl_3 , 68 MHz) δ 13.76 (q, CH_3), 18.10 (t), 18.42 (t), 27.72 (t), 29.39 (t), 37.82 (t), 80.27 (d), 171.96 (s); IR(neat) 1732 cm^{-1} ; EIMS (relative intensity) m/z 143 ($M^+ + 1$, 3), 124 (4), 114 (12), 99 (100), 70 (33), 55 (22), 42 (28); HREIMS calcd for $\text{C}_8\text{H}_{14}\text{O}_2$ m/z 142.0994, found 142.0983. This compound is commercially available.

***cis*- and *trans*-Tetrahydro-3-methyl-6-propyl-2H-pyran-2-one (2x).** Obtained as a *cis/trans*-isomer mixture in a 47/53 ratio: an oil; ^1H NMR (CDCl_3 , 270 MHz) δ 0.94 (t, *cis* 3H and *trans* 3H, $J = 6.8$ Hz), 1.22 (d, *cis* 3H, $J = 6.8$ Hz), 1.30 (d, *trans* 3H, $J = 7.3$ Hz), 1.35-1.76 (m, *cis* 6H and *trans* 6H), 1.88-2.13 (m, *cis* 2H and *trans* 2H), 2.39-2.49 (m, *trans* 1H), 2.56-2.66 (m, *cis* 1H), 4.25-4.33 (m, *cis* 1H and *trans* 1H); ^{13}C NMR (CDCl_3 , 68 MHz) δ 13.77 (q), 16.11 (q), 17.35 (q), 18.00 (t), 18.30 (t), 25.55 (t), 26.62 (t), 28.46 (t), 29.07 (t), 29.62 (t), 33.10 (d), 36.04 (d), 37.35 (t), 38.33 (t), 77.83 (d), 81.52 (d), 174.41 (s), 176.35 (s); IR(neat) 1732 cm^{-1} ; EIMS (relative intensity) for *cis* isomer m/z 156 (M^+ , 2), 113 (100), 85 (62), 70 (53), 56 (84), 42 (48); EIMS (relative intensity) for *trans* isomer m/z 156 (M^+ , 1), 113 (100), 85 (58), 70 (54), 56 (66), 42 (49).; HREIMS for *cis* isomer calcd for $\text{C}_9\text{H}_{16}\text{O}_2$ m/z 156.1150, found 156.1175.; HREIMS for *trans* isomer calcd for $\text{C}_9\text{H}_{16}\text{O}_2$ m/z 156.1150, found 156.1159.

***cis*- and *trans*-Tetrahydro-3-ethyl-6-propyl-2H-pyran-2-one (2y).** Obtained as a *cis/trans*-isomer mixture in a 41/59 ratio: an oil; ^1H NMR (CDCl_3 , 270 MHz) δ 0.94 (t, 3H, $J = 7.3$ Hz), 0.99 (t, 3H, $J = 7.3$ Hz), 1.36-1.75 (m, 7H), 1.81-2.15 (m, 3H), 2.29-2.44 (m, 1H), 4.24-4.32 (m, 1H); ^{13}C NMR (CDCl_3 , 68 MHz) δ 10.95 (q), 11.48 (q), 13.76 (q, two superimposed lines), 17.99 (t), 18.28 (t), 22.83 (t), 23.77 (t), 24.77 (t), 24.85 (t), 26.64 (t), 28.78 (t), 37.33 (t), 38.28 (t), 39.60 (d), 42.01 (d), 77.66 (d), 80.99 (d), 173.71 (s), 175.60 (s); IR(neat) 1727 cm^{-1} .

Synthesis of Tetrahydro-2-methyl-2-furanmethanol acetate (3z). According to the general procedure, after the standard workup, the ether extract was dried over MgSO_4 . Yields of **3z** and recovered **1z** were quantified by GC using an internal standard (*n*-dodecane) and the

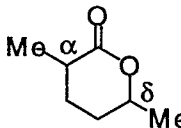
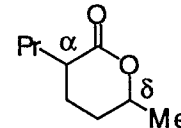
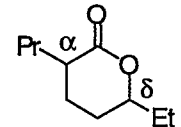
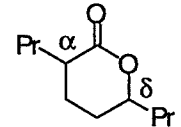
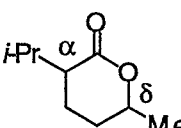
separated samples to calibrate the response of the detector. The spectroscopic data of **3z** isolated by flash chromatography is listed below: a slightly yellow liquid; ^1H NMR (CDCl_3 , 270 MHz) δ 1.44 (s, 3H, CH_3C), 1.46-1.56 (m, 1H), 1.60-1.70 (m, 1H), 1.76-1.84 (m, 1H), 2.03 (s, 3H, CH_3CO), 2.16-2.28 (m, 1H), 3.34 (d, 1H, $J = 11.9$ Hz, OCHHC), 3.49 (td, 1H, $J = 10.4, 2.7$ Hz, OCHHCH_2), 3.78 (td, 1H, $J = 4.4, 10.4$ Hz, OCHHCH_2), 4.02 (dd, 1H, $J = 11.9, 2.0$ Hz, OCHHC); ^{13}C NMR (CDCl_3 , 68 MHz) δ 21.52 (q, CH_3C), 22.18 (q, CH_3CO), 22.28 (t), 33.77 (t), 67.82 (t, OCH_2), 73.62 (t, OCH_2C), 77.93 (s, CH_3C), 170.42 (s); IR(neat) 1735 cm^{-1} ; CIMS (relative intensity) m/z 159 ($\text{M}^+ + 1$, 8), 99 (100), 81 (4), 71 (4), 61 (11); HRCIMS calcd for $\text{C}_8\text{H}_{15}\text{O}_3$ m/z 159.1035, found 159.1028. This compound is already known.¹⁰

With Regard to *cis/trans* Assignments of 2,5-Disubstituted Lactones (2k, 2l, 2w and 2m).

The *cis/trans* assignments of the obtained 2-methyl-5-hexanolide (**2n**) were made rigorously by comparing the obtained spectral and physical data for **2n** with those reported previously by plural groups.⁶ For *cis* and *trans* isomers of **2n**, there exist several significant differences in (i) GC elution orders (*cis* comes out faster than *trans*; with OV-1 column), (ii) ν_{CO} in IR spectra (*cis* has a larger frequency number than *trans*), (iii) ^{13}C NMR chemical shifts of $\text{C}=\text{O}$ (*cis* has a larger δ value than *trans*), and (iv) ^{13}C NMR chemical shifts of $\alpha\text{-C}$ and $\delta\text{-C}$ (*cis* has a smaller δ value than *trans*) (Table, run 1 and 2). The *cis/trans* assignments of the other 2,5-disubstituted lactones, **2k**, **2l**, **2w**, and **2m**, were based on the observed similar propensity. The key data are summarized in Table.

(10) Mihailović, M. L.; Marinković, D.; Konstantinović, S. *Glas. Hem. Drus. Beograd* **1981**, *46*, 397.

Table. The Key Data for 2,5-Disubstituted δ -Lactones

run	δ -lactone	GC elution orders (OV-1)	IR (ν_{CO}) cm^{-1}	^{13}C NMR chemical shift			
				C=O	α -C	δ -C	
1		cis- 2n	2	1732	176.16	32.88	74.34
2		trans- 2n	1	1720	174.29	35.65	78.10
3		cis- 2k	2	1736	175.81	37.95	77.75
4		trans- 2k	1	1728	174.03	40.60	81.02
5		cis- 2l	2	1736	175.83	37.88	79.23
6		trans- 2l	1	1728	174.07	40.60	82.40
7		cis- 2w	2	1736	175.62	37.67	74.22
8		trans- 2w	1	1719	173.95	40.22	77.60
9		cis- 2m	2	1728	174.61	43.93	74.04
10		trans- 2m	1	1724	173.25	46.35	77.29