# Spiro γ-Lactones via Aluminum Enolate–Spiroepoxide Openings

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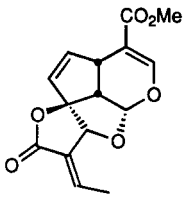
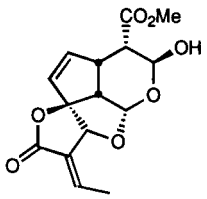
**Abstract:** The opening of several spiroepoxides by aluminum ester enolates is described. The isolated γ-hydroxy esters are cyclized to the corresponding spirolactones with high efficiency. Alternatively, the crude product from epoxide opening may be directly converted to the spirolactone without purification of the intermediate hydroxy ester. This methodology provides another complementary route to 1-oxaspiro[4.n]-2-one systems that are of structural and biological interest.
**Key words:** spiroepoxides, epoxide ring opening, γ-hydroxy esters, 1-oxaspiro[4.n]-2-one spirolactone systems, aluminum ester enolates

Spiro γ-lactones have been shown to be an important class of molecules owing to their interesting structures and biological activity. Some natural products that possess this structural element include the antitumor–antibiotic plumericin **(1)**,[1] the antitumor agent allamandin **(2)**,[2] the norsesquiterpenoids napalilactone **(3)**[3] and pathylactone A **(4)**,[4] and the zedoary extract curcumanolide A **(5)** and its derivatives.[5] Synthetic spiro γ-lactones like **6** and **7** have been employed as templates for the construction of conformationally constrained diacylglycerol mimics for binding protein kinase C (PKC).[6] Many spiro[4.5]decane lactones and ethers have interesting olfactory properties. Over many years, various methods for preparing spiro δ- and γ-lactones have appeared in the literature, but recent reports[7] regarding the synthesis of spirolactones demonstrate that this is still a very active research area and have prompted us to disclose our own efforts in this area.



**1**



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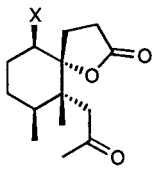
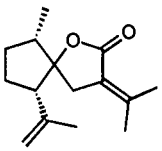


**3** X = Cl
**4** X = OH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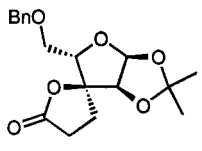

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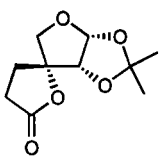
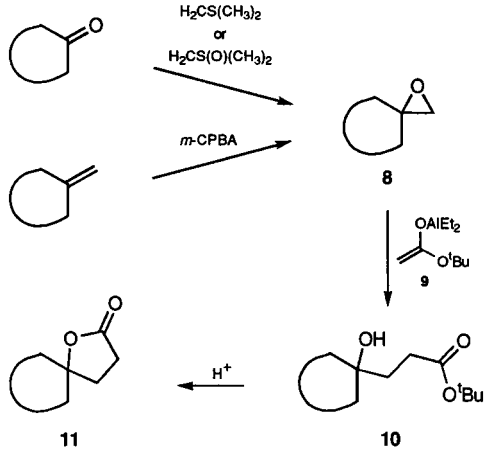

**7**

We have previously explored the opening of monosubstituted epoxides with aluminum ester enolates. This chemistry provides γ-hydroxy esters in good yields and reasonable diastereoselectivity.[8] These hydroxy esters are readily converted to the corresponding γ-lactones by treatment with acid.[9] The utility of the aluminum enolate route to lactones was demonstrated by featuring it as the key step in a short synthesis of (±)-rubrynolide.[10]

In the present work, we have extended the aluminum enolate methodology to *spiro*epoxides **8** which provides tertiary hydroxy esters **10** that yield spiro γ-lactones **11** upon treatment with acid (Scheme). The spiroepoxides **8** are readily obtained from their respective olefins via epoxidation or from treatment of the appropriate ketone with a sulfur ylide. (Scheme). This convenient and versatile approach to starting materials makes the aluminum ester enolate strategy very attractive. This approach also allows for preparation of varied ring sizes in just a few simple steps. A routine literature search revealed just one other approach to spirolactones from spiroepoxides – an isolated study of opening an epoxide with carboxylic acid lithiodianions.[11]



**Scheme**

Spiroepoxides **8** of varying ring sizes and substituents were added to a solution of the diethyl aluminum enolate of *tert*-butyl acetate **9** to give the tertiary γ-hydroxy esters **10** (Table 1). The first set of substrates (entries 1–4) were simple unsubstituted 4- to 7-membered ring systems. The epoxide opening by **9** proceeded smoothly in fair to good yield. These yields are comparable to the yields we have obtained from the aluminum enolate opening of monosubstituted epoxides such as propylene oxide and 1,2-epoxybutane (66% and 71%, respectively).[8]

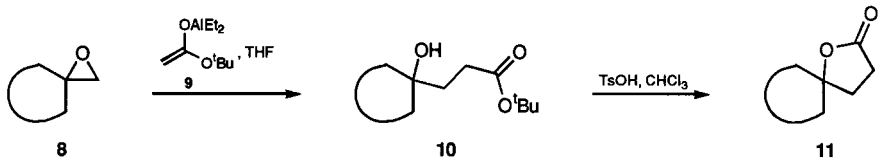
Temperature and reaction time were found to be important variables in this reaction. Maintaining a reaction tempera-

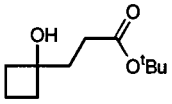
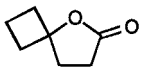
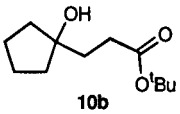
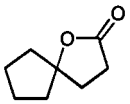
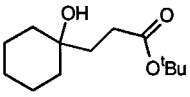
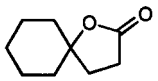
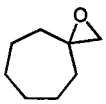
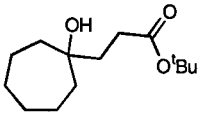
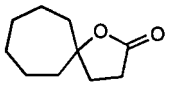
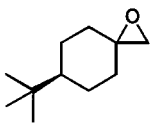
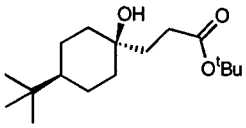
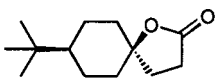
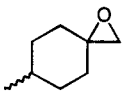
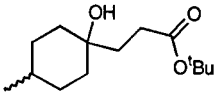
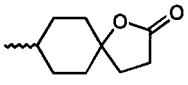
ture between –50 and –35 °C for 4 to 6 hours provided the highest yields of γ-hydroxy ester product. Higher reaction temperatures and/or overnight reaction times tended to increase side product formation from Claisen condensation of the ester and Lewis acid promoted rearrangements. Warming the reaction mixture slowly overnight to room temperature resulted in varying amounts of spontaneous lactonization of the alkoxide ester intermediate.

The isolated hydroxy esters were then lactonized (catalytic TsOH in $CHCl_3$) in good to excellent yield (Table 1). Often it was more convenient to submit the crude product mixture from epoxide opening to the lactonization conditions directly, rather than purifying the hydroxy ester (yields in parentheses Table 1). This protocol not only eliminates a purification step, but the spirolactones are more easily separated (chromatography on silica gel) from the side products formed in the epoxide opening step than are the hydroxy esters.

Entries 5,6 in Table 1 describe the results for 6-substituted 1-oxaspiro[2.5]octanes. Epoxide **8e**, prepared by treat-

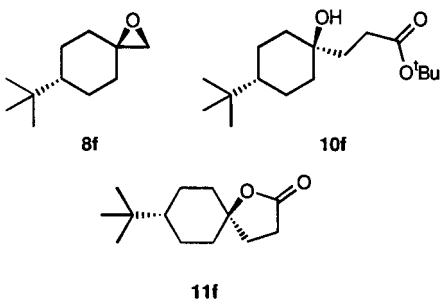
**Table 1.** Hydroxy Ester and Lactone Products




| Entry | Epoxide **8** | Hydroxy Ester **10** | Yield of **10** (%)[a] | Lactone **11** | Yield of **11** (%)[b] | Overall Yield (%)[c] |
|---|---|---|---|---|---|---|
| 1 |  **8a** |  **10a** | 64 |  **11a** | 91 | 58 |
| 2 |  **8b** |  **10b** | 76 |  **11b** | 81 | 62 (63) |
| 3 |  **8c** |  **10c** | 62 |  **11c** | 86 | 54 (58) |
| 4 |  **8d** |  **10d** | –[d] |  **11d** | 99 | (68) |
| 5 |  **8e** |  **10e** | 61 |  **11e** | 99 | 60 |
| 6 |  **8g** |  **10g** | 45 |  **11g** | 99 | 45 |

[a] Yield of pure hydroxy ester **10** isolated from the epoxide opening.
[b] Yield of pure lactone **11** starting from purified hydroxy ester **10**.
[c] Overall yield of lactone **11** from epoxide **8** for the two discrete steps. Yields in parentheses refer to direct lactonizations of crude **10** as described in the text.
[d] This hydroxy ester was isolated in pure form for characterization purposes only.

ment of 4-*tert*-butylcyclohexanone with dimethyloxosulfonium methylide,[12] was opened with aluminum enolate **9** to provide hydroxy ester **10e** in 61% yield. One preparation of **8e** surprisingly resulted in a mixture of **8e** and **8f**, which when reacted with **9** yielded the diastereomeric hydroxy esters **10e** and **10f**. The diastereomers were separated by chromatography in 73% and 17% yields, respectively, taking into account the starting ratio of **8e**/**8f**. The relative configuration of **10e** was confirmed by single crystal X-ray diffraction (Figure 1 and Table 2).[13] These hydroxy esters were lactonized separately to provide **11e** and **11f** as crystalline solids that were subjected to X-ray diffraction to unambiguously determine their diastereomeric relationship (Figure 2 and Table 3).[13] This was especially important to establish since the methyl-substituted epoxide **8g** gave a 1:1 mixture of diastereomers which remained unresolved throughout the synthetic sequence (as was the case in other work[7a]).



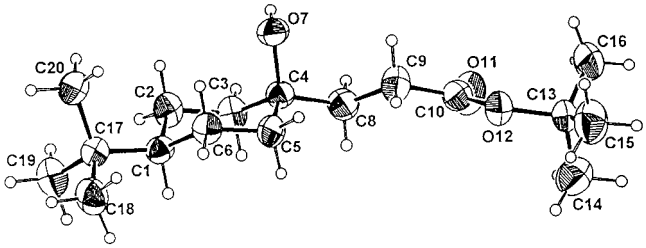




**Figure 1.** ORTEP drawing of hydroxy ester **10e**. Nonhydrogen atoms are represented by ellipsoids corresponding to 50% probability. Hydrogen atoms are represented by spheres of arbitrary size.

**Table 2.** Selected Bond Lengths (Å) and Angles (°) for Hydroxy Ester **10e**.

| | | | |
|---|---|---|---|
| C1–C2 | 1.530(4) | C1–C2–C3 | 111.77(25) |
| C2–C3 | 1.524(4) | C2–C3–C4 | 113.65(26) |
| C3–C4 | 1.526(4) | C3–C4–C5 | 109.27(24) |
| C4–O7 | 1.435(3) | C3–C4–O7 | 110.35(24) |
| C4–C8 | 1.530(4) | C3–C4–C8 | 109.69(24) |
| C8–C9 | 1.519(4) | C4–C8–C9 | 114.69(27) |
| C9–C10 | 1.491(4) | C8–C9–C10 | 113.7(3) |
| C10–O11 | 1.209(3) | C9–C10–O11 | 124.8(3) |
| C10–O12 | 1.336(3) | C9–C10–O12 | 110.63(28) |
| O12–C13 | 1.477(3) | O11–C10–O12 | 124.61(27) |
| | | C10–O12–C13 | 122.50(23) |

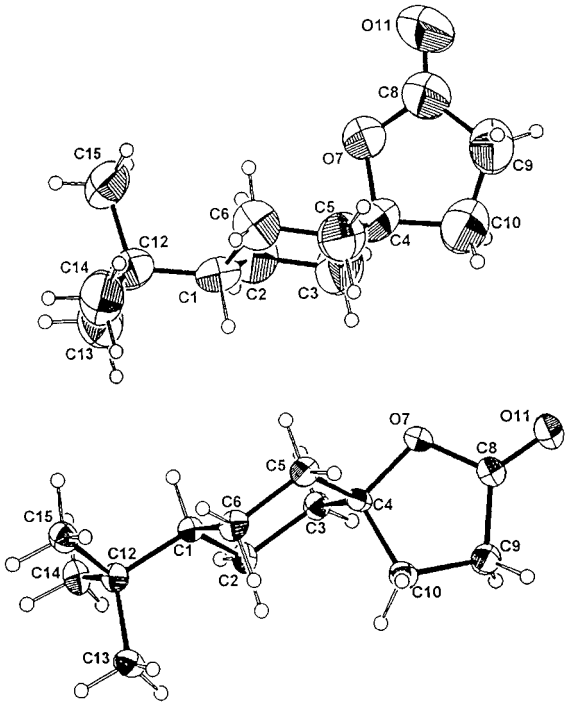



**Figure 2.** ORTEP drawing of spirolactones **11e** (top) and **11f** (bottom). Nonhydrogen atoms are represented by ellipsoids corresponding to 50% probability. Hydrogen atoms are represented by spheres of arbitrary size.

**Table 3.** Selected Bond Lengths (Å) and Angles (°) for Lactones **11e** and **11f**.

| | **11e** | **11f** | | **11e** | **11f** |
|---|---|---|---|---|---|
| C1–C2 | 1.523(5) | 1.536(6) | C1–C2–C3 | 112.4(3) | 111.4(3) |
| C2–C3 | 1.517(5) | 1.530(5) | C2–C3–C4 | 113.2(3) | 112.0(3) |
| C3–C4 | 1.500(5) | 1.519(5) | C3–C4–C5 | 110.2(3) | 110.7(3) |
| C4–C5 | 1.517(6) | 1.512(6) | C3–C4–O7 | 107.5(3) | 106.9(3) |
| C4–O7 | 1.470(4) | 1.481(4) | C3–C4–C10 | 114.0(4) | 113.4(4) |
| C4–C10 | 1.525(5) | 1.536(5) | C4–O7–C8 | 111.0(3) | 111.95(23) |
| O7–C8 | 1.339(5) | 1.346(4) | O7–C8–O11 | 120.8(4) | 121.62(28) |
| C8–O11 | 1.193(4) | 1.202(4) | O7–C8–C9 | 110.2(4) | 110.22(27) |
| C8–C9 | 1.495(6) | 1.495(5) | O11–C8–C9 | 129.0(4) | 128.2(4) |
| C9–C10 | 1.495(7) | 1.529(6) | C8–C9–C10 | 104.0(4) | 104.4(3) |
| | | | C10–C4–O7 | 103.4(3) | 103.4(3) |

In summary, we have demonstrated the utility of the aluminum enolate epoxide opening reaction as a route to the preparation of spiro γ-lactones of various ring sizes. The epoxide openings proceed in moderate to good yield and the hydroxy ester products are efficiently lactonized with acid. The efficiency of the lactone production can be improved by directly treating the crude product mixture from epoxide opening with TsOH.

THF was distilled from sodium/benzophenone under $N_2$ or argon immediately before use. i-$Pr_2$NH was distilled from KOH and stored over 4Å molecular sieves until use. Mps (Mel-Temp) are uncorrected. Spiroepoxide **8a** was prepared by MCPBA epoxidation of methylenecyclobutane.[14] Spiroepoxides **8b–g** were prepared from the corresponding ketones by reaction with dimethyloxosulfonium methylide.[12]

***tert*-Butyl 3-(1-Hydroxycyclobutyl)propanoate (10a); Typical Procedure for Epoxide Openings:**

To a cooled (–78 °C) solution of LDA (15.7 mmol) in THF (40 mL) was added *tert*-butyl acetate (2.0 mL, 15.0 mmol). After 30 min, 1.0 M $Et_2AlCl$ in hexanes (15.0 mL) was added, and the resulting mixture was stirred for an additional 15 min before adding **8a** (1.00 g, 11.9 mmol). The mixture was kept below –35 °C for 6 h. The reaction was quenched by the addition of sat. $NH_4Cl$, diluted with water and warmed to r.t. The resulting gel was dispersed by stirring with 10% HCl (50 mL) until a clear biphasic mixture formed. The layers were separated, and the aqueous layer was extracted with $Et_2O$. The combined organic layers were washed (sat. $NH_4Cl$, sat. $NaHCO_3$, and brine), dried ($MgSO_4$), and concentrated. Flash chromatography (silica gel, hexanes/EtOAc 6:1) provided hydroxy ester **10a** (1.53 g, 64%) as a colorless oil; TLC: $R_f$ 0.25 (hexanes/EtOAc 6:1).

IR (neat, NaCl plates): $\nu$ = 3445 (br, OH), 2978, 2934, 1728, 1368, 1291, 1256, 1154, 1109, 953, 847 $cm^{-1}$.

$^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 2.70 (br s, 1H), 2.31 (t, $J$ = 7.3 Hz, 2H), 1.99 (m, 4H), 1.87 (t, $J$ = 7.3 Hz, 2H), 1.70 (m, 1H), 1.48 (m, 1H), 1.41 (s, 9H).

$^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 174.2, 80.5, 74.6, 35.7, 34.0, 30.2, 28.0, 11.9.

Anal. Calcd for $C_{11}H_{20}O_3$ C, 65.97; H, 10.07. Found C, 65.99; H, 10.13.

***tert*-Butyl 3-(1-Hydroxycyclopentyl)propanoate (10b):**

LDA (20.0 mmol) in THF (50 mL), *tert*-butyl acetate (2.6 mL, 19.3 mmol), 1.0 M $Et_2AlCl$ in hexanes (20.0 mL), and **8b** (1.14 g, 11.6 mmol) provided hydroxy ester **10b** (1.88 g, 76%) as a colorless oil after workup and chromatography using the typical procedure described for **10a**.

IR (neat, NaCl plates): $\nu$ = 3426 (br, OH), 2963, 1726, 1368, 1153 $cm^{-1}$.

$^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 2.39 (t, $J$ = 7.5 Hz, 2H), 1.86 (t, $J$ = 7.5 Hz, 2H), 1.70–1.40 (m, 9H), 1.44 (s, 9H).

$^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 174.8, 83.2, 81.1, 40.3, 36.0, 31.8, 28.2, 23.8.

HRMS (CI, $CH_4$) Calcd for $C_{12}H_{22}O_3$ [M + H – $HOC(CH_3)_3$] 141.0918, found 141.0951.

***tert*-Butyl 3-(1-Hydroxycyclohexyl)propanoate (10c):**

LDA (20.0 mmol) in THF (50 mL), *tert*-butyl acetate (2.6 mL, 19.3 mmol), 1.0 M $Et_2AlCl$ in hexanes (20.0 mL), and **8c** (1.46 g, 13.0 mmol) provided hydroxy ester **10c** (1.85 g, 62%) as a colorless oil after workup and chromatography using the typical procedure described for **10a**.

IR (neat, NaCl plates): $\nu$ = 3410 (br, OH), 2935, 2863, 1730, 1135 $cm^{-1}$.

$^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 2.35 (t, $J$ = 7.5 Hz, 2H), 2.10 (br s, 1H), 1.75 (t, $J$ = 7.5 Hz, 2H), 1.65–1.20 (m, 10H), 1.44 (s, 9H).

$^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 174.1, 80.1, 70.5, 37.3, 36.5, 29.6, 27.9, 26.7, 22.1.

***tert*-Butyl 3-(1-Hydroxycycloheptyl)propanoate (10d):**

LHMDS (10.0 mmol) in THF (10 mL), *tert*-butyl acetate (1.3 mL, 9.65 mmol), 1.0 M $Et_2AlCl$ in hexanes (10.0 mL), and **8d** (5.46 mmol) provided hydroxy ester **10d** and lactone **11d** as a 1.0:1.3 mixture ($^1H$ NMR) (0.74 g, 30% for **10d** and 38% for **11d**) as a colorless oil after workup and chromatography using the typical procedure described for **10a**. Treatment of this mixture with TsOH in $CHCl_3$ resulted in essentially quantitative conversion to pure **11d**. A smaller scale reaction was run to provide pure **10d** for characterization purposes

IR (neat, NaCl plates): $\nu$ = 3450 (br, OH), 2978, 2926, 2857, 1724, 1154 $cm^{-1}$.

$^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 2.35 (t, $J$ = 7.5 Hz, 2H), 1.76 (t, $J$ = 7.5 Hz, 2H), 1.70–1.35 (m, 13H), 1.44 (s, 9H).

$^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 174.2, 80.3, 74.9, 41.1, 37.5, 29.9, 28.0 (2C), 22.5.

HRMS (CI, CH4) Calcd for $C_{14}H_{26}O_3$ [M + H] 243.1959, found 243.1948.

***tert*-Butyl 3-(*cis*-4-*tert*-Butyl-1-hydroxycyclohexyl)propanoate (10e):**

LDA (11.5 mmol) in THF (20 mL), *tert*-butyl acetate (1.95 mL, 13.4 mmol), 1.0 M $Et_2AlCl$ in hexanes (11.5 mL), and **8e** (5.9 mmol) provided hydroxy ester **10e** (1.03 g, 61%) as a crystalline solid (mp 73–76 °C) after workup and chromatography using the typical procedure described for **10a**.

IR (neat, deposited from $CH_2Cl_2$ on NaCl plates): $\nu$ = 3450 (br, OH), 2966, 1724 $cm^{-1}$.

$^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 2.35 (t, $J$ = 7 Hz, 2H), 1.70 (m, 4H), 1.55 (m, 4H), 1.45 (s, 9H), 1.30 (m, 4H), 0.86 (s, 9H).

$^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 174.7, 80.9, 70.5, 48.5, 39.1, 38.1, 33.0, 30.3, 28.7, 28.2, 23.0.

Anal. Calcd for $C_{17}H_{32}O_3$ C, 71.79; H, 11.33. Found C, 72.23; H, 11.00.

Crystallographic Data: triclinic space group $P\bar{1}$ at r.t., a = 10.244(1) Å, b = 14.404(2) Å, c = 6.140(1) Å, $\alpha$ = 97.03(1)°, $\beta$ = 90.67(1)°, $\gamma$ = 103.32(1)°, Z = 2, $\rho_{calcd}$ = 1.081 g/$cm^3$, $\mu$(Mo K$\alpha$) = 0.670 $cm^{-1}$, R = 0.070, $R_w$ = 0.066.

***tert*-Butyl 3-(*trans*-4-*tert*-Butyl-1-hydroxycyclohexyl)propanoate (10f):**

Hydroxy ester **10f** was isolated from a reaction of **9** with a mixture of **8e** and **8f** (see text) as a crystalline solid (mp 86–87 °C) using the typical procedure described for **10a**.

IR (neat, deposited from $CH_2Cl_2$ on NaCl plates): $\nu$ = 3450 (br, OH), 2966, 1722 $cm^{-1}$.

$^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 2.30 (t, $J$ = 7 Hz, 2H), 1.90 (br s, 1H), 1.85–1.65 (m, 8H), 1.45 (s, 9H), 1.35 (m, 3H), 0.85 (s, 9H).

$^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 174.9, 81.0, 72.1, 48.2, 39.3, 32.9, 31.7, 30.2, 28.7, 28.3, 25.0.

Anal. Calcd for $C_{17}H_{32}O_3$ C, 71.79; H, 11.33. Found C, 71.48; H, 11.24.

***tert*-Butyl 3-(1-Hydroxy-4-methylcyclohexyl)propanoate (10g):**

LDA (5.5 mmol) in THF (15 mL), *tert*-butyl acetate (5.5 mmol), 1.0 M $Et_2AlCl$ in hexanes (7.8 mL), and **8g** (3.5 mmol) provided hydroxy ester **10g** (0.381 g, 45%) as a crystalline solid (mp 43–45 °C) after workup and chromatography using the typical procedure described for **10a**.

IR (neat, NaCl plates): $\nu$ = 3455 (br, OH), 2947, 1730 $cm^{-1}$.

$^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 2.40 (t, $J$ = 7.5 Hz, 2H), 1.70 (t, $J$ = 7.5 Hz, 2H), 1.60–1.40 (m, 5H), 1.44 (s, 9H), 1.3–1.2 (m, 5H), 0.90 (d, $J$ = 5 Hz, 3H).

$^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 174.8, 80.9, 70.5, 39.1, 37.5, 32.9, 30.8, 30.3, 28.7, 22.9.

**1-Oxaspiro[4,3]octan-2-one (11a); Typical Procedure for Lactonization:**

TsOH•$H_2O$ (16 mg, 0.08 mmol) was added to a solution of **10a** (435 mg, 2.17 mmol) in $CHCl_3$ (15 mL) and the solution was stirred at r.t. for 24 h. Alternatively, the solution may be refluxed for 30 min to 2 h. to effect the lactonization. The mixture was passed through a plug of silica gel topped with $NaHCO_3$. After solvent removal, flash chromatography (hexanes/EtOAc 3:1) provided **11a** (251 mg, 91%) as a light yellow oil. In some cases passing the crude product through a simple silica gel plug was sufficient to provide analytically pure material. The lactones that follow were prepared by this method in the yields indicated in Table 1. TLC: $R_f$ = 0.5 (hexanes/EtOAc 1:1).

IR (neat, NaCl plates): $\nu$ = 2986, 2942, 2880, 1775, 1422, 1292, 1182, 1146, 1107, 955, 909 $cm^{-1}$.
$^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 2.52 (t, *J* = 7.8 Hz, 2H), 2.50 (m, 2H), 2.27 (t, *J* = 7.8 Hz, 2H), 2.12 (m, 2H), 1.85 (m, 1H), 1.63 (m, 1H).
$^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 176.3, 85.0, 34.5, 33.3, 28.5, 11.9.
Anal. Calcd for $C_7H_{10}O_2$ C, 66.65; H, 7.99. Found C, 66.79; H, 7.75.

*1-Oxaspiro[4.4]nonan-2-one* **(11b)**:[15]
IR (neat, NaCl plates): $\nu$ = 2959, 2874, 1771, 1344, 1283, 1163, 1005 $cm^{-1}$.
$^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 2.60 (t, *J* = 8 Hz, 2H), 2.21 (t, *J* = 8 Hz, 2H), 2.00 (m, 2H), 1.85 (m, 2H), 1.70 (m, 4H).
$^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 176.7, 94.9, 38.3, 32.2, 29.7, 23.7.

*1-Oxaspiro[4.5]decan-2-one* **(11c)**:[7, 16, 17]
IR (neat, NaCl plates): $\nu$ = 2935, 1774 $cm^{-1}$.
$^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 2.60 (t, *J* = 8.5 Hz, 2H), 2.00 (t, *J* = 8.5 Hz, 2H), 1.90–1.70 (m, 4H), 1.70–1.50 (m, 6H).
$^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 177.5, 87.1, 37.6, 33.5, 29.3, 25.6, 23.2.

*1-Oxaspiro[4.6]undecan-2-one* **(11d)**:[16, 17]
IR (neat, NaCl plates): $\nu$ = 2930, 2859, 1769, 1244, 1161 $cm^{-1}$.
$^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 2.57 (t, *J* = 8.3 Hz, 2H), 2.02 (t, *J* = 8.3 Hz, 2H), 2.00–1.80 (m, 2H), 1.75–1.4 (m, 10H).
$^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 176.8, 90.2, 39.8, 34.1, 29.0, 28.6, 22.1.

*cis-8-tert-Butyl-1-oxaspiro[4.5]decan-2-one* **(11e)**:[15, 16]
mp 69–70 °C.
IR (neat, deposited on NaCl plates from $CH_2Cl_2$): $\nu$ = 2943, 2868, 1761 $cm^{-1}$.
$^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 2.52 (t, *J* = 8.3 Hz, 2H), 1.97 (t, *J* = 8.3 Hz, 2H), 1.95 (m, 1H), 1.7–1.3 (m, 8H), 0.87 (s, 9H).
$^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 177.0, 85.6, 47.3, 37.6, 34.2, 32.4, 28.6, 27.5, 23.1.
Anal. Calcd for $C_{13}H_{22}O_2$ C, 74.24; H, 10.53. Found C, 74.43; H, 10.52.
Crystallographic Data: monoclinic space group $P2_{1/\alpha}$ at r.t., a = 10.240(5) Å, b = 6.109(4) Å, c = 20.876(10) Å, $\beta$ = 101.17(3)°, Z = 4, $\rho_{calcd}$ = 1.090 g/$cm^3$, $\mu$(Mo K$\alpha$) = 0.666 $cm^{-1}$, R = 0.082, $R_w$ = 0.079.

*trans-8-tert-Butyl-1-oxaspiro[4.5]decan-2-one* **(11f)**:[15, 16]
mp 97–98 °C.
IR (neat, deposited on NaCl plates from $CH_2Cl_2$): $\nu$ = 2950, 2864, 1774 $cm^{-1}$.
$^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 2.59 (t, *J* = 8.3 Hz, 2H), 2.07 (t, *J* = 8.3 Hz, 2H), 1.9–1.6 (m, 6H), 1.08 (m, 3H), 0.87 (s, 9H).
$^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 176.5, 87.1, 46.7, 36.8, 32.1, 30.2, 28.5, 27.5, 23.0.
Anal. Calcd for $C_{13}H_{22}O_2$ C, 74.24; H, 10.53. Found C, 73.62; H, 10.54.
Crystallographic Data: monoclinic space group $P2_1$ at –165 °C, a = 9.788(3) Å, b = 6.248(2) Å, c = 20.158(6) Å, $\beta$ = 101.72(1)°, Z = 4, $\rho_{calcd}$ = 1.157 g/$cm^3$, $\mu$(Mo K$\alpha$) = 0.707 $cm^{-1}$, R = 0.047, $R_w$ = 0.038.

*8-Methyl-1-oxaspiro[4.5]undecan-2-one* **(11g)**:[7]
IR (neat, NaCl plates): $\nu$ = 2949, 2858, 1769 $cm^{-1}$.
$^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ = 2.60 (t, *J* = 8.5 Hz, 2H), 2.00 (t, *J* = 8.5 Hz, 2H), 1.90 (d, *J* = 11 Hz, 2H), 1.7–1.3 (m, 7H), 0.92 (d, *J* = 5.5 Hz, 3H).
$^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ = 176.9, 85.5, 36.8, 34.0, 31.4, 28.6, 21.8.

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